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# The Journal of Industrial and Engineering Chemistry

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# EDITORIALS

## EDUCATION FOR RESEARCH[1]

The general disturbance in the chemical and pharmaceutical market occasioned by the present European war has sharply emphasized the dependence of many American industries upon the supply of both raw and finished material obtained from abroad. The public is asking the pertinent questions: Why must we import so large a proportion of our coal tar dye stuffs, when we have so much highly colored coal tar at home? Why do we depend upon Germany for lithia salts, when all the lithium-bearing minerals come from America? Why has a European war increased the price of articles not in any way connected with the war?

It is a principle of pedagogy that, to insure the best results when giving instruction, it is necessary to create a receptive attitude on the part of the student; to encourage an inquiring frame of mind. Today there is a keener and broader interest among manufacturers than ever before in determining those factors which have been controlling in giving European nations an advantage in many lines of industry which it would seem the United States is in every way equally fitted to enjoy. The public now possesses that desirable receptive attitude and inquiring frame of mind. It would seem therefore that the present is a psychological moment for a campaign of education which would benefit the chemical profession directly, and the entire community indirectly.

A number of very important factors in successful chemical industry have already been considered by this audience and your able committee has reported its findings and recommendations regarding a so-called anti-dumping clause, an adequate protective tariff and the United States patent law. There are, however, some very general matters bearing upon the subject that may be profitably considered. First, there is the necessity for further education of the public. Notwithstanding all that has thus far been done, the public is, as a whole, ignorant of what a chemist professionally is, and the place he occupies in the community. A great many people do not yet distinguish between a chemist and an apothecary, or between the latter and a dispenser of soda water. A chemical engineer is frequently visualized as a man who runs a so-called chemical fire engine. And yet this same public will talk volubly about the position occupied by Germany in the industrial chemical world and ascribe untold advantages to systems of education and industry which it does not understand. The magnificence of German chemical industry has been compared to the chemical industry of America almost *ad nauseum*. Generally the inequalities are greatly exaggerated and many may be explained without any discredit to the American profession. We are wont to instance the telegraph, the sewing machine, the electric light and such developments, when desiring to find compensating achievements to offset the contributions of Germany to chemical science. But we forget that the sulfite process for obtaining cellulose from wood, the chromium process for leather, calcium carbide, carborundum, and many other chemical industries owe their origin and development to American chemical genius. Nothing succeeds like success; and while we should continue to learn from Germany the many things which she is in position to teach us, we must cease making unfair comparisons and root for the home team.

The increasing appreciation with which the chemically trained man is held by the American manufacturer argues well for the future. Not many years ago if a chemist was employed at all, it was simply and only for so-called control work. The manufacturer was satisfied if he maintained his standard, and turned out a uniform product. There was little inclination to risk money by placing on the market a new product. There has been an encouraging change within the last ten years, and the manufacturing public is awakening to the desirability of progress in both the quality of his product and the methods of his plant; and he is beginning to realize that a man trained in experimental science is a necessary addition to his organization. But the average manufacturer of America still expects bricks without straw. To cite an example of what I mean: A large shoe machinery company known to us thinks nothing of allowing a skilled mechanic two or three years in which to perfect a desired movement or correlation of parts in a machine. Yet this same company was keenly disappointed, even disgusted, because a skilled chemist did not produce in six weeks a special alloy with sharply defined properties. In one case the solution depended upon mechanics which the superintendent understood and could see, while in the other it was chemistry which he did not understand and the action of which he could not follow.

The manufacturer of today is beginning to be strongly attracted by the terms "research" and "research department." He has a sort of conviction that, by adding such an appendage to his organization, he will be insured of progress and will protect himself from difficulties, much in the same way that a good vaccination mark insures against small-pox.

My plea at this time is not so much for greater generosity on the part of the employer in matters of laboratory facilities, special equipment, or a good library, however inportant these are, but rather for a larger appreciation of the conditions which make for ultimate success in research work. Among these conditions may be mentioned, first, the choice of the research worker. I am satisfied that no little harm is done the cause of industrial research by the employment of immature, untrained men, who pass as men skilled in science but who either know no science, or who have had no experience in that very difficult art of applying science to industry. The harm comes not so much because the particular investigation fails, but rather because the

[1] Address at the Joint Meeting of the New York Sections of the American Chemical Society, the Society of Chemical Industry and the American Electrochemical Society, Chemists' Club, December 11, 1914.

management believes it has shown that its problems are not susceptible to solution by scientific research or amenable to the aid which applied science can render. This unfortunate condition is frequently brought about by false economy on the part of the management. A research chemist should in its opinion be obtained with the ease and salary of an apothecary's clerk. A horse suitable for drawing an ice cart is bought and expected to win a Derby.

Another mistake frequently made is in the organization of the research staff, or if done on a less pretentious scale, the research work. Investigation work should never be allowed to interfere with factory production. The average mill superintendent quickly becomes antagonistic to anything which cuts down his output. Yet it is not infrequently the case that a research assistant is placed directly under such a superintendent, and may even report to him exclusively. The superintendent may have won his position on account of his ability to get the maximum of work out of his men, and may have risen in spite of an extreme narrowness of vision, rather than on account of his breadth of view. Or again, the research man may be at the beck and call of the production department and thus be constantly taken away from his real task to do routine testing of the product; or, the purchasing department may have the right to demand such of his time as may be necessary to check up specifications, and purchases made thereunder. Continuous concentrated effort is essential to a successful investigation, and the organization of such work should insure freedom from serious interruption of any kind.

A further tendency on the part of the employer is to expect positive results as soon as the work is well under way; having planted the seed he is impatient to harvest the crop. At best, experimental work is slow and this fact must be cheerfully accepted at the beginning. When considering the large amount of research work done in Germany we forget the great number of men who are there engaged in investigations of every possible type. If we had some means of determining the average yearly output per man, I am sure we would find it extremely small. It is my belief that the *per capita* return for research work is greater in America than it is in Germany. It is only when the results of each individual are multiplied by the great number of men in the work that the enviable amount of scientific work produced yearly in Germany is reached.

As a transition paragraph from the employer to the employee, I shall again emphasize the point already treated elsewhere. For the best results a manufacturer should realize that his organization must teach the college man the details of the work for which he is employed; and the new graduate must realize that there is an enormous lot which he does not yet know, and which the factory superintendent or foreman can best teach him. Fault is frequently found with the college man because he does not know the latest quick analytical methods as used in some large laboratory; that he is not familiar with the types of machines employed in the factory to which he goes. Inasmuch as the average candidate has but four years for his technical training it follows that if he had been taught these details upon which his *immediate* success may possibly depend, it would have been at the expense of a broad, fundamental training in economics and science upon which his final success is sure to depend. On the other hand there is much truth in the oft-repeated assertion that the college graduate "thinks he knows it all." He fails to realize that in every industry there is a great field of knowledge of which he is as yet ignorant but which is familiar to the manager, superintendent or foreman. Not only the details of factory procedure, but matters of finance, salesmanship, advertising and other factors essential to the success of the undertaking are unknown to him.

Finally we come to the education of the man who is to do the research work. At this time it would be out of place to discuss curriculums of study or to outline courses of instruction; but there are two or three points which it may be worth while to consider.

In general it may be said that a man should possess the ability to utilize the knowledge he has acquired in the past in the solution of his present problems. This statement presupposes two things: *first*, the acquisition of knowledge, and *second*, a training in the application or use of this knowledge. Comparatively speaking, the first is easy and the second is difficult. In a limited sense, knowledge can be bought in the form of books, but no one can appropriate to himself a skilled hand or an observant eye or an accurate analytical mind. These are the products of training. There is a regrettable tendency in modern textbooks on elementary chemistry and qualitative analysis to spend an undue amount of time upon the laws of dilute solutions to the exclusion of that training which these subjects are preeminently fitted to give. Not that these laws are of little importance; but fundamental principles and broad generalizations are of value only when they can be visualized in terms of facts and experiences. But the present tendency to overemphasize theory in elementary chemistry and qualitative analysis crowds out that knowledge of facts, and training in observation, in which the beginner is so deficient. The great difficulty with the average student in experimental science is that he sees things as he thinks they ought to be, and not as they are. He does not observe accurately, nor reason logically. He is not resourceful in using the knowledge acquired yesterday in solving the problems of today. Such power can be obtained only by practice; and why postpone the practice of this all-important function until late in the college course? From my experience as a teacher it is my opinion that no subject in the entire curriculum is so well adapted to train a man in keen observation, logical deduction and general resourcefulness, as a broad and sympathetic course in qualitative analysis. The short time usually devoted to this subject should not be consumed in teaching advanced theory which can be better learned later.

A second factor in the education of a research man (but which of course is not limited to a research man) is the necessity of giving him a working knowledge of the general principles of chemistry in the same manner that a mechanical engineer is made familiar with those principles of physics involved in thermodynamics and ap-

plied mechanics. So I use the word *working* advisedly, and mean thereby not only a knowledge of the fundamental theories and laws involved in every-day phenomena, but an acquaintance with them intimate enough to enable him to make daily use of them. The average student knows well the law of conservation of energy and of mass; although his arithmetic is usually poor, the law of multiple proportions is second nature to him and he handles it with ease. This is because the law is valid at all workable concentrations, at all workable pressures, and at all workable temperatures; and he has met with problems for the solution of which its application is imperative. Not so with the laws which he meets later in his work. In his course in Theoretical Chemistry or Physical Chemistry or General Principles of Science, or whatever name it may be called, he learns, for example, the law of mass action; if he solves any problems at all, they involve dilute solutions or low pressures alone. He learns that for concentrated solutions and strongly dissociated salts the law does not hold—and there the matter rests. He learns Henry's law, Raoult's law, the law of electrolytic conductance, transference, osmotic pressure etc., and if the subject is well presented, solves numerical problems to render clear his mental image of these laws; then he learns that under those conditions in which he lives and moves and has his being, they do not quantitatively hold—and there matter rests.

Imparting to the student a knowledge of these general laws of science is one of the most important factors in technical education and must play a leading part in the upper year of college work. But the point I would emphasize is that when these principles are presented, the task is only begun. The first instruction must of necessity be given, set as it were, in dilute solutions. To be of pedagogic value, the work must be quantitative, and accuracy can be realized only in very low concentrations. But here is where the average teacher of so-called theoretical chemistry "lies down on the job." To have a working knowledge of these principles a man must be familiar with their use under the conditions of concentration, temperature and pressure with which he has to deal. He must have a general idea of the deviation from the theoretical which a law will suffer under working conditions. If such laws are not quantitatively applicable, they are at least qualitatively helpful; if they do not determine how far one can go to reach a definite end, they at least indicate the direction he must go. Our experience with men who have had a course in the general principles of chemistry is that they do one of two things—either they attempt to use the knowledge thus obtained, and develop a confidence in their ability to get at the roots of the problem and by applying these general principles determine the lines along which success most probably lies; or to use an analogy, they are afraid to venture into the open ocean of practical experience with a boat which they have sailed only in the closed and secluded harbor of dilute solutions. The result is that they lose interest in the boat and soon entirely forget her. Had they been taught to navigate this boat in times of storm and high tides as well as in the harbor, they might not have attained on the ocean the accurate time they were accustomed to make in the harbor, but they would the more quickly have reached the haven of success which lies on the opposite coast.

It is but a truism to say that the way to acquire an ability to solve problems is in the exercise of this faculty. To become a successful research worker, we must do research work. While in every institution an attempt is made to train students to carry on original work, the four years allotted to the average man are not sufficient for accomplishing very much in this direction. While a genius is born, not made, good experimentalists can be produced from most men of average ability.

It is believed that the training to be obtained from investigation work is largely independent of the particular type of problem undertaken. If one wishes to become a bridge builder by the experience of building bridges, it is not material whether the bridge so built is demanded by the traveling public or not. It is in solving the problems incident to construction, not in the use of the finished structure, that the educational value lies. Thus it is with research work in so-called pure and applied science—whether the results obtained be immediately used, or very remotely used, need not influence the methods employed in the work.

So, in research laboratories, bridges are built not only where the public is anxious to have them built, but where someone is willing to pay for the building. The problems undertaken are brought by manufacturing concerns, and the expenses of the laboratories are met in this way. A two-fold purpose is thus accomplished—the manufacturing public is given facilities for overcoming some of its difficulties, and the more able men of the community are trained to fill the demand, which is constantly growing and now far outmeasures the supply, for men capable of conducting successful original research.

WILLIAM H. WALKER

## CHANGES IN THE EDITORIAL STAFF OF CHEMICAL ABSTRACTS

The resignation of John J. Miller, Editor of *Chemical Abstracts*, to accept a managerial position, seems an appropriate occasion for an appreciation of his services to the Society.

Mr. Miller entered the work five years ago as Associate Editor, during which time the scope of the publication and the labors of the editorial force have grown greatly. Although Mr. Miller has been editor only six months, he had for the previous three years carried a large and increasing amount of editorial responsibility. His editorship was well earned and it is a matter of great regret to us that the Society must lose him.

Mr. Miller's special contribution to the Society's enterprise was executive ability of a high order and an energy that more than kept pace with the growing task. In the early years of the journal the editors used to wonder how the management of the *Zentral-*

*blatt* ever succeeded in publishing their semi-annual index with the last copy. Last year, however, the members of our Society received the much larger *Chemical Abstracts* index before the end of the calendar year. This result was not attained without a systematic improvement from year to year, but that it was achieved at all is due largely to Mr. Miller, assisted by Mr. Crane, and by Miss Laura Collison, who indexes *Abstracts* and the *Journal of our Society* so efficiently. Mr. Miller strove continually to extend the usefulness of *Abstracts* in many other ways, with notable success.

Mr. E. J. Crane, who now becomes Acting Editor, joined the office force as second associate editor something over three years ago. He is a young man of

JOHN J. MILLER

much ability, and naturally suited to editorial work. The writer feels that the Society is to be congratulated in having developed such men as these. A few years ago there was hardly such a thing as a paid chemical editorial position in this country. Now there are a few, and the number is sure to increase as the literature of the science becomes larger and larger. Is it not much better to discover the men that are naturally adapted to this work, train and promote them, than to select men because they have distinguished themselves in some other way in chemistry? For this reason it is a hopeful sign that the principle of promotion is being applied in the office of *Chemical Abstracts;* the Society will thus be best served and a better class of men can be secured to fill the subordinate positions.

AUSTIN M. PATTERSON

## THE ANNUAL MEETING OF THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS

The program of the last meeting of the American Society of Mechanical Engineers contained much material of direct interest to industrial chemists.

One day was devoted, under the direction of the Committee on Public Relations, to a consideration of the engineering questions involved in municipal administration. The purpose of this discussion was to direct the attention of good engineers to municipal opportunities and to get politicians, investigators and reformers to recognize and adopt engineering methods which are constructive instead of destructive, and which are based on facts rather than on opinions.

Another feature of the meeting was the formulation of a standard law for the regulation, construction, operation and inspection of steam boilers and other large pressure vessels, in the interests of public safety. This law was formulated to serve as a model for use by the different state legislatures and thus aid in unifying the existing laws. Many states now have either no laws at all or very bad ones. The present laws of some states even permit them to become the dumping ground for discarded boilers from other states.

The human element, the key to economic problems, was the subject of the presidential address by James Hartness. Mr. Hartness pointed out that the world of mechanism has become so intricate and complex that it has gone beyond the capacity of any single individual; that each person must be content to comprehend only a small part, and that it is only by selecting the character and limiting the amount of material taken into individual minds that the best results can be accomplished. Carrying the principles of the individual into the realm of organized industry, he points out that large organizations are essential as affording the opportunity for the most complete subdivision of work and the greatest degree of specialization, both of which lead to the most efficient employment of human energy. A most important element therefore in a large manufacturing plant is its organization. Without this the buildings and equipment are of little value. The greatest good to the greatest number requires taking into consideration each human being, his desires and his needs in finding the work for which he is best endowed.

President Hartness recommends that in addition to the regular treasurer's report, each industrial unit should have a human report, beginning with a description of the directors and going through the entire organization. It should contain a statement regarding the elements of harmony of the organization, the length of service of manager and workers, frequency of change of methods or articles manufactured, intelligence of executives in the management of men, the degree of contentment of each member, the extent to which each man in the organization approaches the best position for which he is endowed, how nearly he obtains the best remuneration for which he is qualified, the extent to which the management recognizes the inertia of habit of both mind and body, the degree in which the various men in the organization approximate the condition of highest efficiency, the extent to which the management

goes in the expression of appreciation, the degree of its knowledge of the most important characteristics of man as indicated by his inner motives and desires and the condition of his mind as he goes to his home. Finally, all of these elements should be carefully appraised and the average should be the rating of the company. Mr. Hartness thinks that an investor, considering this human rating along with the treasurer's statement, would seldom make a mistake in estimating the true worth of an industrial organization.

# ORIGINAL PAPERS

## PHYSICAL PROPERTIES OF THE METAL COBALT[1]

By Herbert T. Kalmus and C. Harper

Received October 1, 1914

This paper is the third of a series describing investigations of the metal cobalt and its alloys. It is a report on a large number of measurements made at this laboratory of some of the important physical and mechanical properties of metallic cobalt. The properties which have been particularly studied are:

1—Density
2—Hardness
3—Melting Point
4—Tensile Strength
5—Compressive Strength
6—Rolling and Turning Properties
7—Electrical Resistance
8—Magnetic Permeability
9—Specific Heat

### PREPARATION OF METALLIC COBALT FOR THE STUDY OF ITS PHYSICAL PROPERTIES

It is true of cobalt, as of most metals, that its physical properties are often greatly influenced by the presence of small percentages of impurities. It is well known, for example, that less than 0.01 per cent of arsenic in copper is sufficient to account for a drop in its electrical conductivity[2] of 3.3 per cent. Similarly, for cobalt we find that a few tenths of a per cent of impurities often doubles or trebles its electrical resistance (see Tables VI and VII).

The cobalt for these investigations has been prepared by reduction of cobalt oxide, $Co_3O_4$. Commercial oxide was obtained from the smelters, and after a crude purification, was reduced to form what we shall call "commercial cobalt;" also the commercial oxide was purified to a high degree, from which has been prepared what we style "pure cobalt." These two names are used in this paper largely for brevity and convenience; the analysis of each sample is given with the data of its properties. The properties of each of these have been measured and will be discussed separately.

The methods of preparation of the pure and commercial cobalt used in these researches are given in the original paper, and outlined in "Preparation of Metallic Cobalt by Reduction of the Oxide."[1]

color—Pure metallic cobalt very much resembles nickel in color, although, when plated and polished under proper conditions, while beautifully white, it possesses a slightly bluish cast. Sometimes it deposits as a black matte. Metallic cobalt which has been reduced from the oxide at a sufficiently low temperature is a gray powder.

Table I—Density of Cobalt

All samples were cast from just above melting point in an iron mould and allowed to cool in the mould
Except in cases noted, all samples were then turned in the lathe to their final form

| Sample No. | Analysis | | | | Date | Form of sample | Special treatment | Density Value at °C.[2] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| "Commercial Cobalt"—Unannealed | | | | | | | | | | |
| H 109 | Co 96.8<br>Ni 0.56 | Fe 2.36<br>C 0.063 | S 0.022<br>P 0.017 | | Dec. 8, 1913 | Cylindrical bar | None | 8.7997 | 18.5 | See Fig. IX |
| H 130 | Co 96.5<br>Ni 2.0 | Fe 1.27<br>C 0.305 | S 0.054<br>P 0.015 | | Feb., 1914<br>Average of 5 | Thin cylindrical bar | None | 8.7690 | 17.0 | See Fig. IV |
| H 87c | Co 97.8<br>Ni 0.5 | Fe 1.46<br>C 0.18 | S 0.024<br>P Trace | Si 0.02<br>Ca Trace | Feb., 1914<br>Average of 4 | Cylindrical bar | None | 8.6658 | 17.0 | See Fig. VIII |
| Pure Cobalt—Unannealed | | | | | | | | | | |
| H 212 | Co 99.9<br>Ni None | Fe 0.20<br>C None | S 0.017 | Si None<br>Ca None | Jan.-Feb., 1914<br>Average of 6 | Cylindrical bar | None | 8.7562 | 17.0 | See Fig. I |
| H 214 | Co 98.71<br>Ni None | Fe 1.15<br>C 0.039 | S 0.012<br>P 0.010 | Si 0.14<br>Ca None | Apr. 3, 1914 | Wire of 0.0901 cm. diam | Swaged, see p. 11 | 8.8490 | 15.0 | See Fig. III |
| H 193 | Co 99.1<br>Ni None | Fe 0.80 | S 0.021 | Ca Trace | Nov. 15, 1913 | Cylindrical bar | None | 8.7889 | 20.0 | |
| H 213 | Co 99.73<br>Ni None | Fe 0.14<br>C None | S 0.019 | Si 0.02 | Jan.-Feb., 1914<br>Average of 3 | Cylindrical bar | None | 8.7732 | 16.0 | See Fig. II |
| Pure Cobalt—Annealed | | | | | | | | | | |
| H 212 | Co 99.9<br>Ni None | Fe 0.20<br>C None | S 0.017 | Si None<br>Ca None | Jan. 12, 1914<br>from 700° C. | Thin cylindrical bar | Annealed from 700° C | 8.8105 | 14.5 | |
| Pure Cobalt—Rolled | | | | | | | | | | |
| H 213 | Co 99.73<br>Ni None | Fe 0.14<br>C None | S 0.019 | Si 0.02 | Jan. 19, 1914 | Thin cylindrical bar | Swaged | 8.9278 | 14.0 | |
| H 212 | Co 99.9<br>Ni None | Fe 0.20<br>C None | S 0.017 | Si None<br>Ca None | Jan. 23, 1914 | Wire of 0.0840 cm. diam. | Swaged | 8.9227 | 19.0 | |

### 1—DENSITY (SPECIFIC GRAVITY)

The densities of both cast and rolled cobalt were determined in this laboratory by the Archimedes method. A sphere or cylinder of the material was weighed, using a delicate balance, both in air and under water. In the computations the weighings were corrected for the buoyancy of the air, and the measurements reduced so as to be expressed in terms of water at its maximum density. Table I gives the results.

A number of density determinations of metallic cobalt, as made by other investigators, are recorded in the literature, most of which, however, were made at an early date, and very little is said of the nature of the metal. The following table of values is taken

[1] Authors' abstract of report under the above title to the Canadian Department of Mines. Published by permission of the Director of Mines, Ottawa, Canada. This publication is one of a series on the general investigations of the metal cobalt and its alloys, with reference to finding increased commercial usages for them. These are being conducted at the School of Mining, Queen's University, Kingston, Ontario, for the Mines Branch, Canadian Department of Mines. See This Journal, 6 (1914), 107 and 115.

[2] J. H. Dellinger, "The Temperature Coefficient of Resistance of Copper," U. S. Bureau of Standards, *Bull.* 7 (1911), 79.

[1] This Journal, 6 (1914), 107, *Bull.* 259, Mines Branch, Dept. of Mines, Ottawa, Canada.

from the more recent and probably more accurate of them:

DENSITY OF COBALT

| Other workers | | | Kalmus and Harper | | |
|---|---|---|---|---|---|
| Tilden(a) | 8.718 | 21° C. | Unannealed | 8.7918 | 17.0° C. |
| G. Neumann and F. Streintz(b) | 8.6 | ... | Annealed | 8.8105 | 14.5° C. |
| Copaux(c) | 8.8 | 15° C. | | | |
| Winkler(d) | 7.9678 | ... | Swaged | 8.9253 | 16.5° C. |

(a) *Chemical News*, **78** (1898), 16.
(b) *Monatshefte für Chemie*, Vienna, **12** (1891), 642.
(c) *Annalen de Chimie et de Physique*, [8] **6** (1905), 508.
(d) *Berg und hüttenmännische Zeitung*, **39** (1880), 87.

The values from the literature are generally lower than those measured by us, no doubt because of impurities in the metal, or because of the difficulties of casting without occluding a certain amount of gas.

## 2—HARDNESS

Hardness measurements were made in this laboratory on a standard Olsen hardness testing machine of 100,000 lbs. capacity. (Tinius Olsen Co., Philadelphia, Pa.) The machine consists of a framework on which is mounted a lever system. To one end of this lever system a penetrating ball is attached, while at the other, weights are attached, which, when applied, cause motion of the lever system and penetration of the ball into the metal to be tested. An instrument is mounted on the main lever which measures automatically the actual penetration of the steel ball to 0.0001 of an inch.

All hardness measurements of the metal cobalt made by us have been computed in the Brinell system, and have been made with a sphere of one centimeter diameter, and with a load of 3500 pounds, unless stated otherwise.

We have measured the Brinell hardness of a series of common substances under the identical conditions that we have used for cobalt, and a table of these values is given below for comparison. In each instance the value is the mean of a number of observations, and they are reproducible, on the same sample, to within a few per cent. Different samples of most of these materials give values differing considerably among themselves. This table is given merely to serve as a rough basis of comparison.

COMPARISON TABLE OF BRINELL HARDNESS

| | Load, Lbs. | Brinell Hardness | | Load, 3500 lbs. | Brinell Hardness |
|---|---|---|---|---|---|
| Copper | 1000 | 65.6 | Mild Steel | | 109.9 |
| Rolled | 1000 | 67.4 | Cold rolled shafting | | 126.2 |
| Sheet | 3500 | 75.0 | Tool Steel | | 153.8 |
| Unannealed | 3500 | 81.9 | "Crescent" | | 130.2 |
| Swedish Iron | 3500 | 90.7 | Spring Steel | | 160.3 |
| | 1000 | 68.6 | | | 178.0 |
| | | | Tool Steel | | |
| | 3500 | 75.2 | Self Hardening | | 180.0 |
| Wrought Iron | 3500 | 92.0 | "Rex," before hardening | | 162.1 |
| | 1000 | 83.1 | "Rex," after hardening. | | 240.0 |
| | 3500 | 100.2 | | | |
| Cast Iron | 3500 | 97.8 | Self hardening from School | | |
| | 1000 | 84.4 | of Mining Workshop | | 259.0 |
| | 3500 | 104.5 | | | |

COBALT FOR BRINELL HARDNESS MEASUREMENTS—The hardness of cobalt, like that of most other metals, is determined to a greater extent by its physical and mechanical treatment than by slight variations in its chemical composition, if we except the presence of carbon. Even our "commercial cobalt" contains but small percentages of total impurities of which the greater part is iron and nickel, and which, in the small amounts present, would not greatly affect the hardness.

Table II reports the hardness measurements made. In the samples under "commercial cobalt" the percentage of carbon is given throughout, and the other impurities are between the following limits:

TABLE II—BRINELL HARDNESS OF COBALT

All samples were cast from just above melting point, allowed to cool in iron mould and turned in lathe
Special treatments beyond this are noted below. Load 3500 lbs. unless given otherwise

| Sample No. | Analysis | | | | | | Date | Special treatment | Brinell hardness | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| "Commercial Cobalt" | | | | | | | | | | |
| H 109 | C | 0.062 | S | 0.022 | P | 0.017 | 12/ 9/1913 | None | 111.4 | |
| | | | | | | | 1/14/1914 | None | 100.9 | See Fig. IX |
| | | | | | | | 12/11/1913 | None | 104.4 | Metal soft, tough and turns with medium long curling chip |
| | | | | | | | 12/22/1913 | None | 111.7 | |
| | | | | | | | 9/15/1914 | None | 100.2 | |
| H 214c | Co | 97.09 | Fe | 1.45 | Si | 0.011 | 9/15/1914 | Annealed from 850° C. | 138.6 | See Fig. V |
| | Ni | None | C | 0.067 | P | 0.010 | 9/15/1914 | Annealed from 1000° C. | | |
| | Mn | 2.04 | S | 0.012 | Ca | None | | | 136.9 | See Fig. VI |
| | Co | 98.7 | Fe | 1.15 | Si | 0.14 | 9/15/1914 | None | 123.9 | See Fig. III |
| | Ni | None | C | None | P | 0.011 | | | | |
| | | | S | 0.012 | Ca | None | | | | |
| H 211 | C | 0.10 | | | | | 1/14/1914 | None | 128.2 | Metal soft and medium tough. Machines with long curling chip. See Fig. X |
| | | | | | | | 9/15/1914 | None | 130.7 | |
| H 87c | C | 0.13 | S | 0.022 | P | 0.012 | 1/16/1914 | None | 131.0 | Metal medium hard and tough. Machines with curling chip. See Fig. VIII |
| H 87a and e | C | 0.22 | S | 0.03 | P | None | 12/22/1913 | None | 119.3 | |
| | | | | | | | 9/15/1914 | Quenched from 1200° C. | 132.9 | |
| H 130 | C | 0.305 | S | 0.054 | P | 0.015 | 12/11/1913 | Quenched from 1200° C. | 115.0 | Metal short grained, brittle and turns with short chip |
| | | | | | | | 9/15/1914 | Quenched from 1200° C. | 113.8 | |
| | | | | | | | 1/14/1914 | None | 116.6 | Metal soft and tough. Machines with curling chip. See Fig. IV |
| H 87d and b | C | 0.36 | S | 0.016 | P | None | 2/ 1/1913 | None | 112 | Very tough to turn in lathe |
| | C | 0.37 | S | 0.015 | P | None | 2/ 1/1913 | None | 117 | |
| Pure Cobalt | | | | | | | | | | |
| H 193 | Co | 99.1 | Fe | 0.80 | S | 0.02 | 11/15/1913 | None | 129.7 | Load 2500 lbs. Metal soft and brittle. Machines with short chip |
| | Ni | None | C | None | Ca | Trace | | | | |
| | | | | | | | 12/ 9/1913 | None | 133.4 | |
| | | | | | | | 11/15/1913 | None | 131.2 | |
| H 212 | Co | 9.99 | Fe | 0.20 | S | 0.017 | 1/ 9/1914 | None | 105.5 | Load 2500 lbs. |
| | Ni | None | C | None | | | | | | |
| | | | | | | | 1/14/1914 | None | 128.7 | Metal soft and brittle. Machines with short chip. See Fig. I |
| | | | | | | | 1/14/1914 | Annealed from 700° C. | 130.8 | Load 2500 lbs. |
| H 213 | Co | 99.73 | Fe | 0.14 | S | 0.019 | 1/14/1914 | Annealed from 700° C. | 121.0 | Metal soft and brittle. Machines with short chip See Fig. II |
| | Ni | None | C | None | | | | | | |
| H 217 | Co | 99.55 | | | | | 9/15/1914 | Annealed two hours at 600° C., allowed to cool slowly, and again turned in lathe | 125.9 | |
| | | | | | | | 9/15/1914 | None | 109.5 | |

| | | | |
|---|---|---|---|
| S..... | 0.010 to 0.070 per cent | Fe..... | 0.10 to 1.0 per cent |
| Ca..... | Trace to 0.015 per cent | Ni..... | Trace to 0.50 per cent |
| Si..... | Trace to 0.20 per cent | C..... | 0.10 to 0.60 per cent |

The total impurities in any one sample of this "commercial cobalt" rarely exceeded 1.5 per cent.

BRINELL HARDNESS MEASUREMENT—A single measurement of the Brinell hardness is given in full to show the concordance of observations among themselves, and the details of computation. This may be taken as typical of the large number of measurements which were made.

| Sample H 193 Initial reading | Dec. 9, 1913 Reading under load | Load, 3500 Lbs. Indentation (in.) |
|---|---|---|
| 0.0344 | 0.0489 | 0.0145 |
| 0.0333 | 0.0480 | 0.0147 |
| 0.0309 | 0.0465 | 0.0156 |
| 0.0321 | 0.0468 | 0.0147 |

Average, 0.0149 in. = 0.379 mm

$$\text{Brinell hardness by definition} = \frac{\text{total pressure in kg.}}{\text{area of depression in mm.}^2} = \frac{P}{2\pi rh}$$

where, $P$ = Load in kg.
$r$ = radius of indenting ball in mm.
$h$ = depth of depression in mm.

$$\therefore \text{Brinell hardness} = \frac{3500}{22} \times \frac{1}{2 \times \pi \times 5 \times 0.379} = 133.4$$

HARDNESS OF COBALT AS OBSERVED BY OTHER INVESTIGATORS—There is very little in the literature on the hardness of cobalt, except a few more or less qualitative observations. However, a careful measurement seems to have been made by R. Reur and K. Kaneko,[1] from which they compute the Brinell hardness of cobalt to be 132.

COMPARATIVE HARDNESS OF NICKEL AND COBALT—For comparison we have measured the hardness of both cast and sheet nickel under the same conditions that we have used for cobalt, load 3500 lbs., and found them to be, respectively, 83.1 and 85.1 Brinell, the latter for a 1/4 inch sheet. An independent check test on the hardness of cast nickel gave as a result 76.4.

CONCLUSIONS—HARDNESS

I—Table II shows the Brinell hardness of cobalt cast from just above the melting point, and allowed to cool in an iron mould, to be in the neighborhood of 124.0 (load 3500 lbs.). This is the mean of nine observations with an average deviation from the mean of 7.9.

II—The hardness of cobalt cast from just above its melting point is considerably greater than that of either iron or nickel, under corresponding conditions.

III—The effect of the addition of 0.060 to 0.37 per cent of carbon on the hardness of "Commercial" cobalt is not sufficient to offset the effect of slight variations in heat treatment. The measurements are not sufficiently concordant to warrant drawing general conclusions.

3—MELTING TEMPERATURE OF COBALT

A considerable number of melting point determinations of the metal cobalt were made in an Arsem electric vacuum furnace (General Electric Company, Schenectady, N. Y.). These determinations were carried out by the usual cooling or melting curve method, using pure alumina crucibles and alundum lined graphite crucibles.

Cobalt has a very sharp melting point, differing in this respect from iron, which becomes plastic as it approaches its melting point. With iron the actual temperature of melting is not sharply defined, there being a considerable transition region, whereas with cobalt quite the reverse is true. Therefore, the melting point of cobalt may be determined with accuracy by the cooling and melting curve method.

TEMPERATURE MEASUREMENTS—Temperature observations were made with a Wanner optical pyrometer, which was checked against an amyl acetate lamp standard before and after each set of runs, in accordance with a calibration certificate from the Physikalisch-Technische Reichsanstalt, at Charlottenburg. This pyrometer was also used to measure the melting points of copper and nickel during the period of its use for the determinations on cobalt, which measurements agreed with the calibration curve used to within a few degrees. For this work the melting point of nickel was considered to be 1444° C., and of copper to be 1084° C.

The melting point of nickel, considering our calibration curve from the Reichsanstalt to be correct, was determined six times as follows:

| ° C. | Deviation from the mean |
|---|---|
| 1438 | 6 |
| 1437 | 7 |
| 1445 | 1 |
| 1446 | 2 |
| 1448 | 4 |
| 1450 | 6 |
| 1444 Mean | 4.33 C. Average |

The nickel (see Fig. XI) used for these melting point measurements analyzed as follows:

| | | | |
|---|---|---|---|
| Ni..... | 99.29 | Ca..... | None |
| Fe..... | 0.48 | C..... | None |
| S..... | 0.025 | Co..... | None |
| Si..... | 0.042 | Total, 99.84 per cent | |

The cobalt (Sample No. 212—see Fig. I) used for these melting point determinations analyzed as follows:

| | | | |
|---|---|---|---|
| Co..... | 99.9 | Ca..... | None |
| Ni..... | None | Si..... | None |
| Fe..... | 0.20 | C..... | None |
| S..... | 0.017 | Total, 100.12 per cent | |

TABLE III—SUMMARY OF RESULTS OF MELTING POINT DETERMINATIONS

| Date of run | Determined melting point of cobalt | Deviation of single observation from the mean |
|---|---|---|
| Sept. 27, 1912 | 1474° C. | 7 |
| Sept. 30, 1912 | 1472 | 5 |
| Sept. 30, 1912 | 1472 | 5 |
| Oct. 1, 1912 | 1470 | 3 |
| Oct. 1, 1912 | 1472 | 5 |
| Jan. 13, 1914 | 1467 | 0 |
| Jan. 13, 1914 | 1467 | 0 |
| Jan. 14, 1914 | 1460 | 7 |
| Jan. 15, 1914 | 1453 | 14 |
| Jan. 15, 1914 | 1468 | 1 |
| Jan. 15, 1914 | 1468 | 1 |
| Jan. 19, 1914 | 1462 | 5 |
| Jan. 19, 1914 | 1460 | 7 |
| Jan. 19, 1914 | 1470 | 3 |
| Jan. 19, 1914 | 1462 | 5 |
| Jan. 19, 1914 | 1470 | 3 |
| Mean melting temperature, | 1467° C. | Average, 4.4° C. |

From these observations the melting point of pure cobalt would appear to be 1467° C. ± 1.1° C. [Note, however, conclusions below, second paragraph.]

It should be noted that Burgess and Waltenberg[1] use the value 1452° C. as the melting temperature of nickel. If we adopt this value instead of 1444° C. (see below), our value for the melting temperature of cobalt would be practically identical with theirs, namely, 1478° C.

[1] *Trans.*, **10**, [illegible] **1913**, p. 3891.

[1] United States Bureau of Standards, *Bull.* **10** (1913), 6.

THE MELTING POINT OF COBALT AS DETERMINED BY OTHER INVESTIGATORS

| Investigator | Melting temperature | Purity Per cent | Method of measurement |
|---|---|---|---|
| Burgess and Waltenberg(*a*) | 1477° C. | 99.95 | Micropyrometer |
| Burgess and Waltenberg(*a*) | 1478° C. | 99.95 | Crucible melts in electric furnace |
| C. K. Burgess(*b*) | 1464° C. | Very pure | Micropyrometer |
| H. Copaux(*c*) | 1530 | Not given | Interpolation between gold and platinum points |
| Guertler and Tammann(*d*) | 1528 | 98.3 Rest largely Ni and Fe | Cooling curve |
| Guertler and Tammann(*e*) | 1468 | 98.3 | Cooling curve |
| Guertler and Tammann(*f*) | 1505 | 98.3 | Cooling curve |
| Guertler and Tammann(*e*) | 1455 | 98.3 | Cooling curve |
| R. Raer and K. Kaneko(*g*) | 1491 | .. | ..... |

(*a*) Bureau of Standards, *Bull.* **9** (1912), 475; *Bull.* **10** (1913), 13.
(*b*) *Ibid.*, *Bull.* **3** (1906), 350.
(*c*) *Annalen de Chimie et de Physique*, [8] **6** (1905), 508.
(*d*) *Zeitschrift für anorganische Chemie*, **42** (1904), 353.
(*e*) Their value corrected for melting point of nickel = 1451 instead of 1484 as taken by them.
(*f*) *Zeitschrift für anorganische Chemie*, **46** (1905), 223.
(*g*) *Ferrum*, **11** (1913), 33–9.

## CONCLUSIONS—MELTING TEMPERATURE

The melting temperature of cobalt, as determined by us, is 1467 ∓ 1.1° C. This is for metal 99.9 per cent pure, and is the mean of 16 determinations by the cooling and heating curve method.

This value of the melting temperature is based upon pyrometer calibration curves, considering the value of the melting temperature of nickel to be 1444° C. If we adopt the more probable value 1452° C., for the melting temperature of nickel, **our melting temperature for cobalt is 1478° C. ∓ 1.1° C.**

## 4—TENSILE STRENGTH MEASUREMENTS

The tensile strength tests were made on a Riehle universal standard vertical screw power testing machine (Riehle Testing Machine Co., Philadelphia, Pa.), of 100,000 lbs. capacity, operated by direct connection to an electric motor.

TEST BARS—All bars for tensile strength measurements have been "Proportional Bars," as recommended and adopted by the International Association for Testing Materials.

Table IV reports the data for our measurements on "commercial cobalt" and on pure cobalt.

There is almost no literature on the tensile strength of cobalt, although Copaux[1] gives—cobalt 69,000 lbs per sq. in., nickel 58,000 lbs. per sq. in.

We measured the tensile strength of pure iron and pure nickel at this laboratory, under conditions similar

[1] *Annalen de Chimie et de Physique*, [8] **6** (1905), 508.

TABLE IV—TENSILE STRENGTH MEASUREMENTS OF COBALT

All samples (except wires) were cast from just above melting point in an iron mould and allowed to cool in the mould
Special treatments beyond this are noted below

| Sample No. | Analysis | Date | Special treatment | Lbs. per Sq. In. Tensile breaking load | Yield point | Percentage Reduction in area | Elongation in 2 in. | Remarks |
|---|---|---|---|---|---|---|---|---|
| | "Commercial Cobalt"—Unannealed | | | | | | | |
| H 109 | Co 96.8 Fe 2.36 S 0.022 Ni 0.56 C 0.062 P 0.017 Si None Ca None | 12/ 9/1913 | None | 48,700 | 33,800 | 7.7 | 5.5 | Fairly fine-grained fracture |
| | | 12/ 9/1913 | None | 52,800 | 33,800 | 8.7 | 7.0 | Tough and difficult to machine in lathe. Long curling chip |
| | | 12/16/1913 | None | 57,200 | 15,300 | 24.5 | 21.9 | |
| | | 12/22/1913 | None | 64,100 | 9,360 | 25.4 | 27.0 | Fracture coarsely granular and not uniform in appearance |
| H 15 | Co 98.5 Fe 1.0 S 0.020 Ni 0.3 C 0.18 Ca None Si None P None | 2/15/1913 | None | 76,700 | 33,800 | 7.7 | 6.5 | |
| H 87*c* | Co 97.8 Fe 1.46 Si 0.020 Ni 0.5 C 0.18 Ca None S 0.02 P 0.012 | 1/23/1914 | None | 56,100 | 30,600 | 5.3 | 5.0 | Metal medium hard and tough. Long curling chip. See Fig. VIII |
| H 87*f* | Co 98.7 Fe 0.80 Si 0.020 Ni 0.2 C 0.22 P None S 0.029 Ca None | 4/ 5/1913 | None | 75,000 | 33,700 | 25.4 | 29.7 | Very tough to machine in lathe |
| H 87*b* | Co 98.5 Fe 0.80 Si 0.020 | 2/10/1913 | None | 63,200 | 33,100 | 24.1 | 24.0 | |
| H 87*d* | Ni 0.2 C 0.37 P None S 0.016 Ca None | 2/10/1913 | None | 77,700 | 33,900 | 23.8 | 24.0 | |
| H 211 | C 0.18 S 0.08 P 0.031 | 12/22/1913 | None | 31,000 | 31,000 | None | None | Segregation of impurities. See Fig. X |
| | "Commercial Cobalt"—Annealed | | | | | | | |
| H 109 | Co 96.8 Fe 2.36 Si None Ni 0.56 C 0.062 P 0.017 S 0.022 Ca None | 1/ 9/1914 | Annealed from 700° C. | 56,100 | 29,300 | 13.3 | 13.0 | Metal soft and tough. Machines with medium long curling chip |
| | | 1/14/1914 | Annealed from 700° C. | 52,600 | 31,600 | 13.3 | 13.5 | See Fig. IX |
| H 214*c* | Co 97.09 Fe 1.45 Si 0.011 Ni None C 0.067 P 0.10 Mn 2.04 S 0.012 Ca None | 5/19/1914 | Annealed at 850° C. | 70,500 | 37,100 | 5.1 | 8.0 | Very fine grain, uniform. See Fig. V |
| | | 5/19/1914 | Annealed at 1000° C. | 75,200 | 25,500 | 6.1 | 10.0 | Very fine grain, uniform. See Fig. VI |
| H 87*c* | Co 97.8 Fe 1.46 Si 0.020 Ni 0.5 C 0.18 P 0.012 S 0.02 Ca None | 4/22/1914 | Annealed at 850° C. | 60,200 | 40,800 | 1.5 | 1.5 | Very fine grain, uniform. See Fig. VII |
| | | 5/19/1914 | Annealed at 850° C. | 53,700 | ..... | ..... | 2.0 | |
| | | 6/ 2/1914 | Annealed at 850° C. | 63,800 | 61,300 | 0.61 | 0.5 | Very fine grain |
| | | 6/ 2/1914 | Annealed at 850° C. | 58,000 | 56,100 | 1.5 | 0.3 | Very fine grain |
| | | 6/10/1914 | Annealed at 950° C. | 57,000 | 18,000 | 2.57 | 2.0 | Fracture fine-grained but not uniform in appearance |
| | | 6/10/1914 | Annealed at 950° C. | 58,500 | 20,400 | 3.4 | 2.0 | |
| | | 6/15/1914 | Annealed at 1000° C. | 65,000 | 55,000 | 3.1 | 1.9 | |
| | | 6/15/1914 | Annealed at 1000° C. | 62,300 | 40,800 | 3.1 | 1.9 | |
| | | 6/17/1914 | Annealed at 1000° C. | 42,600 | 40,800 | 0.61 | 0.5 | Fine-grained fracture |
| | | 6/18/1914 | Annealed at 1000° C. | 56,000 | 46,000 | 1.3 | 1.0 | |
| | Pure Cobalt—Unannealed | | | | | | | |
| H 212 | Co 99.9 Fe 0.20 Ni None C None S 0.017 | 1/ 9/1914 | None | 29,600 | 10,200 | 1.5 | 2.0 | Fracture coarse-grained and crystalline |
| | | 1/16/1914 | None | 35,400 | 31,400 | 0.5 | 4.0 | Metal soft and brittle. Short chip |
| | | 1/23/1914 | None | 43,400 | 43,400 | None | None | Fracture coarse-grained and crystalline |
| | | 1/23/1914 | None | 45,800 | 25,500 | 1.5 | 0.5 | Fracture coarse with radially crystalline structure |
| | | 1/26/1914 | None | 23,000 | 23,000 | None | None | Fracture coarse with radially crystalline structure. Metal soft and brittle. Short chip |
| H 213 | Co 99.73 Fe 0.14 Ni None C None S 0.019 | 2/ 3/1914 | None | 37,900 | 37,900 | None | None | Fracture good with fine grain. See Fig. I |
| | | 1/23/1914 | None | 30,600 | 30,600 | None | None | Fracture coarse-grained, crystalline. |
| | | 1/23/1914 | | 30,100 | 30,100 | None | None | Metal soft and brittle. Machines with short chip |
| | | 1/23/1914 | None | 23,000 | 23,000 | None | None | |
| | | 2/ 3/1914 | None | 45,300 | 23,000 | 3.0 | 3.6 | Fracture good, fine-grained. See Fig. II |
| | Pure Cobalt—Annealed | | | | | | | |
| H 212 | Co 99.9 Fe 0.20 Si None Ni None C None Ca None S 0.017 | 1/14/1914 | Annealed from 700° C. | 41,200 | 41,200 | None | None | Fracture coarse-grained, crystalline |
| | | 1/27/1914 | Annealed from 700° C. | 28,100 | 28,100 | None | None | Fracture fairly fine structure. See Fig. I |
| H 217 | Co 99.2 Fe 0.730 Si 0.091 Ni None C 0.036 P 0.0077 Al 0.021 S 0.016 Ca None | 6/16/1914 | Annealed at 950° C. | 34 800 | 26,600 | 0.30 | 0.25 | Fracture fine-grained and uniform |
| | | 6/17/1914 | Annealed at 950° C. | 43,600 | 30,600 | 1.3 | 1.0 | |
| Wires | | | | | | | Diam. | |
| H 213 | Co 99.73 Fe 0.14 Ni None C None S 0.19 | 1/29/1914 | Swaged to wire after special treatment (see pp. 11 & 12) | 101,800 | ..... | 5.0 | 8.2 | 0.117 in. |
| | | 2/11 1914 | | 77,000 | | 1 0 | 2 0 | 0 124 in |
| | | 3/24 1914 | | 90,500 | | 8 3 | | 0 076 in. Fine-grained fracture |

to those for our cobalt tensile strength measurements. The iron used for these measurements analyzed:

| | | | |
|---|---|---|---|
| Fe..... | 99.9 per cent | Mn..... | 0.031 per cent |
| S..... | 0.023 per cent | Cu..... | 0.028 per cent |
| P..... | 0.004 per cent | Si..... | Trace |
| C..... | 0.010 per cent | Ni and Co | None |

The nickel (see Fig. XI) used for the tensile strength tests was the same as that used for the melting point determinations.

A large series of measurements on nickel and iron would be required to fix the values of the tensile strengths with any definiteness; our measurements show them to be approximately as follows:

Cast Nickel—Tensile Breaking Load 18,000 Lbs. per Sq. In.
Cast Iron—Tensile Breaking Load 23,000 Lbs. Per Sq. In.

The rate of cooling of cast metals from the fluid to the solid state is such an important factor in determining the mechanical properties of the metal, that it is just as necessary to know the dimensions of the test bars as it is to know the chemical composition. The above values, for iron, nickel and cobalt, all of which have been made under exactly the same conditions, with a standard "proportional" test bar, are strictly comparable, although they should not be compared with values obtained by other observers on bars of different sizes.

### CONCLUSIONS—TENSILE STRENGTH

PURE COBALT. I—The tensile strength of pure cobalt, cast and unannealed, is in the neighborhood of 34,400 lbs. per sq. in. This is the average of 10 measurements on cobalt cast from just above its melting point, allowed to cool in iron mould, and machined in lathe to test bars.

II—The effect on the tensile strength of annealing cast cobalt is to increase its value slightly, although this effect is not marked. The average value of our determinations was 36,980 lbs. per sq. in. for the annealed samples, as compared with 34,400 lbs. per sq. in. for the unannealed samples.

III—The percentage reduction in area and elongation are small for cast pure cobalt as would be expected for the pure metal.

IV—The tensile yield point for pure cobalt is in general very close to the tensile breaking load.

V—The tensile strength of pure cobalt increases very rapidly as the metal is rolled, as is common for most metals. It may easily reach over 100,000 lbs. per sq. in. by being swaged down to a wire.

VI—The tensile breaking load of pure cobalt, cast from just above the melting temperature, allowed to cool in iron mould and turned in lathe to test bar, is greater than either that of iron or nickel prepared and tested under the same conditions.

"COMMERCIAL COBALT." VII—The effect of the addition of carbon is to increase the tensile breaking strength of cobalt very markedly, the value rising from 34,400 lbs. per sq. in. for the pure cast and unannealed metal to in the neighborhood of 61,000 lbs. per sq. in. for cobalt carrying from 0.060 to 0.30 per cent carbon. More exactly, the average of eight measurements, with a carbon content of approximately 0.062 per cent, is 59,700 lbs. per sq. in. Similarly, the average of fifteen measurements, with a carbon content varying in the neighborhood of 0.25 per cent, is 61,900 lbs. per sq. in. However, the average deviation of these individual measurements among themselves is such that no more specific conclusion can be attached thereto. These values refer to cobalt cast from just above the melting point, allowed to cool in iron mould, machined in a lathe, and tested unannealed. The increased tensile strength may not be entirely due to the presence of carbon, for these tests were made on "commercial cobalt."

VIII—The effect of carbon and other impurities in the "commercial cobalt" is to greatly increase the percentage reduction and elongation, which rises in most cases well above 20 per cent.

### 5—COMPRESSIVE STRENGTH MEASUREMENTS

The measurements of the compressive strength of cobalt were made in the same Riehle universal standard vertical screw power testing machine, of 100,000 lbs. capacity, that was used for the tensile strength measurements.

TEST BARS—All bars for compressive strength measurements were $1^1/_2$ in. long and $^3/_4$ in. in diameter.

There is practically no literature on the compressive strength of cobalt.

We measured the compressive yield point of pure nickel (see Fig. XI) under conditions identical with the above measurements for cobalt and found it to be 20,000 lbs. per sq. in. This was for a sample cast from just above the melting temperature, allowed to cool in iron mould, and tested unannealed.

### CONCLUSIONS—COMPRESSIVE STRENGTH

PURE COBALT. I—The compressive strength of pure cobalt, cast and unannealed, is in the neighborhood of 122,000 lbs. per sq. in. This is the average of 5 measurements on cobalt cast from just above its melting point, allowed to cool in iron mould, and machined in lathe to test bars.

II—The effect of annealing on the compressive strength of cast pure cobalt is not very marked; the average of 5 measurements of the compressive strength of annealed cast cobalt is 117,200 lbs. per sq. in. There seems to be a tendency to lower the compressive strength by annealing.

III—The compressive yield point of pure cobalt is 56,100 lbs. per sq. in. for the annealed samples, compared with 42,200 lbs. per sq. in. for the unannealed samples. Thus the yield point seems to be slightly raised by annealing.

IV—The compressive yield point of pure cobalt, cast from just above the melting temperature, allowed to cool in iron mould and machined in lathe to test bar, is considerably greater than that of either pure iron or nickel prepared and tested under the same conditions.

"COMMERCIAL COBALT." V—The effect of the addition of carbon is to increase the compressive breaking strength of cobalt, the value rising well above 175,000 lbs. per sq. in. by the addition of from 0.060 to 0.30 per cent carbon. These values refer to cobalt cast from just above the melting point, allowed to cool in

iron mould, machined in lathe, and tested unannealed. The increased compressive strength may not be entirely due to the presence of carbon, for these tests were made on "commercial cobalt."

VI—The effect of carbon and other impurities in the "commercial cobalt" does not seem greatly to affect the yield point through the range of our observation, although on the average from 0.20 to 0.30 per cent of carbon, with the other impurities shown, tends to lower it from 5 to 10 per cent for both annealed and unannealed metal.

VII—The effect of annealing "commercial cobalt" is to lower its compressive strength, our values averaging 140,000 lbs. per sq. in. for the annealed samples, compared with 183,000 lbs. per sq. in. for the unannealed samples.

VIII—The compressive yield point of "commercial cobalt," similarly to that for the pure metal, is slightly raised by annealing; our values average 39,000 lbs. per sq. in. for unannealed samples, compared with 53,000 lbs. per sq. in. for the annealed samples.

TABLE V—COMPRESSIVE STRENGTH MEASUREMENTS OF COBALT

All samples cast from just above melting point, allowed to cool in iron mould and turned in lathe

| Sample No. | Analysis | Date | Special treatment | Lbs. Per Sq. In. Compressive breaking load | Yield point | Remarks |
|---|---|---|---|---|---|---|
| "Commercial Cobalt"—Unannealed | | | | | | |
| H 87b | Co 98.5 Fe 0.80 S 0.014 Si 0.020 Ni 0.20 C 0.37 P None Ca None | 2/10/1913 | None | 172,000 | 29,000 | |
| H 87c | Co 97.8 Fe 1.46 S 0.020 Si 0.020 Ni 0.50 C 0.18 P 0.012 Ca None | 1/16/1914 | None | 178,000 | 52,100 | Metal medium hard and tough. Machines with medium long curling chip |
| H 87a and e | Co 98.7 Fe 0.80 S 0.030 Si 0.020 Ni 0.20 C 0.23 P Trace Ca None | 12/22/1913 | None | 184,000 | 47,600 | |
| H 87d | Co 98.5 Fe 0.80 S 0.016 Si 0.020 Ni 0.20 C 0.37 P None Ca None | 2/10/1913 | None | 184,000 | 31,200 | |
| H 109 | Co 96.8 Fe 2.36 S 0.022 Ni 0.56 C 0.062 P 0.017 | 12/22/1913 | None | 197,500 | 35,000 | |
| H 211 | S 0.080 C 0.17 P 0.031 | 12/22/1913 | None | 92,000 | 41,000 | Low value due to segregation of impurities. Fig. X |
| H 130 | Co 96.52 Fe 1.27 S 0.053 Ni 2.00 C 0.305 P 0.015 | 12/22/1913 | None | 94,000 | 36,000 | Metal short-grained and brittle. Machines with short chip |
| "Commercial Cobalt"—Annealed | | | | | | |
| H 211 | C 0.17 S 0.080 P 0.031 | 1/10/1913 | Annealed from 700° C. | 98,200 | 54,300 | Impurities segregated. See Fig. X |
| H 214 | Co 98.71 Fe 1.45 S 0.012 Si 0.011 Ni None C 0.067 P 0.010 Ca None Mn 2.04 | 4/21/1914 | Annealed at 850° C. | 144,000 | 40,700 | Fine-grained and uniform |
| H 87c | Co 97.8 Fe 1.46 S 0.020 Si 0.0 Ni 0.50 C 0.18 P 0.012 Ca None | 5/19/1914<br>6/17/1914 | Annealed at 850° C.<br>Annealed at 950° C. | 124,000<br>148,000 | 56,500<br>61,000 | |
| Pure Cobalt—Unannealed | | | | | | |
| H 212 | Co 99.9 Fe 0.20 S 0.017 Si None Ni None C None Ca None | 1/10/1913<br>1/24/1914 | None<br>None | 88,900<br>104,800 | 40,700<br>40,700 | Metal soft and brittle, turned with very short chip |
| H 213 | Co 99.73 Fe 0.14 S 0.019 Ni None C None | 1/24/1914 | None | 154,000 | 36,200 | |
| H 193a | Co 99.6 Fe 0.41 S 0.025 Si None | 12/ 9/1913 | None | 135,800 | 39,200 | |
| H 193 | Ni Trace C None P Trace Ca None | 1/10/1913 | None | 123,900 | 54,200 | |
| Pure Cobalt—Annealed | | | | | | |
| H 212 | Co 99.9 Fe 0.20 S 0.017 Si None Ni None C None Ca None | 1/16/1914 | Annealed from 700° C. | 129,100 | 63,400 | |
| H 213 | Co 99.73 Fe 0.14 S 0.19 Ni None C None | 1/16/1914 | Annealed from 700° C. | 114,300 | 65,600 | Metal soft and brittle. Machines with short chip |
| H 217 | Co 99.20 Fe 0.730 S 0.016 Si 0.091 Ni None C 0.036 P 0.0077 Ca None Al 0.021 | 5/19/1914<br>5/20/1914<br>6/17/1914 | Annealed at 850° C.<br>Annealed at 850° C.<br>Annealed at 950° C. | 102,000<br>106,000<br>134,800 | 45,200<br>65,600<br>40,700 | |

## 6—MACHINING, ROLLING AND SWAGING OF METALLIC COBALT

TURNING PROPERTIES—Pure metallic cobalt may be readily machined in the lathe, although it is somewhat brittle and yields a short chip. The addition of small amounts of carbon renders cobalt less brittle and the metal then yields a longer curling chip upon turning.

SWAGING OF COBALT—Cast cobalt of extreme purity, which has been cast either in iron or sand moulds, whether cooled slowly or rapidly, cannot be directly swaged down to a fine wire without special mechanical heat treatment.

On the other hand, "commercial cobalt" containing small percentages of carbon as described in this paper, may be readily swaged down from cast bars to wire of any desired diameter.

SWAGING MACHINES—For our experiments on the swaging of cobalt, we used a No. 3 Dayton swaging machine, manufactured by the Excelsior Needle Company of Torrington, Conn.

With this machine the metal is not drawn out, as is the case with wire-drawing machines, but is rather hammered down by being placed within a pair of dies, carried in a slot in the face of a revolving mandrel, outside of which is an annular rack containing a number of hardened steel rollers. The dies thus revolve rapidly around the work which is hammered by them as they pass between opposite pairs of rolls on either side of it.

With this machine it is comparatively easy to swage hard steel into fine wires. The steel will pass through the dies either hot or cold. However, when a bar of pure cobalt, which has been turned in a lathe to give it a smooth uniform surface, was placed in the swaging machine cold, it cracked along its entire length, and broke off at many places. This was repeated several times with different bars of the metal, each time with the same result, showing that the metal could not be swaged cold.

It became evident that pure cobalt must be given some heat treatment before it could be swaged at all. Hence a bar was first annealed from a temperature of 700° C., by heating it slowly to this temperature in a gas muffle furnace, holding it there for a short time, and then allowing it to cool with the furnace, during several hours. It was then heated to different temperatures before being placed in the swaging machine, with the following results:

At 900° C., the metal crumbled in the machine as

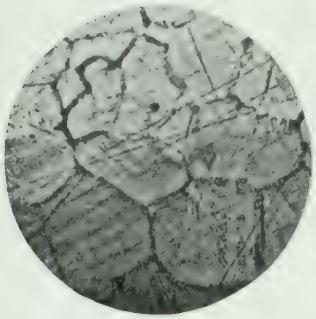

FIG. I × 130 PURE COBALT H 212

Exposure—1 sec., May 8, 1914
Etching—Strong iodine for 3 minutes
Analysis—Co, 99.9; Fe, 0.20; S, 0.017; Ni, C, Ca, Si, None
Density—8.7562 at 17° C.
Brinell Hardness—128.7
Tensile Breaking Load—37,900 lbs. per sq. in.
Melting Point—1478° C. ±1.1° C.
Specific Electrical Resistance—88.08 × 10⁻⁷ ohms per cm³.

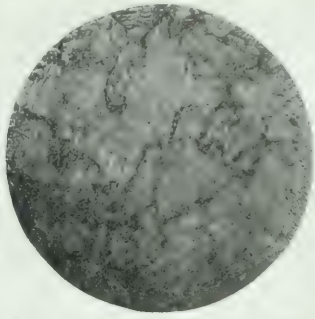

FIG. II × 130 COMMERCIAL COBALT H 213

Exposure—1 sec.; May 9, 1914
Etching—Strong iodine for 5 seconds
Analysis—Co, 99.73; Fe, 0.14; S, 0.019; Si, 0.020; Ni, C, Ca, P, None
Density—8.7732 at 16° C.
Brinell Hardness—121.0
Tensile Breaking Load—45,300 lbs. per sq. in.

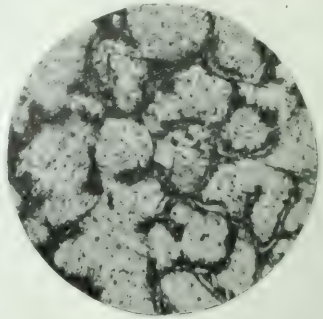

FIG. III × 130 COMMERCIAL COBALT H 214

Exposure—2 sec.; May 1, 1914
Etching—Strong iodine for 14 minutes
Analysis—Co, 98.7; Fe, 1.15; Si, 0.14; S, 0.012; P, 0.011; Ni, Ca, C, None
Density—8.8490 at 15° C.

This sample shows polyhedral crystalline structure, with impurities rejected to the boundaries of the crystalline grains.

though it were extremely hot short, although the sulfur content was as low as 0.018 and 0.020 per cent.

At 700° C. to 800° C. it still cracked and broke very badly in the machine.

At 500° C. to 600° C., however, the bar could be passed through one or two dies without any apparent cracking. It would not go further than this, although the bar was reannealed after each pass, and reductions in diameter of only 0.002 to 0.003 in., on a $^3/_8$ in. bar were made at each pass. At lower temperatures than this the metal would crack still more, and hence it is obvious that the metal must be given some special treatment to render it more ductile before it can be swaged down to a wire.

Cobalt, like iron and certain other metals, will absorb considerable quantities of gases when it is in the molten state; and as the gases in the metal will, in all probability, have a bad effect on its swaging properties, an attempt was made to remove any of these gases that may have been dissolved in the metal and which still remained in the solid bar. With this in view, a bar which had been cast in an iron mould was heated slowly in a good vacuum to a temperature of about 700° C., where it was held for several hours, at the end of which time the bar was allowed to cool slowly in the furnace. This treatment is claimed to have rendered tungsten more ductile; but on attempting to swage a cobalt bar which had been treated thus, very little, if any, improvement was observed in its swaging properties.

The method which finally succeeded consisted in slowly cooling the bar from a high temperature, 1100° to 1150° C., under a high pressure. This was accomplished in the following way: The bar was placed within an iron mould, squeezed tightly by means of clamps, and the whole heated slowly to the above temperature. The mould, with bar, was then removed from the furnace, and the outer portions of the mould chilled while the inner portion still remained hot. The consequent contraction through cooling of the outer portion exerted a considerable pressure on the inner hot bar of metal. The cooling under this pressure continued for three of four hours, after which the metal swaged at a dull red heat with very little difficulty.

The process of swaging consisted in passing the metal, heated to a dull red heat, through successive dies, which hammered it down until a wire of the required diameter was obtained. However, the temperature at which the bar was passed through the dies had to be carefully regulated, as the metal apparently would not swage at all when cold, and when hot only between 500° and 600° C. By thus controlling the temperature, and feeding in the bar very slowly good, smooth, uniform wires were obtained.

### CONCLUSIONS—MECHANICAL AND SPECIAL TREATMENTS

I—Pure cobalt may be machined in a lathe as readily as pure nickel or pure iron, although it is somewhat brittle and yields a short chip.

II—"Commercial cobalt," containing small percentages of carbon, machines very readily after the manner of mild steel.

III—Cast cobalt of extreme purity cannot be rolled or swaged without developing cracks, unless given a special mechanical heat treatment.

IV—Cast cobalt of extreme purity may be rolled or swaged to any extent by cooling the casting under extreme pressures, followed by passing through rolls or dies at temperatures between 500 to 600° C., reducing the bar by small percentages at each pass.

V—"Commercial cobalt," containing small percentages of carbon, may be rolled or swaged down from cast bars to any extent, provided that the metal be worked at a red heat.

### 7—MEASUREMENT OF ELECTRICAL RESISTANCE

The potentiometer method of electrical measurement, which is in reality a measurement of the drop

in potential along a known length of wire when a definite current is flowing through it, was employed for our measurements on pure and "commercial" cobalt.

DESCRIPTION OF APPARATUS—Fig. A is a diagrammatic sketch of the electrical circuits as they were used in the potentiometer method of measuring the electrical resistance of cobalt.

W is a storage battery, two volts, which sends a current through the circuit WRDAMCBW, which flows in the direction from R to B. This circuit is known as the potentiometer circuit. AC is a series of fifteen 5 ohm resistance coils, and CB is a 5 ohm slide-wire, consisting of several turns of constantan wire mounted on a marble cylinder. St'd is a cadmium standard cell, electromotive force 1.0189 volts, which bears the certificate of the United States Bureau of Standards. The standard cell is connected from a point X in the coils AC to the switch T, which is set at a point in the resistance DTA, such that the electromotive force between T and X, due to the battery W, is exactly equal to that of the standard cell. This balanced condition is determined by the galvanometer G which is connected in the circuit of the standard cell by throwing the switch U into the dotted position. The resistance R is adjusted until there is no deflection of the galvanometer, which signifies the balanced condition above mentioned.

The resistance coils from A to C are a set of fifteen 5 ohm coils, and the point X is such that ten of them are included between A and X. ATD is a standard resistance such that there is included between A and T exactly 0.945 ohm. When the balance was made, there flowed, therefore, through the potentiometer circuit, a current I = 1.0189/50.945 = 1/50 ampere. This adjustment is made so that for this current in the potentiometer circuit, the drop in potential across any two adjacent coils along AC is exactly 1/10 of a volt.

The switch used is now thrown to connect an unknown electromotive force (E. M. F. in the diagram) through the galvanometer, and in such a way that the current from the new source flows in the same direction as that from the standard cell. The sliding contact $M^1$ is brought to the zero end of the slide wire, and the moving contact M is shifted from C towards A, step by step, until the galvanometer deflection is reversed in direction. M is left at the last point for which a galvanometer deflection is in the same direction as when M was at C. Then the contact $M^1$ is moved along the slide wire until the galvanometer deflection is zero.

The reading of the contact point M gives the value of the electromotive force in tenths of a volt, and that of $M^1$ from hundredths to hundred-thousandths of a volt. Thus a very accurate measurement of the unknown electromotive force is obtained in terms of the known standard.

The unknown electromotive force in these experiments is not a cell, but is the drop in potential along S. S is a given length of the cobalt wire, whose resistance is to be measured, through which a small current is passing from battery $W^1$ connected as shown in the diagram. In this latter circuit $W^1S$ there is also connected a standard resistance $S^1$ of 0.1 ohm. By throwing the switch $U^1$ into the dotted position the drop in potential along $S^1$ was measured. Knowing the drop in potential along S and also along $S^1$, when the same current is passing through each, the resistances are known from the following equation:

$$\frac{\text{Unknown Resistance S}}{\text{Known Resistance } S^1} = \frac{\text{Drop in Potential along S}}{\text{Drop in Potential along } S^1}$$

METHOD OF COMPUTATION—The length S between two knife edges, which formed the contact points between which the electromotive force was determined, was carefully measured to tenths of a millimeter. The average diameter of the wire was measured to thousandths of a millimeter, and from these data the specific resistance of the wire in ohms per cubic centimeter was calculated to be

$$R = \mu\frac{l}{A} \text{ or } \mu = \frac{RA}{l},$$

where
R = total resistance of S in ohms,
$l$ = length of S in centimeters,
A = average cross section of S in square centimeters,
U = specific resistance in ohms per centimeter cube.

After this measurement the wire was cut to the exact length S, carefully weighed to the nearest milligram, and the density of the wire determined by the Archimedes principle. From these data the resistance

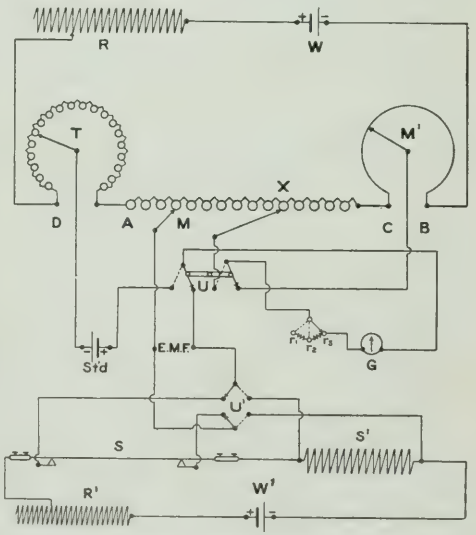


FIG. A—ARRANGEMENT OF CIRCUITS FOR ELECTRICAL RESISTANCE MEASUREMENTS

W and $W^1$—2 Volt and 4 Volt Storage Batteries, Respectively
R and $R^1$—Adjustable Rheostats
U and $U^1$—Double-Throw Switches
G—Galvanometer
R and $R^1$—Small Resistances for Protection of Galvanometer in Making Adjustments
St'd—Standard Cell, E. M. F. = 1.0189 Volts
S—Wire Tested
$S^1$—Standard Resistance of 0.1 Ohm Correct to 1/25 of One Per Cent, and with No Temperature Coefficient

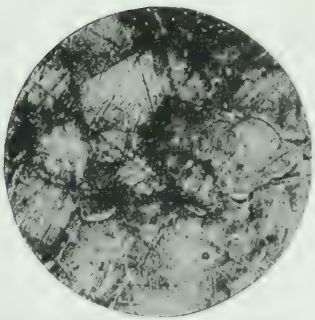

FIG. IV × 130 COMMERCIAL COBALT H 130

Exposure—2 sec.; May 1, 1914

Etching—Strong iodine for 7 min

Analysis—Co, 96.5; Ni, 2.0; Fe, 1.27; C, 0.305; S, 0.054; P, 0.015

Density—8.7690 at 17° C.

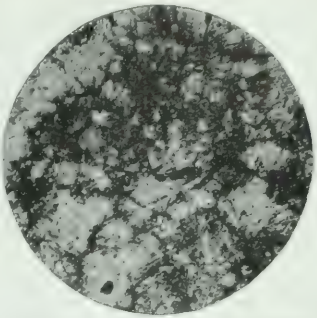

FIG. V × 130 COMMERCIAL COBALT H 214 *c*

Exposure—1 sec; May 6, 1914

Etching—Strong iodine for 5 min.

Analysis—Co, 97.09; Fe, 1.45; C, 0.067; S, 0.012; Mn, 2.04; Si, 0.011; P, 0.010; Ni, Cu, None

Annealed at 850° C.

Tensile Breaking Load—70,500 lbs. per sq. in.

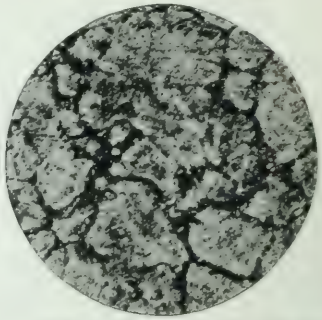

FIG. VI × 130 COMMERCIAL COBALT H 214 *d*

Exposure—2 sec.; May 2, 1914

Etching—Strong iodine for 9 min.

Analysis—Co, 97.09; Fe, 1.45; C, 0.067; S, 0.012; Mn, 2.04; Si, 0.011; P, 0.010; Ni, Ca, None

Annealed at 1000° C.

Tensile Breaking Load—75,200 lbs. per sq. in.

of the wire in ohms per meter gram was calculated as follows:

$$R = \mu \frac{l}{A},$$

$$D = \frac{M}{V} = \frac{M}{lA}, \text{ or } A = \frac{M}{Dl},$$

from which

$$R = D\mu\frac{l^2}{M} = \frac{kl^2}{M}, \text{ or } k = \frac{RM}{l^2},$$

where $R$ = Resistance of S in ohms,
$M$ = Mass of S in grams,
$D$ = Density of S,
$k$ = Specific resistance of S in ohms per meter gram,
$V$ = Volume of S in cubic centimeters.

For a comparison of $k$ and $\mu$ it should be noted that $k$ is equal to $\mu$ multiplied by the density of the wire times $10^4$.

The following values of the specific resistances of cobalt and nickel are taken from the literature:

SPECIFIC ELECTRICAL RESISTANCE

| | Temperature | Specific resistance in ohms per centimeter cube: Cobalt | Nickel |
|---|---|---|---|
| Copaux(*a*) | Room | 55 × $10^{-7}$ | 64 × $10^{-7}$ |
| Reuer and Kaneko(*b*) | Room | 64 × $10^{-7}$ | 77.2 × $10^{-7}$ |
| Hofman(*c*) | Room | 97 × $10^{-7}$ | 70 × $10^{-7}$ |
| Knott, C. G.(*d*) | 100° C. | 121 × $10^{-7}$ | |
| Knott, C. G.(*d*) | 200° C. | 159 × $10^{-7}$ | |
| Reichardt (*e*), 99.8% Co | 20° C. | 97 × $10^{-7}$ | |
| Fleming(*f*) | 0° C. | | 69 × $10^{-7}$ |
| Niccolai(*g*) | 0° C. | | 119 × $10^{-7}$ |
| Harrison, E. P.(*h*) | 0° C. | | 103 × $10^{-7}$ |

(*a*) *Annalen de Chimie et de Physique*, [8] **6** (1905), 508.
(*b*) *Ferrum*, **10**, 257; *Chem. Abs.*, **113**, 3591.
(*c*) "General Metallurgy," **1913**, p. 29.
(*d*) *Proceedings of the Royal Society of Edinburgh*, **18** (1891), 303.
(*e*) *Annalen de Physik*, [4] **6** (1901), 832.
(*f*) *Proceedings of the Royal Society*, **66** (1900), 50.
(*g*) *Lincei Rend.*, [1] **16** (1906), 757; [2] (1907), 185.
(*h*) *Proceedings of the Physical Society*, **18** (1902), 57; *Philosophical Magazine*, [6] **3** (1902), 177.

The samples of metal which were used were all cast from just above their melting points, allowed to cool slowly in an iron mould, and thereafter swaged down to wires of given diameters according to the method described under "Swaging of Pure Cobalt." Our results are given in Tables VI and VII.

ANNEALING OF WIRES—The effect of annealing on the conductivity of both pure and "commercial" cobalt was studied. In this connection the annealing was accomplished by two methods.

(1) PASSING A SUITABLE ELECTRIC CURRENT THROUGH THE WIRE IN VACUO—The annealing furnace used consisted of a cylindrical glass tube about 4 ft. long and 2 in. in diameter, and sealed off at the ends with rubber stoppers. Through the ends protruded copper leads and a connection to a vacuum pump. The slack in the cobalt wire, developed upon heating, was taken up by a coiled spring. The approximate temperature was measured by a thermocouple placed against the annealing wire.

TABLE VI—ELECTRICAL RESISTANCE OF UNANNEALED COBALT

| Sample No. and analysis | Date: Nov., 1913 and Apr., 1914 | Wire Data: Temp. ° C. | Length Cm. | Aver. cross section Sq. cm. | Weight Grams | Resistance in Ohms per: Centimeter Cube | Meter Gram |
|---|---|---|---|---|---|---|---|
| "COMMERCIAL COBALT" | | | | | | | |
| H 192 | 11/7 | 21.2 | 83.25 | 0.005568 | 3.9881 | 229.6 × $10^{-7}$ | 1.977 |
| Co 99.63 | 11/7 | 21.0 | 50.20 | 0.005568 | 2.4051 | 231.2 × $10^{-7}$ | 1.992 |
| Ni None | 11/7 | 21.8 | 50.20 | 0.005568 | 2.4051 | 231.5 × $10^{-7}$ | 1.993 |
| Fe 0.60 | | | | | | | |
| S 0.023 | | | | | | | |
| C 0.09 | | | | | | | |
| Si Trace | | | | | | | |
| Ca Trace | | | | | | | |
| H 193 | 11/8 | 21.9 | 75.07 | 0.01885 | 12.3871 | 144.4 × $10^{-7}$ | 1.271 |
| Co 92.36 | 11/8 | 22.0 | 51.67 | 0.01885 | 8.526 | 144.5 × $10^{-7}$ | 1.271 |
| Ni 2.73 | | | | | | | |
| Fe 4.49 | | | | | | | |
| S 0.018 | | | | | | | |
| C None | | | | | | | |
| H 214 | 4/3 | 22.5 | 74.95 | 0.006374 | 4.304 | 105.8 × $10^{-7}$ | 0.9530 |
| Co 98.71 | 4/3 | 22.5 | 74.95 | 0.006374 | 4.304 | 105.8 × $10^{-7}$ | 0.9530 |
| Ni None | 4/3 | 22.0 | 52.64 | 0.006419 | 3.023 | 105.1 × $10^{-7}$ | 0.9545 |
| Fe 1.15 | 4/3 | 22.0 | 52.64 | 0.006319 | 3.023 | 104.8 × $10^{-7}$ | 0.9524 |
| Si 0.14 | 4/6 | 16.0 | 82.56 | 0.006319 | 4.723 | 104.2 × $10^{-7}$ | 0.9431 |
| Ca None | 4/6 | 15.5 | 82.56 | 0.006319 | 4.723 | 103.8 × $10^{-7}$ | 0.9403 |
| S 0.012 | 4/7 | 18.0 | 59.95 | 0.006305 | 3.429 | 104.7 × $10^{-7}$ | 0.9502 |
| C 0.039 | 4/7 | 18.0 | 59.95 | 0.006305 | 3.429 | 104.7 × $10^{-7}$ | 0.9502 |
| P 0.010 | | | | | | | |
| PURE COBALT | | | | | | | |
| H 212 | 1/22 | 17 | 92.81 | 0.005890 | 4.863 | 87.27 × $10^{-7}$ | 0.7766 |
| Co 99.9 | Same | 17 | 92.81 | 0.005890 | 4.863 | 88.04 × $10^{-7}$ | 0.7834 |
| Ni None | Same | 17 | 50.23 | 0.005890 | 2.631 | 88.08 × $10^{-7}$ | 0.7838 |
| Fe 0.20 | Same | 17 | 50.23 | 0.005890 | 2.631 | 88.22 × $10^{-7}$ | 0.7840 |
| S 0.017 | Same | 14 | 79.41 | 0.005822 | 4.113 | 86.66 × $10^{-7}$ | 0.7713 |
| C None | Same | 14 | 79.41 | 0.005822 | 4.113 | 86.80 × $10^{-7}$ | 0.7727 |
| Si None | Same | 14 | 48.98 | 0.005822 | 2.538 | 85.80 × $10^{-7}$ | 0.7637 |
| Ca None | Same | 14 | 48.98 | 0.005822 | 2.538 | 85.55 × $10^{-7}$ | 0.7616 |
| H 215 | 4/2 | 22 | 95.38 | 0.006547 | 5.432 | 89.17 × $10^{-7}$ | 0.7756 |
| Co 99.6 | 4/4 | 22 | 95.38 | 0.006547 | 5.432 | 89.98 × $10^{-7}$ | 0.7826 |
| Ni None | 4/4 | 23.0 | 95.38 | 0.006547 | 5.432 | 89.98 × $10^{-7}$ | 0.7826 |
| Fe 0.19 | 4/4 | 23.0 | 95.38 | 0.006547 | 5.432 | 90.26 × $10^{-7}$ | 0.7852 |
| S 0.012 | | | | | | | |
| C None | | | | | | | |
| Si 0.084 | | | | | | | |
| Ca None | | | | | | | |
| P 0.0066 | | | | | | | |

(2) HEATING WITHIN AN ELECTRIC FURNACE IN A $CO_2$ ATMOSPHERE—The furnace used consisted of an iron tube about 4 ft. long and 2 in. in diameter, wound with suitable insulated nichrome wire. The ends, which

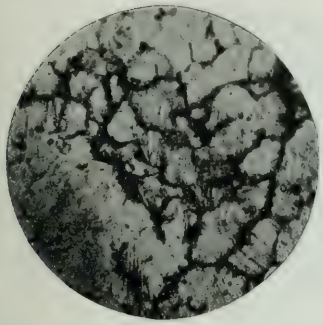

FIG. VII × 130 COMMERCIAL COBALT H 87 *c*

Exposure—1 sec.; May 6, 1914
Etching—Strong iodine for 10 min.
Analysis—Co, 97.8; Ni, 0.50; Fe, 1.46; S, 0.020; C, 0.18; Si, 0.020; Ca, P, Trace.
Annealed at 850° C.
Density—8.6658 at 17° C.
Tensile Breaking Load—60,200 lbs. per sq. in.

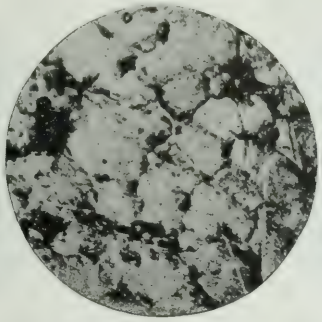

FIG. VIII ×130 COMMERCIAL COBALT H 87 *c*

Exposure—2 sec.; May 5, 1914
Etching—Strong iodine for 1 min.
Analysis—Co, 97.8; Fe, 1.46; Ni, 0.50; C, 0.18; S, 0.020; Si, 0.020; P, 0.012; Ca, None
Tensile Breaking Load—56,100 lbs. per sq. in.

FIG. IX × 130 COMMERCIAL COBALT H 109

Exposure—1/2 sec.; May 6, 1914
Etching—Strong iodine for 30 sec.
Analysis—Co, 96.8; Ni, 0.56; Fe, 2.36; S, 0.022; C, 0.063; P, 0.017
Density—8.7997 at 18.5° C.
Brinell Hardness—107
Tensile Breaking Load—52,600 lbs. per sq. in.

were sealed off with rubber stoppers, were water cooled and contained a suitable gas inlet and outlet.

## CONCLUSIONS—ELECTRICAL RESISTANCE

PURE COBALT. I—The specific electrical resistance of cobalt wires of extreme purity is $89.64 \times 10^{-7}$ ohms per centimeter cube, or 0.7769 ohms per meter gram,

TABLE VII—ELECTRICAL RESISTANCE OF ANNEALED COBALT

| Sample No. and analysis | Date Apr. 1914 | Wire Data: Temp. ° C. | Length. Cm. | Av. cross section. Sq. cm. | Wt. Grams | Resistance in Ohms per: Centimeter Cube | Meter Gram | Annealed: At ° C. | For hrs. | In |
|---|---|---|---|---|---|---|---|---|---|---|
| "COMMERCIAL COBALT" | | | | | | | | | | |
| H 214 | 11 | 13.0 | 74.65 | .006333 | 4.260 | 91.76 ×10⁻⁷ | .8286 | 350 | 2 | Vac. |
| Co 98.71 | 11 | 13.0 | 47.50 | .006376 | 2.713 | 91.49 ×10⁻⁷ | .8205 | 350 | 5 | Vac. |
| Ni None | 21(*a*) | 21.5 | 83.69 | .006461 | 4.845 | 104.1 ×10⁻⁷ | .9325 | 200 | 5 | $CO_2$ |
| Fe 1.15 | 21 | 21.5 | 49.97 | .006461 | 2.888 | 103.7 ×10⁻⁷ | .9264 | 200 | 5 | $CO_2$ |
| Si 0.14 | 22 | 19.2 | 82.80 | .006447 | 4.799 | 102.6 ×10⁻⁷ | .9225 | 300 | 2 | $CO_2$ |
| Ca None | 22 | 19.2 | 45.86 | .006447 | 2.657 | 102.9 ×10⁻⁷ | .9249 | 300 | 2 | $CO_2$ |
| S 0.012 | 23 | 19.0 | 82.40 | .006390 | ..... | 100.7 ×10⁻⁷ | .9090 | 400 | 2 | $CO_2$ |
| C 0.039 | 23(*a*) | 19.0 | 54.94 | .006404 | ..... | 100.2 ×10⁻⁷ | .9019 | 400 | 2 | $CO_2$ |
| P 0.01 | 24 | 18.5 | 78.11 | .006291 | 4.478 | 98.42 ×10⁻⁷ | .8969 | 500 | 2 | $CO_2$ |
| | 24 | 18.5 | 56.35 | .006291 | 3.230 | 98.14 ×10⁻⁷ | .8941 | 500 | 2 | $CO_2$ |
| | 25 | 19.3 | 81.65 | .006319 | 4.664 | 93.34 ×10⁻⁷ | .8437 | 600 | 1 | $CO_2$ |
| | 25(*b*) | 19.3 | 57.50 | .006319 | 3.285 | 93.63 ×10⁻⁷ | .8466 | 600 | 1 | $CO_2$ |
| | 27 | 15.6 | 66.67 | .006291 | 3.801 | 91.44 ×10⁻⁷ | .8285 | 700 | 1 | $CO_2$ |
| | 27 | 15.8 | 51.01 | .006291 | 2.907 | 90.50 ×10⁻⁷ | .8232 | 700 | 1 | $CO_2$ |
| | 28 | 18.4 | 53.55 | .006263 | 3.046 | 90.35 ×10⁻⁷ | .8204 | 800 | 1 | $CO_2$ |
| PURE COBALT | | | | | | | | | | |
| H 215 | 13 | 17.7 | 85.21 | .006475 | 4.834 | 85.03 ×10⁻⁷ | .7449 | 350 | 5 | Vac. |
| Co 99.6 | 13 | 17.7 | 85.21 | .006475 | 4.834 | 85.18 ×10⁻⁷ | .7463 | 350 | 5 | Vac. |
| Ni None | 13 | 17.7 | 50.2 | .006475 | 2.848 | 84.92 ×10⁻⁷ | .7424 | 350 | 5 | Vac. |
| Fe 0.19 | 13 | 17.7 | 50.2 | .006475 | 2.848 | 85.04 ×10⁻⁷ | .7436 | 350 | 5 | Vac. |
| S 0.012 | 21 | 19.0 | 74.48 | .006151 | 4.224 | 97.42 ×10⁻⁷ | .8988 | 400 | 2 | $CO_2$ |
| C None | 21 | 18.8 | 39.89 | .006221 | 2.264 | 97.94 ×10⁻⁷ | .8938 | 400 | 2 | $CO_2$ |
| Si 0.084 | 22 | 21.2 | 73.99 | .006249 | 4.162 | 101.0 ×10⁻⁷ | .9108 | 500 | 1.5 | $CO_2$ |
| Ca None | 22 | 21.2 | 49.41 | .006249 | 2.779 | 101.1 ×10⁻⁷ | .9176 | 500 | 1.5 | $CO_2$ |
| P 0.0066 | 23 | 15.4 | 72.75 | .006249 | 4.080 | 93.54 ×10⁻⁷ | .8395 | 600 | 1 | $CO_2$ |
| | 23(*b*) | 15.4 | 52.23 | .006221 | 2.930 | 93.85 ×10⁻⁷ | .8460 | 600 | 1 | $CO_2$ |
| | 24 | 19.0 | 51.37 | .006235 | 2.875 | 94.06 ×10⁻⁷ | .8442 | 700 | 1 | $CO_2$ |
| | 24 | 19.0 | 74.08 | .006291 | 4.145 | 93.33 ×10⁻⁷ | .8360 | 700 | 1 | $CO_2$ |
| | 28 | 16.5 | 73.11 | .006207 | 4.080 | 91.36 ×10⁻⁷ | .8203 | 800 | 0.5 | $CO_2$ |
| | 28 | 16.5 | 54.15 | .006207 | 3.022 | 91.65 ×10⁻⁷ | .8240 | 800 | 0.5 | $CO_2$ |

(*a*) Samples H 214 series, Apr. 21–23, are all the same wire, annealed and unannealed.
(*b*) Note drop in resistance between 500° and 600° C.

at 18° C. This is the average of twelve observations agreeing well among themselves, and is for wires unannealed after swaging. This is approximately five times that of pure copper.

II—The effect of annealing cobalt wire of extreme purity *in vacuo*, at about 350° C. for several hours, by passing an electric current through the wire is to diminish its electrical resistance by about 5 per cent. This is not as much as is true of some metals, as for example, aluminum, the resistance of which is diminished about 10 per cent by annealing for 2 hours at 250° C.[1]

III—The effect of annealing cobalt wires of extreme purity in an atmosphere of carbon dioxide gas by heating from an external source is at first to increase the resistance, but with continued annealing at increasingly higher temperatures up to 800° C., the specific resistance drops again. It is particularly noticeable that there is a drop of about 7 per cent in the specific electrical resistance of cobalt wire of extreme purity, annealed in a carbon dioxide atmosphere at 600° C. compared with one similarly annealed at 500° C. This drop was from $101 \times 10^{-7}$ ohms to $93.5 \times 10^{-7}$ ohms per centimeter cube.

IV—The fact that annealing *in vacuo* diminishes the electrical resistance of pure cobalt, whereas annealing in an inert gas at low temperatures increases its electrical resistance, which is again lowered by heating at higher temperatures, tends to show that the specific electrical resistance of cobalt is largely influenced by the presence of occluded or absorbed gases.

"COMMERCIAL COBALT." V—The specific electrical resistance of cobalt, as with copper and most other metals, increases tremendously by the addition of small percentages of impurities. Less than 0.5 per cent of impurities may treble the electrical resistance.

VI—The specific electrical resistance of "commercial cobalt" varies between $231 \times 10^{-7}$ and $103 \times 10^{-7}$ ohms per centimeter cube, for the cases we have studied, depending upon the nature of the small percentages of impurities present. These figures are for wires unannealed after swaging.

VII—The effect of annealing "commercial cobalt" by passing an electric current through the wire *in vacuo*, is to greatly reduce its specific electrical resistance. Annealing in this way at 350° C. for 5 hours

[1] H. Gwercke, *Electrician*, **72**, 450; *Chem. Abs.*, **1914**, 1049.

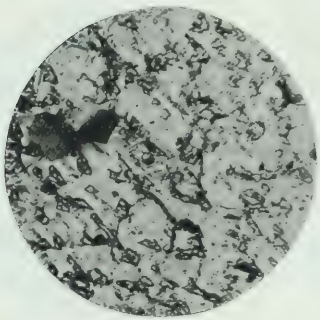

FIG. X × 130 COMMERCIAL COBALT H 211

Exposure—1 sec.; May 5, 1914 Etching—Strong iodine for 1 min.
Brinell Hardness—128.2 Analysis—C, 0.18; S, 0.080; P, 0.031
Tensile Breaking Load—31,000 lbs. per sq. in.
This sample shows "ghosts" or "ghost lines" because of its impurities, C, S, and P. Metals of this kind are usually brittle, weak and hard, which are the characteristics of this particular sample as shown under the tables of measurements preceding.

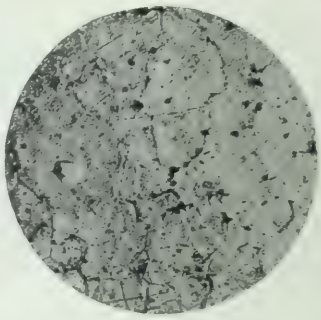

FIG. XI × 130 PURE NICKEL

Exposure—2 sec.; May 7, 1914 Brinell Hardness—83.1
Etching—Nitric acid (sp. gr. 1.42) for 4 sec.
Analysis—Ni, 99.29; Fe, 0.48; S, 0.025; Si, 0.042; Co, Ca, C, None
Tensile Breaking Load—18000 lbs. per sq. in.
Melting Point—1444° C.
This nickel shows polyhedral crystalline structure of the pure metal.

reduced the specific resistance by approximately 14 per cent.

VIII—The effect of annealing "commercial cobalt" in an atmosphere of carbon dioxide gas by heating from an external source is in general to decrease its resistance. As in the case of pure cobalt, there is a sharp decrease in resistance in the sample annealed in an atmosphere of $CO_2$ gas at 600° C. compared with that similarly annealed at 500° C.

These conclusions all refer to measurements on wires made from bars cast from just above melting temperature, allowed to cool in an iron mould, and then swaged to wires of approximately 0.03 in. diameter, in the manner described on pages 11 and 12.

### 8—MAGNETIC PERMEABILITY AND HYSTERESIS MEASUREMENTS OF PURE COBALT

A considerable series of measurements on the magnetic properties of pure cobalt have been made in this laboratory, but as they are extended in length, and as they have bearing on certain interesting magnetic cobalt alloys, which are also being studied, these measurements will form part of an independent paper, which is in process of writing.

### 9—SPECIFIC HEAT MEASUREMENTS

The specific heat of cobalt was determined by the method of mixtures, and the result is probably accurate to within 0.5 per cent.

The method employed consisted in heating a weighed amount of metallic cobalt in the form of short pieces of wire to 100° C., by bringing them into temperature equilibrium with steam at normal temperature and pressure, at the same time having them enclosed so that they were perfectly dry. This was accomplished by a simple boiler device.

When the metal was thus brought to 100° C., which temperature was read on a suitable thermometer, and after constant temperature readings on this thermometer had been obtained for a period of minutes, it was dropped directly from the heater into a suitable calorimeter. Prior to dropping the cobalt at 100° C. into the calorimeter, preliminary temperature readings of the water in the calorimeter were made over a period of minutes. These readings were continued with uniform stirring of the calorimeter liquid, after the introduction of the cobalt, until the final equilibrium calorimeter temperature had been reached.

The thermometer was read to 0.01° C., and readings were taken every 20 seconds. This method obviously gives us the mean specific heat between 100° C. and room temperature, approximately 15° C.

MATERIAL—The cobalt used for the specific heat measurements was Sample No. H 213 (see Fig. II) and analyzed as follows:

| | | | |
|---|---|---|---|
| Co | 99.73 | C | None |
| Ni | None | Si | 0.040 |
| Fe | 0.14 | Ca | None |
| S | 0.019 | P | None |

The mean of a series of specific heat measurements, made as indicated above, gives us the

Mean Specific Heat of Cobalt between 15–100° C. = 0.1053.

with an average deviation of single observations from the mean of about 0.5 per cent.

The writers wish to acknowledge their indebtedness to Professor W. J. Drisko of the Department of Physics, Massachusetts Institute of Technology, Boston, who was good enough to have several specific heat measurements of our material made under his direction at the Massachusetts Institute of Technology. These measurements were made on the same material as above. Following are the measurements:

SAMPLE H 213, MARCH 18, 1914

| Specific heat of cobalt | Deviation of a single observation from the mean |
|---|---|
| 0.1070 | 0.0014 |
| 0.1037 | 0.0019 |
| 0.1058 | 0.0002 |
| 0.1060 | 0.0004 |
| Mean, 0.1056 | Average, 0.0010 |

Mean Specific Heat of Cobalt between 15–100° C. = 0.1056 ∓ 0.0005.

The following values of the specific heat of cobalt are taken from the literature:

| Observer | Temperature Range °C. | Specific Heat | Observer | Temperature Range °C. | Specific Heat |
|---|---|---|---|---|---|
| Tilden(*a*).. | —182 to 15 | 0.0822 | Copaux(*c*).. | 500 | 0.1451 |
| | — 78 to 15 | 0.0939 | | 800 | 0.1846 |
| | 15 to 100 | 0.1030 | | 1000 | 0.204 |
| | 15 to 185 | 0.1047 | Copaux(*d*).. | 20 to 100 | 0.104 |
| | 15 to 350 | 0.1087 | Kalmus and | | |
| | 15 to 435 | 0.1147 | Harper... | 15 to 100 | 0.1053 |
| | 15 to 550 | 0.1209 | Drisko..... | 15 to 100 | 0.1053 |
| | 15 to 630 | 0.1234 | | | |
| Tilden(*b*).. | 20 to 200 | 0.104 | | | |

(*a*) *Proceedings of Royal Society*, **66** (1900), 244.
(*b*) *Ibid.*, **71** (1903), 220.
(*c*) *Compt. rend.*, **140** (1905), 657.
(*d*) *Annalen de Chimie et de Physique*, [8] **6** (1905), 508.

From these figures the true specific heat at any temperature may be computed from 0° to 890° C.

$$\text{Specific Heat} = 0.1058 + 0.0000457t + 0.0000000661t^2.$$

MICROPHOTOGRAPHS

No attempt has been made to make a minute or complete microphotographic study or analysis of cobalt with the small percentages of impurities with which we have to do in this paper. Such a study would be decidedly interesting but, unfortunately, is not possible in the time at our disposal. The microphotographs shown (Figs. I to XI) are rather characteristic, and require no further explanation than the notes accompanying them and the references in the text and tables.

The analyses throughout this paper were made by Mr. R. C. Wilcox, part-time assistant in this laboratory; valuable assistance was rendered in certain of the experiments by Mr. W. L. Savell, B.Sc., and by Mr. K. B. Blake, S.B., likewise both part-time assistants. The authors wish to acknowledge their indebtedness to these gentlemen.

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QUEEN'S UNIVERSITY, KINGSTON, ONTARIO

## THE SEPARATION OF THE ILLUMINANTS IN MIXED COAL AND WATER GAS[1]

By G. A. BURRELL AND I. W. ROBERTSON

In this paper are shown experiments, made by the Bureau of Mines, that resulted in separating the illuminants in the artificial gas of Pittsburgh. This gas is made by mixing 1 part carbureted water gas with three parts of coal gas. The separation was made by fractionally distilling the gas in a vacuum at low temperatures, and follows the method detailed by the Bureau in separating natural gases.[2]

In both the natural gas work and coal gas work, advantage was taken of the work on the subject by P. Le Beau and A. Damiens,[3] who separated mixtures of the paraffin hydrocarbons and coal gas by the same method. The Bureau, however, separated the paraffin hydrocarbons into single constituents and found it necessary to refractionate distillates and residues in all cases to obtain pure gases. Le Beau and Damiens make no mention of this latter necessity and separated the paraffins in pairs. Further, there is shown in this paper a simple method for the determination of benzene in artificial gas. The principle of the procedure rests on the fact that the gases at different stages in the analysis are subjected to temperatures at which certain constituents can be removed by a mercury pump from certain others which have lower vapor tensions at the temperatures selected. It was found impossible to make a clean separation in any case at one fractionation, hence distillates and residues were refractionated until the separation was as complete as was desired.

The following groups show the constituents in artificial gas that can be separated at different temperatures. The first column shows the distillates that can be obtained at a particular temperature and the second column the residues, *i. e.*, those gases that have appreciable vapor pressures at the temperatures given:

TABLE I—GROUPS SEPARATED FROM ARTIFICIAL GAS AT VARIOUS TEMPERATURES

| Distillates | | Residues | | | |
|---|---|---|---|---|---|
| Name and formula | Boiling point ° C. | Name and formula | B. P. ° C. | Name and formula | B. P. ° C. |
| Liquid air temperature, —185° C. | | | | | |
| Methane, $CH_4$... | —165 | Ethane, $C_2H_6$..... | —93 | Ethylene, $C_2H_4$.. | —103 |
| Nitrogen, $N_2$..... | —195 | Propane, $C_3H_8$.... | —45 | Propylene, $C_3H_6$ | —51 |
| Oxygen, $O_2$..... | —183 | *N*-butane(*a*), $C_4H_{10}$ | 1 | Iso-butylene(*a*), | |
| Carbon monoxide, CO..... | —190 | Iso-butane, $C_4H_{10}$ | —10 | $C_4H_8$..... | —4 |
| Hydrogen, $H_2$... | —253 | | | Benzene, $C_6H_6$... | 80 |
| Below —140° C. | | | | | |
| Ethylene, $C_2H_4$... | —103 | Propane, $C_3H_8$.... | —45 | Propylene, $C_3H_6$ | —51 |
| Ethane, $C_2H_6$.... | —93 | *N*-butane, $C_4H_{10}$.. | 1 | Iso-butylene, | |
| | | Iso-butane, $C_4H_{10}$ | —10 | $C_4H_8$..... | —4 |
| | | | | Benzene, $C_6H_6$.. | 80 |
| Below —120° C. | | | | | |
| Propane, $C_3H_8$... | —45 | *N*-butane, $C_4H_{10}$.. | 1 | Iso-butylene, | |
| Propylene, $C_3H_6$.. | —51 | Iso-butane, $C_4H_{10}$ | —10 | $C_4H_8$..... | —4 |
| | | | | Benzene, $C_6H_6$.. | 80 |
| —78° C. | | | | | |
| *N*-butane, $C_4H_{10}$. | 1 | Benzene, $C_6H_6$.... | 80 | | |
| Iso-butane, $C_4H_{10}$ | —10 | | | | |
| Iso-butylene, $C_4H_8$ | —4 | | | | |

(*a*) The boiling point of *N*-butylene could not be found in the literature. The *N*-butylene was not separated from the iso-butylene; neither was the *N*-butane separated from the iso-butane.

TABLE II—COMPOSITION OF THE ARTIFICIAL GAS OF PITTSBURGH AS ANALYZED BY ORDINARY METHODS (SEPTEMBER 1, 1914)

| Constituents | Per cent | Constituents | Per cent |
|---|---|---|---|
| Carbon dioxide, $CO_2$..... | 2.64 | Methane, $CH_4$..... | 30.96 |
| Oxygen, $O_2$..... | 0.81 | Ethane, $C_2H_6$..... | 1.82 |
| Illuminants..... | 8.67 | Nitrogen, $N_2$..... | 4.72 |
| Carbon monoxide, CO..... | 13.34 | | |
| Hydrogen, $H_2$..... | 37.04 | Total, | 100.00 |

In making the analysis in Table II the carbon dioxide was removed by the caustic potash solution, the oxygen by alkaline pyrogallate solution, the illuminants by fuming sulfuric acid, the hydrogen by absorption in colloidal palladium[1] solution, the methane and ethane by slow combustion, and the nitrogen by difference.

The above gas was next subjected to fractional distillation at various low temperatures in the apparatus shown at Fig. I. At *a* is shown a Dewar flask to hold the refrigerant used in cooling the gases; *b* is the bulb in which the gases were cooled; *d* is a gas-analysis burette and *c* another gas container for measuring the gases prior to cooling; *e* is a pressure gauge for registering pressures in the Töpler pump; *f* is a drying tube containing phosphorus pentoxide for removing the water vapor from the gases; *g*, *h* and *i* are containers for trapping the gases over mercury as they were removed from the pump; *h* and *i* are provided with 3-way stopcocks. The particular advantage of containers such as are shown at *h* and *i*

[1] Presented at the meeting of the American Gas Institute, October 20, 1914, New York City, with the permission of the Director of the U. S. Bureau of Mines.

[2] Burrell, G. A. and Seibert, F. M., "Gas Analysis by Fractional Distillation at Low Temperatures," *J. Am. Chem. Soc.*, **36** (1914), 1538–1548.

[3] *Compt. rend.*, **156** (1913), 325; **156** (1913), 797.

[1] See Burrell, G. A. and Oberfell, G. G., "The Absorption of Hydrogen by Colloidal Palladium Solution," THIS JOURNAL, **6** (1914), 992.

lies in the fact that they can be filled with mercury by forcing down on them with the stopcock open to the air, finally filling the capillary tubes with mercury. The gas from the pump can then be introduced into them by means of the goose-neck tube attached to *l*, leaving a mercury seal in the capillary tube all the time; *i* is a pressure gauge which is of principal use in the benzene determination; *o*, *n* and *m* are 3-way stopcocks. A counterpoise, *p*, attached to the mercury reservoir of the Töpler pump greatly facilitates the working of the pump.

Fig. II shows the various steps in the main separation of the gas.

SERIES I—The original volume of sample (2048 cc.) was first freed of the carbon dioxide by passing

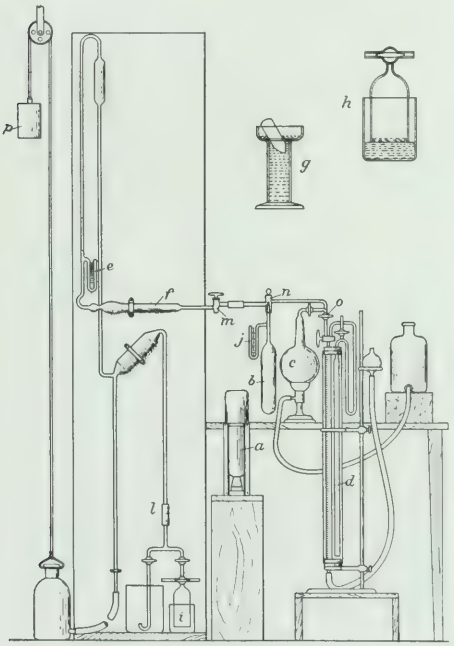


FIG. I—APPARATUS FOR LIQUEFACTION AND FRACTIONATION OF GASES

it through caustic potash solution: 53 cc. of carbon dioxide were removed, leaving 1995 cc. The latter quantity of gas was then cooled in the bulb *b* (Fig. I) (about 300 cc. at a time), at the temperature of liquid air. After the introduction of each 300 cc., pumping was started and as much of the gas removed as possible. There resulted a distillate, A, and a residue, B. The distillate A was fractionated at the temperature of liquid air, resulting in two more fractions, C and D. D was added to the residue B, and the total again fractionated at the temperature of liquid air. The distillate F thus obtained was added to the distillate C, and the total again fractionated at the temperature of liquid air. The residue thus obtained (10 cc.) was added to the residue E, and the total again fractionated. There resulted a distillate, G, of 3 cc. which was added to the distillate I, making a total of 1782 cc. This first series of fractionations shows the general procedure. At the temperature adopted, in this case the temperature of liquid air, the gases were repeatedly fractionated until no more distillate of consequence could be obtained: 3 cc., the final distillate obtained, is only 0.15 per cent of the original quantity of gas (2048 cc.) taken for the experiment. The total distillate obtained at the temperature of liquid air was 1782 cc., and consisted of those gases that have an appreciable vapor tension at that temperature. This fraction, when calculated to the original quantity of gas taken, consisted of 0.81 per cent oxygen, 13.25 per cent carbon monoxide, 37.33 per cent hydrogen, 31.13 per cent methane, and 4.23 per cent of nitrogen. It will be observed that the quantities of these constituents check very well with the quantities of the same constituents found in the ordinary analysis of the coal gas (page 17). The residue H of the first series of fractionations (191.6 cc.) should consist of those gases and vapors that do not have an appreciable vapor pressure at the temperature of liquid air. They are $C_2H_6$, $C_3H_8$, $C_4H_{10}$, $C_2H_4$, $C_3H_6$, $C_4H_8$ and $C_6H_6$; in other words, the so-called illuminants of coal gas with the addition of ethane and probably propane.

SERIES II—The residue H (191.6 cc.) was next cooled at a temperature not higher than —140° C. and as much gas removed as possible with the mercury pump. Distillates and residues were repeatedly fractionated until there was obtained 167.0 cc. of gas consisting of ethane and ethylene. The fraction was analyzed in two ways: *first* by burning the entire fraction with oxygen, and *second*, by first removing the ethylene with fuming sulfuric acid and then burning the ethane in oxygen. The data covering these methods are given in Table III:

TABLE III—ANALYSIS OF ETHANE AND ETHYLENE FRACTION

| COMBUSTION | Cc. | ABSORPTION AND COMBUSTION | Cc. |
|---|---|---|---|
| Sample taken | 15.12 | Sample taken | 34.18 |
| Oxygen added | 94.42 | After absorption in $H_2S_2O_7$ | 8.85 |
| Total volume | 109.54 | Absorbed by $H_2S_2O_7$ | 25.33 |
| Volume after burning | 78.00 | Oxygen added | 76.28 |
| Contraction produced | 31.54 | Total volume for combustion | 85.13 |
| Volume after KOH absorption | 48.27 | Volume after burning | 64.95 |
| Carbon dioxide produced | 29.73 | Contraction | 20.18 |
| | | Volume after KOH absorption | 49.02 |
| | | Carbon dioxide produced by burning | 15.93 |
| | Per cent | | Per cent |
| Ethane | 23.90 | Ethane | 23.3 |
| Ethylene | 74.40 | Ethylene | 74.1 |

It will be observed that the ethane and ethylene as found by the two methods of analysis check very well, showing that other gases were not present in the distillate in significant amounts. The percentages as found above were averaged and calculated to percentages of the original quantity of gas taken.

SERIES III—After the removal of the ethane and ethylene, there remained 24.4 cc. of gas which was fractionated at a temperature not higher than —120° C. The distillate, 21.1 cc., was analyzed by burning it in oxygen, and measuring the resulting contraction and carbon dioxide and calculating to

propane and propylene. This method does not isolate the gases and hence does not show that other gases than these two were not present. In working on the separation of the paraffin hydrocarbons, however, the Bureau found that propane could be separated from ethane at temperatures between —130° C. and —120° C. Propylene has a boiling point very close to that of propane, and the boiling point of ethylene is not far different from that of ethane; hence it is assumed that propylene and ethylene would respond to the same treatment as the propane and ethane.

SERIES IV — After removing the propylene and propane, there remained a residue of 2.3 cc., only 0.11 per cent of the original quantity of gas (2048.0 cc.). This residue was analyzed by burning it in oxygen, and the contraction and carbon dioxide calculated to butylene. The observed data are given in Table IV.

TABLE IV—ANALYSIS OF BUTYLENE RESIDUE

| | Cc. |
|---|---|
| Volume taken for analysis | 2.3 |
| Oxygen added | 93.81 |
| Total volume | 96.11 |
| Volume after burning | 90.53 |
| Contraction produced | 5.58 |
| Volume after KOH absorption | 82.86 |
| Carbon dioxide produced by burning | 7.67 |

According to the reaction $C_4H_8 + 6O_2 = 4CO_2 + 4H_2O$ there result three volumes contraction and four volumes carbon dioxide, when butylene reacts with oxygen. The contraction and carbon dioxide observed in the above analysis, 5.58 cc. and 7.67 cc., is almost in the ratio of 3 : 4, within the error of making the analysis, hence the data were calculated to butylene. Such a small quantity of gas was available to work upon that there might easily have been a trace of butane present. However, the total quantity compared to the original volume was only 0.11 per cent, or a practically insignificant amount. Benzene that should have appeared in the last fraction did not appear satisfactorily; hence a separate portion of gas was taken for this analysis, as is described later.

The total number of cubic centimeters of gas from the various fractions equals 1782 + 167 + 21.1 + 2.3 = 1972.4 cc. This is exclusive of the benzene. The benzene as found by using a separate portion of the coal gas is 1.33 per cent of the coal gas. Then 2048 cc. × 1.33 per cent = 27.2 cc., and 1972.4 cc. + 27.2 cc. = 1999.6 cc., or within about 4.6 cc. of the amount (1995 cc.) that was fractionated. Considering the number of times the different fractions of gas were handled and measured in the fractionation analysis, this is not a bad check on the operation.

### DETERMINATION OF BENZENE

For the benzene determination a separate quantity of gas was used, and advantage taken of an apparatus suggested by Dr. G. A. Hulett, Chief Chemist of this Bureau, for the determination of water vapor in air. Dr. Hulett suggested that air with its moisture be cooled at the temperature of liquid carbon dioxide, that the air be then removed with a mercury pump, and the water vapor be determined, after removing the cooling medium, by measuring its pressure. It was a simple matter to apply this principle to the determination of benzene in coal gas. The procedure was to free the coal gas of water vapor and introduce it into the liquefaction bulb *b* (Fig. I), cool it at a temperature of —78° C. and remove as much gas with the pump as possible. The stopcock *n* on the bulb was then closed and the Dewar flask containing the cooling medium removed. The condensed liquid in the bulb was then vaporized and its pressure read on the manometer *j* (Fig. I). This pressure compared with the original pressure of the gas gave the percentage of benzene

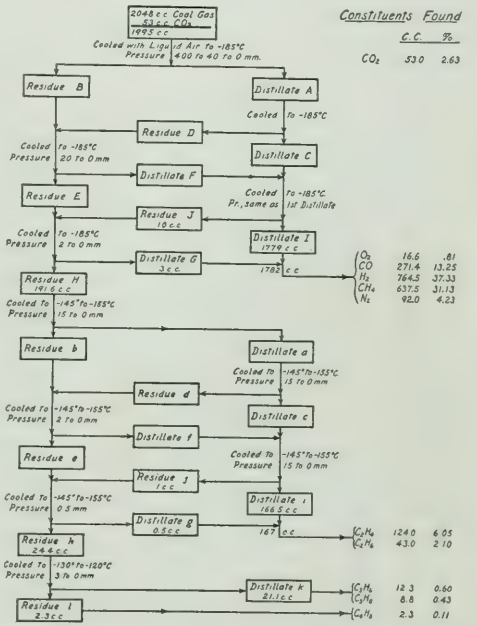


FIG. II—DIAGRAM SHOWING VARIOUS STEPS IN THE FRACTIONATION OF THE COAL GAS OF PITTSBURGH

in the gas. The results of two determinations are shown in the following table:

TABLE V—BENZENE DETERMINATION IN PITTSBURGH GAS

| | | |
|---|---|---|
| Original pressure of gas, mm. Hg | 744 | 744 |
| Partial pressure of benzene vapor | 10 | 9 |
| Illuminants in distillate—per cent of total gas | 7.32 | 7.39 |
| PER CENT BENZENE | $\frac{10 \times 100}{744} = 1.34$ | $\frac{9 \times 100}{744} = 1.31$ |

The total illuminants in the gas of Pittsburgh as found by absorption in fuming sulfuric acid is 8.67 per cent (page 17). The distillate from the benzene determination was analyzed by absorbing the remaining illuminants in fuming sulfuric acid. There was removed 7.32 and 7.39 per cent of the distillates. These amounts when added to the benzene found, 1.31 and 1.34 per cent, equals 8.66 and 8.70 per cent, or almost identically the same quantities as the total illuminants in the coal gas. Benzene reacts with oxygen as follows:

$$C_6H_6 + 7.5O_2 = 6CO_2 + 3H_2O$$

The contraction is 2.5 volumes and the carbon dioxide is 6 volumes. The following data show the results of analysis of the residual vapor that was held in the liquefaction bulb (Fig. I) when the coal gas was cooled at a temperature of —78° C. Before analysis the benzene vapor was diluted with air.

TABLE VI—ANALYSIS OF BENZENE VAPOR

| | Cc. |
|---|---|
| Volume taken for analysis | 28.29 |
| Oxygen added | 51.94 |
| Total volume | 80.23 |
| Volume after burning | 75.47 |
| Contraction due to burning | 4.76 |
| Volume after KOH absorption | 64.25 |
| Carbon dioxide produced by burning | 11.42 |

It will be observed that the ratio between the carbon dioxide and contraction is almost exactly 6 : 2.5, showing that the vapor obtained in the determination was benzene. Traces of other easily condensable vapors may have been present but apparently in such small quantities as to be negligible. The authors of this publication were unable to find the vapor pressure of benzene at —78° C., but apparently it is very small. Benzene boils at 80° C. At —20° C. the tension is 5.76 mm.[1] The authors prepared saturated vapors of benzene by shaking pure benzene with dry air. It was a simple matter to prepare unsaturated vapors of benzene by merely diluting the saturated vapors with air. The quantity of benzene in the air was checked by combustion analysis. A number of tests were made of the benzene in air by the method just described. It was found that at —78° C. all of the benzene could be separated from the air. Analyses were made of the distillates and residues to make sure that all of the benzene remained in the liquefaction bulb at the temperature of —78° C. The foregoing method therefore seems to be well adapted for the benzene determination. There is needed a mercury pump, a liquefaction bulb, a gas burette for introducing the gases, and a Dewar flask for holding the refrigerant. A temperature of —78° C. can be easily obtained by mixing solid carbon dioxide with acetone. The coal gas does not even have to be measured and its exact volume determined. It is sufficient to introduce it into the liquefaction bulb at atmospheric pressure and then to read the barometer.

The complete analysis of the artificial gas as found by the foregoing methods is given in Table VII.

TABLE VII—COMPLETE ANALYSIS OF ARTIFICIAL GAS OF PITTSBURGH

| Constituent | Per cent | Constituent | Per cent |
|---|---|---|---|
| Carbon dioxide, $CO_2$ | 2.63 | Ethylene, $C_2H_4$ | 6.05 |
| Oxygen, $O_2$ | 0.81 | Propylene, $C_3H_6$ | 0.60 |
| Carbon monoxide, CO | 13.25 | Butylene, $C_4H_8$ | 0.11 |
| Hydrogen, $H_2$ | 37.33 | Benzene, $C_6H_6$ | 1.33 |
| Methane, $CH_4$ | 31.13 | Nitrogen, $N_2$ | 4.23 |
| Ethane, $C_2H_6$ | 2.10 | | |
| Propane, $C_3H_8$ | 0.43 | TOTAL | 100.00 |

## ANALYSIS OF A DIFFERENT SAMPLE OF ARTIFICIAL GAS

Table VIII gives the analysis of a sample of the artificial gas of Pittsburgh collected at a different date than the one already given. It is interesting as showing the marked uniformity of the gas as collected on two days about seven weeks apart. The benzene was not determined in this analysis because the method had not been perfected.

[1] Landolt and Börnstein, "Physikalish-Chemische Tabellen," 1905, p. 143 (according to Regnault).

TABLE VIII—ANALYSIS OF A SAMPLE OF ARTIFICIAL GAS OF PITTSBURGH MADE ON JULY 10, 1914

| Constituent | Per cent | Constituent | Per cent |
|---|---|---|---|
| Carbon dioxide, $CO_2$ | 2.40 | Ethane, $C_2H_6$ | 1.92 |
| Oxygen, $O_2$ | 0.61 | Propane, $C_3H_8$ | 0.32 |
| Carbon monoxide, CO | 13.63 | Ethylene, $C_2H_4$ | 6.36 |
| Hydrogen, $H_2$ | 37.13 | Propylene, $C_3H_6$ | 0.70 |
| Methane, $CH_4$ | 30.92 | Butylene, $C_4H_8$ | 0.12 |

## HEATING VALUE OF THE ILLUMINANTS IN THE GAS OF PITTSBURGH

In calculating the heating value of artificial gas from the analysis as ordinarily made, a value is usually assigned to the illuminants that is an approximation because the constituents that make up the illuminants have not been exactly known. With these data at hand for the gas of Pittsburgh the authors show below a value calculated from the complete analysis:

TABLE IX—HEATING VALUE OF THE ILLUMINANTS IN ARTIFICIAL GAS

| Constituents | B. t. u. per cu. ft. at 0° C. and 760 mm.(a) | Per cent present in the gas | Heating value of constituents present in the gas |
|---|---|---|---|
| Ethylene | 1673 | 6.05 | 101.21 |
| Propylene | 2509 | 0.60 | 15.05 |
| Butylene | 3265 | 0.11 | 3.59 |
| Benzene | 4012 | 1.33 | 53.36 |
| Propane | 2654 | 0.35 | 9.29 |
| Total | | 8.44 | 182.50 |

(a) These heating values were calculated from the values as found by Thomsen. His values are given in Landolt and Börnstein's "Physikalish-Chemische Tabellen," 1905, p. 425. They are given in large calories per gram-molecule.

According to the above calculations the illuminants have a heating value at 0° C. and 760 mm. of pressure of $\frac{182.50 \times 100}{8.44} = 2162$ B. t. u. The authors have included propane in the illuminants as ordinarily determined by absorption in fuming sulfuric acid because propane dissolves to a certain extent in the acid. Just how much is not known. It was found that the methane and ethane[1] were soluble to a slight extent. Unquestionably propane is much more so because the higher paraffins are more soluble than the lower ones. Excluding propane, the heating value of the illuminants becomes $\frac{173.2 \times 100}{8.09} = 2141$ B. t. u. per cubic foot at 0° C. and 760 mm. pressure.

## ADDITIONAL DETAILS OF THE EXPERIMENT

Temperatures higher than the temperature of liquid air were obtained by cooling a natural gas condensate. This condensate was obtained from a natural gas gasoline plant by subjecting natural gas (casing-head gas) from an oil well to a pressure of 250 pounds per square inch and then cooling it to ordinary temperatures. A steel cylinder, such as is used in transporting oxygen, was shipped to the natural-gas gasoline plant of the Bessemer Gas Engine Company at Follansbee, West Virginia, for the purpose of collecting the condensate. This condensate is known in the natural-gas gasoline trade as "wild" gasoline. It contains large quantities of liquid propane and the butanes, especially the latter, as well as some of the ordinary gasoline constituents, the pentanes, hexanes, etc. Ordinary refinery gasoline, and other substances such as alcohol, ether, methyl and ethyl chloride, jellied so much at low temperatures that they could not be used satisfactorily. In order to obtain a tem-

[1] See Burrell, G. A. and Seibert, F. M., "The Sampling and Examination of Mine and Natural Gases," U. S. Bureau of Mines, *Bull.* 43, 47.

perature higher than the temperature of liquid air, say —140° C., the condensate was placed in a Dewar flask and stirred with a test tube into which liquid air was run until —140° C. was reached. Upon removal of the test tube containing the liquid air the condensate warmed up slowly, about 5° C. to 10° C. per hour, thereby affording sufficient time for the withdrawal of the vapors. If the condensate rose to a higher temperature than was desired it was a simple matter to introduce a little more liquid air and cool it.

Temperature measurements were made with two pentane thermometers. They agreed with each other and gave within 1.5° C. the true melting points of chloroform and carbon disulfide, and the temperature of solid carbon dioxide and acetone. Fresh liquid air as it usually reached the laboratory from a plant near-by had a temperature of —193° C.

The determinations of the traces of hydrogen sulfide, acetylene, carbon disulfide, ammonia, etc., that might have been present in the gas were not attempted.

Future work on the fractionation of artificial illuminating gas will cover the analyses of gas that is used in other cities than Pittsburgh and the separation of the illuminants in the coal gas before it is mixed with carbureted water gas and in oil gas that is used to enrich water gas.

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## SPECIFIC GRAVITY—ITS DETERMINATION FOR TARS, OILS AND PITCHES

By JOHN MORRIS WEISS

Received September 24, 1914

To the average chemist, the subject of specific gravity is one which, on first glance, seems to present few, if any, difficulties. It is a property which is an absolute quantity for any substance at a given temperature. Unlike many of the other properties of substances determined in the tar industry, it is not an arbitrary figure obtained by a very definite method with very careful attention to manipulative details, but may be determined by any method which is theoretically correct, that is, when the mass and volume relative to water are determined at any specified temperature. Therefore, it would seem that on this test, at least, laboratory workers should have no difficulty in obtaining consistent check determinations, both with themselves and others.

As a matter of fact, it has been the writer's experience, so far as tar products are concerned, that very few tests are susceptible of as grave differences in individual results as the specific gravity test. In the writer's opinion, this is due partly to the fact that all workers do not give sufficient attention to the importance of detail in this test, so that often a method, perfectly correct theoretically, may, by unintentional neglect, give incorrect results when carried out in practice. It is therefore necessary to select a method based on sound theory, which can be carried out with the minimum amount of care by the worker, and then so standardize the details of manipulation that, if directions are followed, the true result will be obtained with a sufficient accuracy for the purposes involved.

It is the writer's intention to review the specific gravity methods now in standard use in the laboratories of the Barrett Manufacturing Company, in the hope that they may be of use to chemists who have to carry out specific gravity determinations on tar and tar products, or other similar materials. Most of the *special methods* described have been developed to a large extent in the writer's own laboratory. The descriptive part of this paper may be divided into two parts: *First*, oils; *Second*, tars and pitches. In the course of the paper, attention will also be given to temperature correction factors, their use and misuse.

### I—OILS

In this connection we shall consider oils from coal tar and other tars, presupposing sufficient quantities of material for the ordinary test. In addition, we shall deal with methods that are used when only small quantities of oil are available (less than 20 cc.) as is the case in road compound testing, where the specification calls for the distillation of 100 g. and a subsequent specific gravity of the distillate oil; and also, when a Hempel distillation, according to the Forest Service method for creosote oils, is carried out, and specific gravities are required on the narrow fractions taken.

A. OVER 100 CC. OF OIL AVAILABLE—For any ordinary work, a standardized hydrometer gives sufficiently accurate results. Our custom for creosote oils is to have a set of three, *i. e.*, 1.000 to 1.080, 1.070 to 1.150, and 1.150 to 1.230, compared to water at 15.5° C. These are approximately 225 mm. long; the stems are about 125 mm. in length and the bulbs 24 mm. in diameter: such dimensions adapt them for use in a 100 cc. cylinder of the ordinary type. They are subdivided to 1 in the third place of decimals. For oils lighter than water, similar hydrometers of different ranges are used.

The standard temperatures at which the specific gravities of creosote oils are taken are 15.5° C./15.5° C., and 38° C./15.5° C. As most oils are liquid at 38° C., there is no reason why specific gravities should not, when that temperature is required, be taken at that exact point. If, however, for any reason the reading is taken at a point above the one desired, as is often the case, a correction may be made by adding 0.0008 for every degree Centigrade the temperature is above the standard. To express this in a formula:

$$\text{Sp. gr. } 15.5°/15.5° = \text{Sp. gr. } X°/15.5° + 0.0008\,(X° - 15.5°)$$

If, for any reason, a specific gravity bottle or pycnometer is used at a temperature higher than normal, this correction cannot be applied directly. It is clear that with a pycnometer, the oil must be compared with water at the same temperature, owing to the fact that the absolute capacity of any container varies with the temperature. It is necessary first to calculate the specific gravity X/15.5° from the found figure of X/X and then apply the correction factor given

above. This can be done conveniently by multiplying the figure at X/X by the specific gravity of water at X° compared to water at 15.5°. The figure for water can be obtained or calculated from density tables given in many reference books. That is:

Sp. gr. 15.5°/15.5° = Sp. gr. X/X × Sp. gr. water X/15.5° + 0.0008 (X—15.5°)

It should be borne in mind that this correction factor of 0.0008 per degree centigrade is to be used only on coal tar creosote oils. It is necessary because these oils are frequently solid at 15.5° C., and the specific gravity must of necessity be taken at a higher temperature. Coal tar light oils and distillates from other tars are usually liquid, and can be taken at 15.5° C. Therefore, no very exact correction figure for such substances has been determined. However, if great accuracy is not desired, the same factor can be used for these other materials, if suitable means of cooling are not at hand.

B. LESS THAN 100 CC. BUT NOT MORE THAN 20 CC. OF OIL AVAILABLE—Such cases are comparatively rare, the occasions being when a two-ounce mailing sample is received by a laboratory, and, therefore, there is insufficient for a hydrometer test. Here it is best to use a Westphal balance with the regular plummet. It is necessary in this case to take the specific gravity compared to water at the same temperature, and correct to the desired temperature in the same way as described under A, for the correction of pycnometer gravities.

C. LESS THAN 20 CC. OF OIL AVAILABLE—The method described can be used when as little as 8 cc. of oil are available, and is rapid, convenient, and sufficiently accurate. Any laboratory possessing a Westphal balance can readily use it. As its largest use is in taking specific gravities of small fractions obtained from a Hempel distillation of creosote oil, and as these frequently have limpid points above 50° C., we

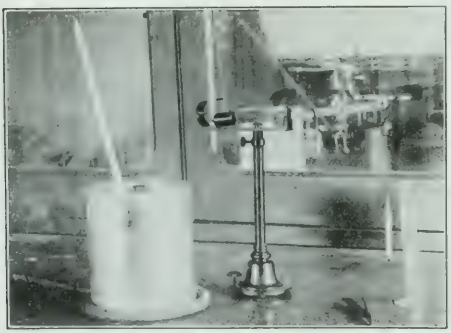


FIG. I

have fixed on 60° C. as the standard temperature at which to make such measurements. A special plummet is used, which is small enough to go in an ordinary 10 cc. cylinder. This plummet can be made readily by any laboratory worker with elementary glass-handling knowledge.

A piece of ordinary glass tubing of about 7 mm. outside diameter is sealed at one end with a short platinum wire melted into the glass where sealed. This is allowed to cool, and about 9–10 g. of mercury,

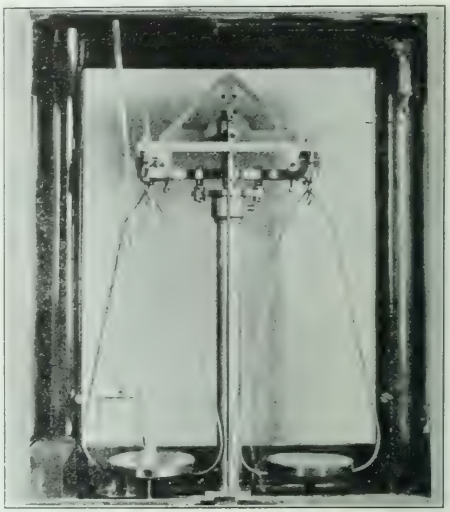


FIG. II

making a column about 35–40 mm. high, is placed in the tube. It is now cut off to within 20 mm. of the top of the mercury, and sealed off with a blowpipe flame. The plummet when completed is about 55–60 mm. long over-all, and should have a weight of from 10 to 12 g. A picture of the Westphal balance equipped with such a plummet, is shown in Fig. I. Beside the balance is shown the heating bath used, which consists of a quart open-top tin can and a ring burner.

In using the plummet, the weight necessary to balance it in both air and water at 60° C. is noted. Similarly, the weight required to balance the plummet in oil at 60° C. is observed. Then

If $a$ = weight required to balance plummet in air,
$b$ = weight required to balance plummet in water,
$c$ = weight required to balance plummet in oil,

$$\text{Specific Gravity of Oil} = \frac{c - a}{b - a}.$$

That this is theoretically correct may be shown by the following reasoning: $b - a$ represents the lifting force exerted by water on the plummet, or, a volume of water equal to that of the plummet has a weight which is represented by $b - a$. Similarly, $c - a$ represents the weight of a volume of oil equal to the volume of water whose weight is represented by $b - a$. As with equal volumes, specific gravity is taken as the relative weight of the substance to water,

$$\text{Specific Gravity of Oil} = \frac{c - a}{b - a}, \text{ as given above.}$$

Occasionally, especially in road compound speci-

fications, the specific gravity of the oil at 15.5°/15.5° is required. This may be obtained approximately by multiplying the figure found at 60°/60° by the specific gravity of water at 60°/15.5°, and adding 0.036 to the result.

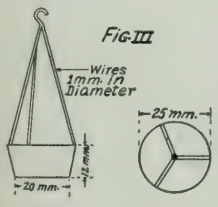
Sometimes there is even too little of the fraction for this method, in which case recourse must be had to some other device. A 1 cc. specific gravity bottle may be used, but we have found that a 1 cc. pipette and a piece of sealed glass tubing, as shown in Fig. II, is very convenient for this purpose. The pipette is standardized by drawing water at 60° C. up into the pipette several times to warm it, then adjusting to the mark, wiping off the outside with a bit of soft paper, inserting it in the glass tube sealed at one end, and weighing it on the balance. The pipette is then dried and the process repeated with the oil to be tested. A piece of rubber tubing on the end of the pipette, which is removed before weighing, serves to protect it from the moisture of the mouth. A small piece of German silver wire, twisted about the pipette near the top, is formed into a ring to support it from the hook above the balance pan (see Fig. II). With this arrangement, results accurate only in the second place of decimals can be obtained.

### II—TARS AND PITCHES

A. TARS—With tars, the method used depends on the consistency of the materials handled. For thin materials, like water gas tars, a specific gravity bottle which is a combination of the Regnault and the Hubbard types, of approximately 50 cc. capacity, is usually employed, filling the bottle with tar and adjusting to the mark at the specified temperature of 15.5° C. The water content of the bottle having been predetermined at the same temperature, a simple division gives the specific gravity.

For the more viscous coal tars, such a method is not applicable. Our standard practice on these materials is to use the same type specific gravity bottle[1] and partially fill with tar, adjusting to the mark with water. This method, however, has several disadvantages, *i. e.*, it is slow and tedious, the large-mouth bottle has a tendency to leak if the stopper is not very carefully ground, and there is considerable breakage of the bottles.

Accordingly, we developed in our laboratory what we call the "platinum pan method," and use it almost exclusively for viscous tars and pitches. A drawing of this pan is shown in Fig. III, and a picture of the same in use in Fig. IV. It is made entirely of platinum, and the supporting wires are joined to the pan and to each other by heavy platinum solder. It has a total weight of about 7 g.




The method of use is simple. It is suspended from the balance pan by a fine, waxed silk thread, and its weight in air and water at 15.5° C. determined. The pan is then ignited over a burner, let cool, and filled with tar. The weight of the pan filled with tar is taken first in air and then in water at 15.5° C.

Let $a$ = weight of pan in air.
$b$ = weight of pan in water.
$c$ = weight of pan plus tar in air.
$d$ = weight of pan plus tar in water.

$$\text{Then Specific Gravity of Tar} = \frac{c - a}{(b + c) - (a + d)}$$

After the test, the pan is held by a pair of tongs and warmed over a burner, the tar poured out, the pan dipped in benzol or naphtha, and burned off, the entire cleaning operation being complete in two minutes. One standardization suffices for a considerable period of time, and need be repeated only when a new thread is taken, or when high-ash materials, such as blast furnace tar, are being handled. The method is quick, clean and accurate.

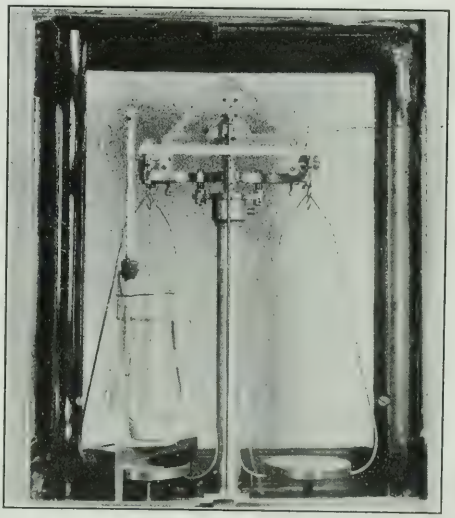


Fig. IV

The use of the hydrometer on tars, though close enough for very rough work, is not to be recommended. For coal tar works tests, it is sometimes used, a factor of 0.000685 per degree centigrade being used as a temperature correction.

B. PITCHES—Here the bottle method is standard for the softer pitches, with the alternative of suspension by a thread in air and water for pitches which are hard enough. For the same general reasons given under tars, we find the pan method more convenient and equally accurate. A lump of the pitch, if hard enough, is used without melting. In the harder pitches, good checks are not obtained as readily as with softer ones. This is because in cooling the melted material, voids are formed in the interior, due to contraction after the surface has hardened. For ordinary work, our practice is to take a lump of the pitch as it comes to hand, though in some very exact work we have slowly

[1] S. R. Church, THIS JOURNAL, 3 (1911), 227; 5 (1913), 195.

cooled the pitch under slight pressure, to avoid the formation of voids. The slow cooling always caused a marked increase in apparent specific gravity with the harder pitches, while with soft pitches the difference is negligible.

The writer hopes that this paper on the homely subject of specific gravity will be useful in some measure to workers in general, and can state that, in his experience, the methods recommended here are rapid, convenient, and sufficiently accurate.

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## OILS OF THE CONIFERAE: IV. THE LEAF AND TWIG OILS OF DIGGER PINE, LODGEPOLE PINE, AND RED FIR

By A. W. SCHORGER

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It is well known at the present time that the oleoresins of the digger pine (*Pinus sabiniana*) and Jeffrey pine (*Pinus jeffreyi*) yield oils consisting almost entirely of *n*-heptane. Examination of the leaf and twig oil of the digger pine has revealed the very interesting fact that heptane was present in the sample to the extent of only about 3 per cent, the remainder of the oil consisting of aromatic bodies which are principally terpenes. It may be assumed with safety that this small percentage of heptane was derived from the small twigs during distillation, since the latter were not separated from the leaves. The phytochemical processes taking place in the leaves and in the woody portions of the tree are, accordingly, entirely different, since the oil from the former consists of aromatic compounds and the oil from the latter of aliphatic derivatives.

Anisic acid was obtained by oxidation of certain fractions of the oils from digger and lodgepole pines. Lack of material prevented obtaining conclusive evidence as to the parent substance from which the anisic acid was derived, and for the same reason the presence of borneol and certain terpenes can not be shown with absolute certainty. The data obtained, however, should be of important assistance to the chemist who is fortunate enough to obtain material for further investigation.

### LEAF AND TWIG OIL OF DIGGER PINE (*Pinus sabiniana*, DOUGL.)

The physical and chemical constants of the oils are given in Table I.

The sample of 238 grams gave the following fractions: 100°–152°, 6.0 per cent; 152°–160°, 10.0 per cent; 160°–170°, 52.0 per cent; 170°–188°, 15.0 per cent; 188°–235°, 8.5 per cent; 235°–290°, 2.3 per cent; residue, 6.0 per cent.

HEPTANE—The lower boiling portions of the oil were fractionally distilled and repeatedly treated with concentrated sulfuric acid. By this treatment 7.2 grams (3.0 per cent) of oil were finally obtained, having the specific gravity 0.7013 at 15° and boiling between 98.5° and 101°. Pure *n*-heptane boils at 98.4° and has a specific gravity at 15° of 0.6880.

α-PINENE—The fraction boiling at 156–157° had $d_{15°}$ 0.8618 and $\alpha_{D20°}$ —26.24°. A good yield of pinene nitrosochloride was obtained. The nitrosochloride was thoroughly washed with methyl alcohol and dissolved in a small amount of hot chloroform. The crop

TABLE I—THE PHYSICAL AND CHEMICAL CONSTANTS OF THE LEAF AND TWIG OILS

| Sample | Sp. gr. 15° | Ref. Ind. 15° | Optical rotation $\alpha_{D20°}$ | Acid No. | Ester No. | Ester No. after acetylation | Per cent yield of oil |
|---|---|---|---|---|---|---|---|
| DIGGER PINE: | | | | | | | |
| 2493 | 0.8566 | 1.4670 | —20.93° | 2.05 | 11.98 | 37.16 | 0.102 |
| 2494 | 0.8543 | 1.4708 | —38.36° | 1.91 | 9.48 | 29.84 | 0.085 |
| 2496 | 0.8517 | 1.4671 | —30.75° | 1.47 | 6.77 | 25.86 | 0.078 |
| LODGEPOLE PINE: | | | | | | | |
| 2495 | 0.8690 | 1.4831 | —17.84° | 0.90 | 6.02 | 32.30 | 0.234 |
| RED FIR: | | | | | | | |
| 2529 | 0.8665 | 1.4861 | —16.70° | 0.75 | 9.93 | 36.22 | 0.154 |

of crystals obtained on cooling, after washing with alcohol, melted at 104–105°. From the chloroform mother liquor a further amount of crystals was obtained on addition of methyl alcohol. These crystals after washing with methyl alcohol melted at 105°. The nitrolpiperidine derivative melted at 117°. The total α-pinene fractions amounted to 58 to 59 per cent.

The relatively small amount of oil boiling between 160–170° was examined for β-pinene with negative results.

LIMONENE—The total limonene fractions amounted to about 24 per cent. The fraction boiling at 170–175° and having $\alpha_{D21°}$ —40.79° gave negative results for phellandrene. Sylvestrene was apparently absent since the dihydrochloride obtained melted at 49–50°. The fraction boiling at 175–177° yielded a tetrabromide melting at 104°, the melting point of limonene tetrabromide.

ESTER FRACTION—The portion boiling at 206–235° was saponified and distilled with steam. The recovered oil was then oxidized with a saturated solution of potassium permanganate and again distilled with steam. Only a few drops of oil having the odor of camphor were obtained. On acidifying the oxidation liquor an acid was obtained that crystallized from hot water in thin needles and sublimed readily, giving crystals melting at 183–184°. A portion of the acid weighing 0.1637 g. required 10.62 cc. of *N*/10 NaOH for neutralization, giving a neutralization equivalent of 154.2. The properties of the acid showed it to be anisic acid, $C_6H_4\begin{cases}OCH_3\\COOH\end{cases}$, the latter melting at 183–184° and having a neutralization equivalent of 152.

The boiling point of the fraction, and other considerations, render it probable that the anisic acid was derived from methylchavicol, the latter boiling at 215–216°. Lack of material, however, prevented obtaining conclusive evidence on this point. Methylchavicol has never been previously detected in the needle oils of the coniferae but was found by Schimmel and Company[1] in "pine oil."

"GREEN OIL"—Only a few drops of oil distilled between 235 and 265°. Between 265 and 290°, 5.4 grams (2.3 per cent) of a light green oil were obtained. When a drop of the oil was dissolved in glacial acetic acid

[1] Report for April, 1910.

and a drop of concentrated sulfuric acid was added the solution turned saffron, then crimson.

LEAF AND TWIG OIL OF LODGEPOLE PINE
(*Pinus contorta*, LOUD.)

The physical and chemical constants of the lodgepole pine oil are given in Table I.

The sample examined amounted to 414 g. and gave the following results on distillation: 164°–170°, 40 per cent; 170–175°, 27 per cent; 175–183, 10.5 per cent; 183–205°, 5.5 per cent; 205–235°, 7 per cent; 235–255°, 0.5 per cent; 255–284°, 6.5 per cent.

FURFURAL—A qualitative test for furfural was obtained in the aqueous extract of the first fraction by means of aniline and hydrochloric acid.

α-PINENE—After repeated fractionation, 12.6 g. (3 per cent) of oil were obtained, having the following properties: b. p. 156–160°, $d_{15°}$ 0.8662, $\alpha_{D25°}$ —24.85°. α-Pinene was identified by means of the nitrosochloride melting at 103.0–103.5° and the nitrolpiperidine melting at 118°.

CAMPHENE—The fraction distilling at 160–164° and having $d_{15°}$ 0.8692, $\alpha_{D25°}$ —23.77°, weighed 22.7 g. (5.5 per cent). This oil was treated with glacial acetic acid-sulfuric acid mixture. On distilling the saponified oil with steam, the greater portion of the distillate came over as an oil. The small amount of solid isoborneol that formed in the condenser melted at 205–207° after one crystallization from petroleum ether.

β-PINENE—The greater portion of the original oil consisted of β-pinene, 205.5 g. (49.6 per cent) being collected between 164–170°. One hundred grams of oil boiling at 166–168° and having $d_{15°}$ 0.8680, $\alpha_{D24°}$ —21.16°, were oxidized with alkaline potassium permanganate. The crystalline sodium nopinate obtained yielded on acidification nopinic acid melting at 127°.

PHELLANDRENE—This terpene was found to be present in considerable amounts in the fractions boiling between 170–180°. The fraction boiling at 170–173° and having $\alpha_{D25°}$ —19.94° gave the largest yield of phellandrene nitrite, the latter melting at 102°.

DIPENTENE—Apparently, owing to the presence of considerable phellandrene, it was not possible to obtain a crystalline tetrabromide. The following fractions were examined: (1) b. p. 173–175°, $d_{15°}$ 0.8577, $\alpha_{D25°}$ —22.06°, weight 33.6 grams; (2) b. p. 175–180°, $d_{15°}$ 0.8577, $\alpha_{D25°}$ —21.85°, weight 19.8 g. By dissolving a portion of fraction (2) in dry ether and saturating with dry HCl gas it was possible to obtain dipentene dihydrochloride melting at 49°.

ESTER FRACTION—The fraction boiling at 205–235° was saponified with alcoholic potash. The oil recovered by steam distillation, having the rotation $\alpha_{D25°}$ —15.58°, was treated with a saturated solution of potassium permanganate until reduction of the solution ceased. On steam distillation a small amount of oil having a strong camphor odor was obtained, but the quantity was too small for further identification. The oxidation liquor was then filtered hot to remove manganese sludge and after cooling extracted with ether. The ether extract gave a little viscous oil having a cinnamon odor. The aqueous solution when acidified gave a copious crystalline precipitate that after sublimation melted at 183–184° and was identified as anisic acid. It is very probable that in this case, as well as in that of the needle oil of digger pine above, the anisic acid may be attributed to the presence of methylchavicol.

CADINENE—The fractions boiling between 265 and 284° were rich in cadinene, the oil having the rotation $\alpha_{D21°}$ +14.69°. The crystals obtained on treatment with HCl gas melted at 117–118° and had in ethereal solution the specific rotation $[\alpha]_D$—45.66° calculated from the following values:

$$\begin{matrix} \alpha = -1.375° \\ l = 1 \end{matrix} \qquad \begin{matrix} p = 4.125 \\ d = 0.7300 \end{matrix}$$

LEAF AND TWIG OIL OF RED FIR (*Abies magnifica*, MURR.)

The oil examined had a light green color and a pungent, unpleasant odor. The physical and chemical constants are given in Table I.

The sample weighing 193 grams distilled as follows: 167–170°, 10 per cent; 170–181°, 47.5 per cent; 181–190°, 12.0 per cent; 190–236°, 9.0 per cent; 236–260°, 13 per cent.

FURFURAL—This aldehyde was qualitatively detected in the first fraction.

α-PINENE—By repeated fractionation 3.6 g. of oil were obtained which boiled at 160–164°. When treated with ethyl nitrite and hydrochloric acid an intense green coloration characteristic of the formation of pinene nitrosochloride developed, but no crystals deposited. There is little doubt that, with sufficient oil for a careful fractionation, the presence of α-pinene could be definitely established.

β-PINENE—The oil boiling at 164–168° had $\alpha_{D24°}$ —25.54°, $d_{15°}$ 0.8620, and yielded sodium nopinate on oxidation. The free nopinic acid melted at 126–127° which proved the presence of β-pinene. From 16–18 per cent of this terpene is present in the oil.

PHELLANDRENE—Phellandrene was the only terpene that could be detected in the fractions boiling above 168° and constitutes about 52 per cent of the original oil. The fraction boiling at 173–177°, $d_{15°}$ 0.8537, $\alpha_{D24°}$ —21.42°, gave a copious precipitate of phellandrene nitrite melting at 102–103°. Dipentene could not be detected as either the dihydrochloride or tetrabromide.

BORNEOL—Saponification of the fraction, boiling point 206–236°, followed by steam distillation yielded an oil. The oil was then oxidized and distilled with steam. The amount of solid camphor that collected in the receiver was too small for further investigation.

"GREEN OIL"—There were obtained between 255° and 260°, 22.3 g. of a deep green oil having the following properties: $d_{15°}$ 0.8963, $n_{D15°}$ 1.4952, specific rotation $[\alpha]_D$ —6.05°. When a drop of the oil was dissolved in glacial acetic acid and treated with bromine vapors the solution first turned purple, then deep blue. No crystalline derivative was obtained.

SUMMARY

The constituents present in the oils examined, with their approximate percentages, are the following:

| Leaf and Twig Oils of<br>Constituents Present | Digger Pine<br>Per cent | Lodgepole Pine<br>Per cent | Red Fir<br>Per cent |
|---|---|---|---|
| Furfural | ... | Trace | Trace |
| *n*-Heptane | 3 | ... | ... |
| *l*-α-Pinene | 58–59 | 3 | ? |
| *l*-Camphene | ... | 5–6 | ... |
| *l*-β-Pinene | ... | 49–50 | 16–18 |
| *l*-Phellandrene | ... | 19 | 52 |
| Dipentene | ... | | 0 |
| *l*-Limonene | 18 | ... | ... |
| Bornyl ester (as acetate) | 3.5 | 2 | 3.5 |
| Free alcohol (as *l*-borneol) | 6 | 7.5 | 7.5 |
| Methylchavicol | ? | ? | ... |
| "Green oil" | 2–3 | ... | 13 |
| Cadinene | ... | 7 | ... |
| Losses by polymerization, etc. | 9.5 | 6 | 6 |

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## THE ELECTROLYTIC SEPARATION OF ZINC, COPPER AND IRON FROM ARSENIC

By A. K. Balls and C. C. McDonnell

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Satisfactory electrolytic methods for the quantitative separation of zinc and iron from arsenic have not been developed up to this time. With respect to the separation of copper from arsenic, several methods are in use, namely, in acid solution according to Freudenberg,[1] and in ammoniacal and cyanide solutions as first suggested by Smith and Frankel,[2] and McCay.[3]

The idea of separating arsenic from other metals by using an electrolyte of sodium or potassium hydroxide, although by no means novel, has not previously been developed to a workable basis except in the separation of tin and arsenic by Lampèn,[4] whose work seems to have been overlooked by more recent writers. A Fischer[5] says relative to separating zinc from arsenic that it has never been investigated and is only conceivable in an alkaline zincate solution with a definite voltage.

The precipitate formed on adding potassium or sodium hydroxide to the solution of a heavy metal is in the case of some metals soluble in an excess of the precipitant, forming a strongly alkaline solution from which the metal can be deposited by the electric current. Zinc and lead are examples of this, while arsenic, on the other hand, exists in solution as an alkaline arsenate or arsenite, and therefore travels toward the anode. With many metals, such as iron and copper, the precipitate is not dissolved by an excess of caustic alkali, but its formation may often be prevented by the action of certain organic substances, particularly citric and tartaric acids, and from these solutions the metal is easily deposited. Alkaline electrolytes are capable, therefore, of rather wide application.

In this paper we wish to describe the conditions which were found to give excellent results in the separation of arsenic from copper, from iron, and more especially from zinc. Some work is being done upon other metals, notably lead, but this is not yet ready for publication.

In all of these separations the arsenic must exist in the higher state of oxidation, otherwise a small quantity will be found in the cathode deposit, and some may also be volatilized.

### ZINC FROM ARSENIC

It is necessary in connection with our official work in this laboratory to examine numerous samples of zinc arsenite and products containing it. It was in the course of investigations conducted on methods for analyzing these substances that the following experiments were undertaken.

The deposition of zinc from a caustic electrolyte in the absence of arsenic has been so fully discussed by others that we shall not take it up here except to say that we have found it entirely satisfactory.

Since a platinum electrode is injured by the deposition of zinc, the cathode used was a nickel dish, preferably with a surface which has been roughened either by etching or sand blasting. The experiments recorded here were very satisfactorily carried out in ordinary nickel crucibles of about 125 cc. capacity, offering to the deposit about 90 cm². of surface. The anode consisted of a No. 14 (B. & S.) platinum wire bent in the shape of a flat oval-shaped paddle, whose blade is about 2.5 × 2.0 cm., and suspended from the spindle of the rotating mechanism so that the paddle blade is just completely immersed in the liquid. This form of apparatus, besides being readily obtainable, has the advantage of permitting an unusually rapid agitation of the electrolyte.

PREPARATION OF SOLUTIONS—For the zinc solution a weighed amount of very pure zinc oxide[1] was dissolved in dilute sulfuric acid and made to a definite volume.

For the arsenic a solution of pure arsenic acid was used, which was standardized by the iodometric method described later.

Measured amounts of the zinc and arsenic solutions were mixed and sodium hydroxide or potassium hydroxide (50 per cent solution) added until the solution became clear, and then in excess to the extent of about 20 g. The solution was diluted to about 95 cc. and electrolyzed. The electrolysis was thus started at room temperature, but the liquid quickly became heated nearly to boiling.

It was found, as mentioned by Amberg,[2] that by using potassium hydroxide decidedly better zinc deposits were obtained than with sodium hydroxide. When sodium hydroxide was used, the deposit frequently showed a tendency to be spongy, although this could be remedied somewhat by increasing the rate of anode rotation. The presence of many organic substances in small quantities will also greatly increase the adherence of the deposit.[3] We found that glycerol and a mixture of equal parts of glycerol and alcohol worked very well in these experiments. Even alcohol alone had the same effect, but in this case a reddish brown resinous body was formed during the electrolysis. This did not vitiate the results, but rendered the siphonate more difficult to handle.

[1] *Z. physik. Chem.*, **12** (1893), 117.
[2] *Amer. Chem. Jour.*, **13** (1890), 428.
[3] *Chem. Ztg.*, **14** (1890), 509.
[4] *Chemische Industrie*, **1907**, 128.
[5] *Electroanalytische Schnellmethoden*, **1908**, 246.

[1] The zinc oxide was analyzed by several methods with the greatest care and found to contain 99.84 per cent ZnO and 0.14 per cent moisture.
[2] *Ber.*, **36** (1903), 2489.
[3] Cf. Gmelin-Kraut, "Handbuch der anorg. Chemie," **4** (1), s. 559 *et seq.* (1911).

According to Amberg,[1] and Spear and Strahan,[2] nitrates should be absent. While we have found that the last trace of zinc is deposited very slowly in the presence of as little as 0.2 g. $KNO_3$, with such small quantities a particularly smooth and adherent deposit is obtained, and since the amount not deposited in a reasonable time should not exceed 0.5 mg., and is usually much less, this error is sometimes allowable. Consequently 0.1 to 0.2 g. of $KNO_3$ may be added to the solution in order to improve the quality of the deposit, without sensibly sacrificing accuracy, unless working upon small amounts of metal or small aliquots. In general, however, we prefer the use of potassium hydroxide, in which case the addition of any of these substances is unnecessary.

The most prolific source of error in all such determinations is undoubtedly in the weighing of the large dishes used as cathodes. The following procedure was found satisfactory. The weighings were made with two dishes, one of which was used always as a counterpoise. The dishes, which weighed approximately 70 g., were washed with absolute alcohol, dried in the air, heated for half an hour in an air oven at 110° and placed in a desiccator over sulfuric acid for at least an hour. They were then removed and weighed immediately. The zinc deposits, after the electrolytes had been siphoned out and replaced by distilled water, were washed well with absolute alcohol, dried in the air, heated in the oven at 110° and weighed as before. It is not necessary to use ether in drying the deposits, nor does any oxidation occur in the oven. Zinc deposits heated for 24 hrs. at a temperature of 140° C. did not show any change in weight.

The zinc was dissolved in strong nitric acid and tested for arsenic with ammonium molybdate. For comparison, similar tests were made on solutions containing known amounts of arsenic oxid. (0.1 mg. $As_2O_5$ was readily detected by this test). In many zinc deposits no arsenic at all was found and in no case did it exceed 0.2 mg.

Hydrogen sulfide was passed into the siphonates from several experiments and the amount of zinc shown to be present never exceeded 0.2 mg. (Such an amount of zinc in a liter of solution gives a distinct opalescence.)

DETERMINATION OF ARSENIC—The method employed for the determination of the arsenic was essentially that of Gooch and Browning[3] and was briefly as follows:

Evaporate the siphonate to about 200 cc. and acidify with sulfuric acid, adding 8 to 10 cc. of concentrated acid in excess. Then add 2 to 3 g. of potassium iodide, and boil down slowly until the volume is reduced to about 90 cc. Cool the solution and destroy the iodine remaining by adding sodium thiosulfate solution from a burette. Immediately add sodium bicarbonate in considerable excess, and titrate with standard iodine. Care should be taken not to continue the evaporation too far, as the large amount of alkali salts present may cause the solution to become superheated, with consequent loss of arsenious iodide.

[1] *Loc. cit.*
[2] THIS JOURNAL, **4** (1912), 889.
[3] *Am. Jour. Science*, **40** (1890), 66.

Number 15 in Table I is the analysis of a commercial zinc arsenite. A two-gram sample was dissolved in sulfuric acid (1 to 5), made to 250 cc., caustic soda added to a 50 cc. aliquot, the arsenic oxidized by warming with a little sodium peroxide, and the solution electrolyzed. The results agreed with those obtained by standard gravimetric methods.

As lead and zinc are frequently found together in combination with arsenic, a few experiments were made to see what effect the lead would have on the procedure. In an alkaline solution lead separates out on the cathode. Cathodic lead tends to be spongy. Gartenmeister[1] has remedied this in an acid electrolyte by adding gallic or tannic acid. While we have found that the same substances will also make the deposit from an alkaline solution smooth, it is doubtful whether the deposited metal is free from organic impurities. If, however, the quantity of lead be quite small in comparison with the surface of the cathode (not more than 0.1 g. metal per 100 sq. cm.) the deposit will be satisfactory without the addition of any extraneous material. Cathodic lead also oxidizes so readily that it must be dried with the greatest care; but if a small quantity of lead is present with a larger amount of zinc, the lead deposits first and is subsequently coated by the zinc, which prevents its oxidation. The combined deposits are weighed, dissolved in dilute nitric acid and the lead determined electrolytically as peroxide.[2] If it is desired to determine directly the zinc, which will be in the siphonate from the $PbO_2$, this may be done by driving off the nitric acid and again using a caustic electrolyte to which about 5 g. of Rochelle salt have been added to hold up traces of nickel dissolved by the acid from the first cathode used.[3] Experiment 16 in Table I is an example of a determination of this kind. To obtain the best results a quantity of zinc at least equal to the lead should be present.

A description of the conditions employed and examples of the results obtained in separating zinc from arsenic are given in Table I.

### IRON FROM ARSENIC

Iron deposits free from arsenic from a solution containing a large excess of caustic potash or soda in which precipitation of iron hydroxide has been prevented by previously adding tartaric acid.[4] The iron so obtained always contains carbon, unless the current is kept below 1.7 amperes per 100 sq. cm. If this is done, the amount of carbon present is negligible. The best results are obtained with a current density of less than 1 ampere per 100 sq. cm. With such a small current, however, the deposition is necessarily very slow, and the use of a rotating electrode unnecessary. It is often necessary to run such determinations over night. The iron may be in either the ferrous or ferric condition. The apparatus used was that described by Smith.[5] It consisted of an ordinary platinum dish cathode and

[1] *Chem. Ztg.*, **37** (1913), 1281.
[2] E. F. Smith, "Electroanalysis," 5th Ed., **1911**, p. 234.
[3] Cf. Vortmann, *Monats.*, **14** (1893), 536.
[4] Vortmann, *Loc. cit.*
[5] "Electroanalysis," 5th Ed., p. 42.

a spiral anode which could be rotated or not as desired.

In the experiments tabulated below the tartaric acid was added to the solution containing a known amount of pure Mohr's salt and a definite quantity of the arsenic acid solution, and this was poured into the caustic potash solution. If a precipitate is once allowed to form it can be redissolved only with the greatest difficulty. An excessive amount of sulfate is to be avoided, as sulfates of the alkalis are insoluble in strong caustic solutions. Occasionally, a deposit of iron oxide was observed at the anode but this can be prevented by the addition of a few cc. of alcohol. As a check on the purity of the deposit, in a number of cases the iron was dissolved in sulfuric acid, reduced with zinc, and titrated with potassium permanganate; and in other cases dissolved in hydrochloric acid and determined as ferric oxide.

Many iron deposits were tested for arsenic in the same manner as the zinc deposits and more than 0.2 mg. of $As_2O_5$ was never found.

TABLE I—SEPARATION OF ZINC FROM ARSENIC

| | Volume of Solution—95 cc. Grams Zn | | Grams $As_2O_5$ | | Conditions of electrolysis | | | | Electrolyte | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Added | Found | Added | Found | Volts | Amps. $ND_{100}$ | Time Min. | Anode rotation, R.P.M | Excess KOH Gms. | Excess NaOH Gms. | Additions |
| 1 | 0.3000 | 0.2996 | 0.0500 | 0.0508 | 5.5 | 5.5 | 90 | 900 | 20 | | |
| 2 | 0.1989 | 0.1992 | 0.0500 | 0.0498 | 4.5 | 4.4 | 60 | 800 | 20 | | |
| 3 | 0.2984 | 0.2985 | 0.1968 | 0.1948 | 4.0 | 2.2 | 90 | 600 | | 21 | 3 cc alcohol |
| 4 | 0.2984 | 0.2986 | 0.1968 | 0.1965 | 4.5 | 4.0 | 70 | 700 | | 21 | 3 cc. alcohol |
| 5 | 0.2984 | 0.2983 | 0.1968 | 0.1962 | 4.5 | 3.2 | 75 | 600 | | 21 | 2 cc. alcohol<br>2 cc. glycerol |
| 6 | 0.2984 | 0.2980 | 0.2172 | 0.2163 | 4.0 | 2.2 | 90 | 800 | 20 | | 2 cc. alcohol<br>2 cc. glycerol |
| 7 | 0.2984 | 0.2990 | 0.2088 | 0.2102 | 4.6 | 4.4 | 45 | 900 | 20 | | 0.2 gm. $KNO_3$ |
| 8 | 0.2984 | 0.2984 | 0.2088 | .... | 4.2 | 3.1 | 60 | 700 | 20 | | 0.2 gm. $KNO_3$ |
| 9 | 0.2984 | 0.2989 | 0.2172 | 0.2180 | 4.5 | 4.0 | 70 | 800 | 20 | | |
| 10 | 0.2984 | 0.2984 | 0.2172 | 0.2178 | 4.5 | 4.0 | 70 | 800 | 20 | | |
| 11 | 0.2000 | 0.2008 | 0.5000 | 0.4995 | 5.5 | 5.5 | 135 | 1000 | 20 | | |
| 12 | 0.1989 | 0.1992 | 0.5000 | 0.5020 | 5.0 | 5.5 | 135 | 900 | 20 | | |
| 13 | 0.1000 | 0.1004 | 0.5000 | 0.4992 | 4.5 | 4.4 | 120 | 900 | 20 | | |
| 14 | 0.0995 | 0.0997 | 0.5000 | 0.5009 | 4.5 | 4.4 | 120 | 900 | 20 | | |
| 15 | 0.1416(a) | 0.1415 | 0.1054(b) | 0.1053 | 4.0 | 2.0 | 60 | 600 | .. | 15 | 5 gm. $Na_2O_2$ |
| 16 | 0.1989 | 0.1991 | 0.1968 | 0.1976 | 4.0 | 2.2 | 60 | 600 | 20 | .. | 0.0717 gm. Pb added<br>0.0712 gm. recovered |

(a) Determination (after removal of arsenic) as carbonate. See Treadwell (Hall), Vol. II, 3rd Ed., p. 142.
(b) Determination as pentasulfid. Neher, *Z. anal. Chem.*, **1893**, s. 45.

TABLE II—SEPARATION OF IRON FROM ARSENIC

| | Volume of Solution—100 cc | | | | | Conditions of electrolysis | | | Electrolyte Grams | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Grams iron | | | Grams $As_2O_5$ | | | | | | |
| No. | Taken | Found | Detd. | Taken | Found | Volts | Amps. $ND_{100}$ | Time. Hrs. | Anode rotation, R.P.M. | Tartaric acid. | Excess KOH. |
| 1 | 0.2000 | 0.1997 | 0.1998 | 0.0500 | 0.0508 | 1.2 | 0.4 | 18 | 0 | 3 | 20 |
| 2 | 0.2000 | 0.2009 | 0.1993 | 0.0434 | 0.0441 | 2.4 | 0.8 | 18 | 0 | 3 | 10 |
| 3 | 0.2000 | 0.1996 | 0.1986 | 0.1086 | 0.1084 | 1.8 | 0.5 | 18 | 0 | 3 | 20 |
| 4 | 0.3000 | 0.3011 | 0.2996 | 0.2172 | 0.2178 | 2.8 | 0.8 | 18 | 0 | 5 | 15 |
| 5 | 0.2000 | 0.1990 | 0.1992 | 0.1968 | 0.1968 | 2.8 | 1.7 | 31/2 | 700 | 5 | 10 |
| 6 | 0.2000 | 0.2004 | 0.1990 | 0.1968 | 0.1968 | 2.8 | 0.8 | 11 | 0 | 5 | 10 |
| 7 | 0.2000 | 0.2007 | 0.2001 | 0.2172 | 0.2169 | 2.8 | 0.8 | 18 | 0 | 3 | 15 |
| 8 | 0.2000 | 0.2006 | 0.2000 | 0.2172 | 0.2181 | 2.5 | 1.3 | 18 | 0 | 3 | 20 |
| 9 | 0.2000 | 0.2011 | 0.1998 | 0.2172 | 0.2169 | 2.8 | 0.8 | 6 | 0 | 3 | 20 |
| 10 | 0.2000 | 0.1991 | | 0.3932 | 0.3922 | 0.8 | 0.3 | 18 | 0 | 3 | 10 |
| 11 | 0.2000 | 0.2003 | 0.2007 | 0.3932 | 0.3928 | 0.8 | 0.3 | 13 | 0 | 3 | 10 |
| 12 | 0.2000 | 0.2002 | 0.1994 | 0.3932 | 0.3927 | 1.0 | 0.4 | 18 | 0 | 3 | 20 |
| 13 | 0.0800 | 0.0808 | | 0.3932 | 0.3936 | 0.8 | 0.3 | 18 | 0 | 3 | 10 |
| 14 | 0.0800 | 0.0805 | 0.0800 | 0.3932 | 0.3932 | 0.8 | 0.3 | 20 | 0 | 3 | 20 |
| 15 | 0.0800 | 0.0806 | 0.0792 | 0.5000 | 0.4993 | 1.0 | 0.5 | 24 | 0 | 3 | 20 |

The arsenic was determined iodometrically as before. The presence of tartaric acid does not interfere with the titration.

Details of the method and results obtained are tabulated in Table II.

### COPPER FROM ARSENIC

The same general method applies equally well to copper, the precipitation of hydroxide from the alkaline solution being prevented by tartaric acid. The copper separating from a caustic electrolyte tends to be spongy, and in order to get a firmly adherent deposit the anode is rotated quite rapidly (1000–1600 R. P. M.) and about two grams of potassium nitrate are introduced into the solution. The effect here seems to be, as with zinc, to decrease the rapidity of the decomposition while increasing the adherence of the deposit, but all the copper can be removed from the solution easily in a reasonable length of time.

The standard copper solution was prepared by dissolving a weighed amount of pure copper sulfate in water and making up to a definite volume. The copper content was verified by a number of electrolytic determinations in both nitric acid and potassium cyanide electrolytes. The arsenic solution was the same as that used in the work on zinc and iron.

The arsenic in the siphonate was determined iodometrically, as before.

The copper deposits were tested for arsenic with ammonium molybdate, as described previously, and they all showed less than 0.2 mg. of arsenic pentoxide.

The results obtained and details of the experiments are given in Table III.

In general, the successful carrying out of these separations depends principally upon having all the arsenic in the pentavalent form, upon the presence of a sufficient excess of alkali, and upon maintaining the conditions which produce an adherent deposit.

Should the arsenic be present in its lower form of oxidation it will invariably contaminate the deposit, and this will also occur, particularly in the case of iron, if too small an excess of alkali is used. A large excess is always advisable as it does not exert any harmful effect even when the electrolysis is unnecessarily prolonged. The voltage used does not, as far as we have experimented, have any important bearing on the results. Except in the case of iron, the current density may vary between wide limits; however, it occasionally happens that when too large, metallic arsenic will separate on the anode and finally appear in the solution. The time required for an electrolysis depends very largely on the amount of arsenic present, since the arsenates retard the deposition apparently in

TABLE III—SEPARATION OF COPPER FROM ARSENIC

| | Volume of Solution—100 cc. | | | | Conditions of electrolysis | | | | Electrolyte Grams | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Grams Cu | | Grams $As_2O_5$ | | | | | | | | |
| No. | Taken | Found | Taken | Found | Volts | Amps. N.D 100 | Time. Min. | Anode rotation, R.P.M. | $KNO_3$. | Tartaric acid. | Excess KOH. |
| 1 | 0.2061 | 0.2055 | 0.0434 | 0.0446 | 5.5 | 6.0 | 35 | 1200 | 1 | 1 | 20 |
| 2 | 0.2000 | 0.1992 | 0.0500 | 0.0508 | 4.5 | 4.0 | 40 | 1600 | 1 | 1 | 10 |
| 3 | 0.2061 | 0.2059 | 0.1086 | 0.1078 | 5.2 | 5.8 | 30 | 1100 | 1 | 1 | 20 |
| 4 | 0.2061 | 0.2065 | 0.1303 | 0.1307 | 3.6 | 4.0 | 40 | 1300 | 2 | 1 | 20 |
| 5 | 0.2065 | 0.2061 | 0.2088 | 0.2084 | ... | 3.0 | 35 | 1000 | 1 | 1 | 20 |
| 6 | 0.2065 | 0.2064 | 0.2088 | 0.2088 | 4.0 | 4.0 | 30 | 1100 | 1 | 2 | 20 |
| 7 | 0.1993 | 0.1989 | 0.1968 | 0.1968 | 4.0 | 4.0 | 20 | 900 | 0 | 4 | 20 |
| 8 | 0.2065 | 0.2062 | 0.2088 | 0.2084 | 4.0 | 4.5 | 25 | 1100 | 1 | 1 | 20 |
| 9 | 0.2065 | 0.2063 | 0.2088 | 0.2090 | 4.0 | 4.0 | 30 | 1000 | 1 | 1/2 | 20 |
| 10 | 0.2000 | 0.2005 | 0.3932 | 0.3922 | 4.5 | 4.0 | 40 | 1560 | 1 | 1 | 10 |
| 11 | 0.2000 | 0.1994 | 0.3932 | 0.3934 | 4.8 | 5.0 | 40 | 1400 | 1 | 1 | 10 |
| 12 | 0.2000 | 0.2000 | 0.5000 | 0.4993 | 4.8 | 5.0 | 55 | 1400 | 1 | 1 | 10 |
| 13 | 0.0800 | 0.0806 | 0.3932 | 0.3948 | 4.5 | 4.0 | 30 | 1500 | 1 | 1 | 10 |
| 14 | 0.0800 | 0.0796 | 0.3932 | 0.3943 | 4.5 | 4.0 | 35 | 1500 | 1 | 1 | 10 |

much the same way as the nitrates. The drying of the deposits presents no special difficulty, but the weighings should be made with more than ordinary care.

### CONCLUSION

Zinc, iron, copper, and small amounts of lead have all been successfully separated from arsenic in the electrolytic way by using an electrolyte containing a large excess of potassium or sodium hydroxide. The arsenic is determined in the solution from the electrolysis. Conditions have been worked out which insure good deposits, and we believe that the methods will often greatly simplify the course of analysis for many substances containing these metals.

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## THE STANDARDIZATION OF ALKALIMETRIC SOLUTIONS

By FRANCIS D. DODGE

Received October 19, 1914

The text-book methods for determining the value of the acid and alkali solutions employed in volumetric analysis are not perfectly satisfactory as regards ease and convenience of manipulation. This will be admitted by most technical chemists, and will no doubt account for the numerous suggestions which have appeared in the chemical literature in recent years and which have as their object the simplification or improvement of known processes with respect to accuracy as well as convenience.

Any criticism of these methods is not in relation to accuracy of results, because in general that is merely a matter of manipulative skill; but, if one has convenience or economy of time in mind, it would seem that the amount of time and care required is disproportionate, or excessive, as compared with the theoretical simplicity of the end to be attained. Hence it is presumed that an account of some attempts made towards this very desirable simplification may be not without interest.

All methods so far proposed fall naturally into two classes which can be called direct and indirect. The direct methods involve the use of a standard pure substance, which can be weighed with all desirable accuracy and directly titrated. This appears to be the simplest and most desirable way, provided a thoroughly suitable standard substance can be found.

Of the indirect methods, the following may be noted:

PHYSICAL

Determination of specific gravity.

CHEMICAL

Gravimetric determination as $BaSO_4$, or AgCl.

Electrolysis of $CuSO_4$.

Evaporation with $NH_3$, and weighing $(NH_4)_2SO_4$.

Distillation of $NH_3$, etc.

Iodometric, involving the use of iodic acid and iodates, and thiosulfates.

Sodium oxalate, ignited to carbonate.

All these propositions are lacking in simplicity; under special conditions, some of them may, of course, be useful.

As already indicated, the value of a direct method will depend on the availability of the standard substance. A little consideration will show that the latter should comply as far as possible with the following specifications:

1—The standard should be *easily* obtained in a state of sufficient purity.

2—It should be *unalterable* in the air, at ordinary or moderately high temperatures, *i. e.*, neither hygroscopic nor efflorescent. Hence, hydrated compounds are, in general, undesirable.

3—It should be readily soluble in water and alcohol, thus allowing immediate titration in the cold.

4—It should have a high molecular, or equivalent weight, thus lessening the effect of small errors in weighing.

5—On titration, no interfering product, as carbonic anhydride, should be present.

6—The standard should be free from color, before and after titration, to avoid interference with indicators.

As far as the writer has been able to ascertain, no standard substance so far suggested answers perfectly these requirements.

Brief consideration and criticism of the degrees of approximation to the ideal exhibited by the compounds already proposed are presented below:

| | STANDARD SUBSTANCE | Equivalent weight | Fails to pass Specification No. | | | | |
|---|---|---|---|---|---|---|---|
| | FOR ACIDS | | | | | | |
| 1 | Sodium carbonate | 53 | 1 | 2 | | | 5 |
| | Sodium metal | 23 | | 2 | | 4 | |
| | Magnesium metal | 24 | 1 | | | 4 | |
| | Borax | 191 | | 2 | | | |
| | Calcium carbonate (Iceland spar) | 50 | | | | | 5 |
| | FOR ALKALIES | | | | | | |
| | Oxalic acid, anhydrous | 45 | 1 | 2 | | 4 | |
| | hydrated | 63 | 1 | 2 | | 4 | |
| | Acid oxalates | | 1 | 2 | | | |
| | Succinic acid | 59 | | | | 4 | |
| | Malonic acid | 52 | 1 | | | 4 | |
| | Benzoic acid | 122 | | | 3 | | |
| | Phthalic acid | 83 | | | 3 | | |
| | Phthalic anhydride | 74 | | | 3 | | |
| | Salicylic acid | 138 | | | 3 | | |
| | Nitro and amino acids | .. | 1 | | | | |
| | Picric acid | 212 | | | | | 6 |
| | Potassium bichromate | 146 | | | | | 6 |
| | Potassium bitartrate | 188 | | | 3 | | |
| | Betain hydrochloride | 153.5 | 1 | 2(?) | | | |

The use of potassium acid tartrate has been strongly recommended by Borntraeger,[1] and the writer has obtained excellent results with it. Its purification is not exactly easy, but the main objection is its great

[1] *Zeit. anal. Chem.*, **25**, 334.

insolubility in water and in alcohol, which makes the titration tedious. As an improvement on this, it seemed that an analogous compound might be more convenient as regards solubility, and the acid phthalates appeared worthy of examination.

The acid phthalate of potassium has not apparently been described. It is readily obtained by half-neutralization of a solution of phthalic anhydride and crystallizes nicely in hexagonal plates.

### ACID POTASSIUM PHTHALATE

PREPARATION—50 g. resublimed phthalic anhydride are dissolved in about 200 cc. of water. The solution is exactly neutralized with a solution of about 60 g. of pure potassium hydroxide in an equal amount of water; 50 g. more of anhydride are then added, and the heating continued until all crystals are dissolved. The solution is now made up to about 550 g. with water, filtered hot, if necessary, and let cool, with continuous agitation to promote the formation of small crystals. When cold, the latter are filtered by suction or centrifuge. The yield is about 125 g. The product is recrystallized from 300 cc. of hot water and dried at 110°.

The salt is anhydrous $KHC_8H_4O_4$ with mol. wt. 204. It is soluble in 10 to 11 parts of water at ordinary temperatures, and in about 400 parts alcohol.

This compound seems to approximate the ideal substance, as shown by the following facts:

1—As regards purity, the sublimed anhydride is an admirable raw material and not expensive. Recrystallization of the salt is hardly necessary as the impurities derived from the alkali used should be minimal.

2—The salt is stable, anhydrous, not hygroscopic.

3—The solubility in water is sufficient.

4—The molecular weight is higher than that of any compound so far proposed, except picric acid.

5—It behaves like a monobasic acid, and can be titrated with all desirable sharpness.

6—It is colorless.

7—The writer has found it to work well in practice.

The acid phthalate of sodium was obtained by Wislicenus[1] as a by-product, and described as glassy, prismatic crystals, containing $2H_2O$. Salzer,[2] however, reports the salt as anhydrous. It is easily prepared in the manner described for the potassium salt, substituting sodium hydroxide or carbonate. In all cases, however, the writer found the fine transparent prisms to contain $^1/_2H_2O$. The salt is soluble in about 9 parts water at 25° and analyzed for moisture as follows:

| Wt. of salt Grams | Treatment | Time Hrs. | Loss in Weight Gram | Per cent |
|---|---|---|---|---|
| 5 (air-dry) | Desiccator | 115 | 0.0055 | 0.11 |
| | Heated at 50° C. | 24 | 0.0070 | 0.14 |
| | Heated at 100–110° C | 12 | 0.2410 | 4.82 |
| 1.97 (air-dry) | Heated at 110° C. | 12 | 0.0950 | 4.82 |
| Moisture calculated for $NaHC_8H_4O_4.^1/_2H_2O$ | | | | 4.57 |

The salt is thus fairly stable up to 50°; at 100–110° the crystals lose $^1/_2H_2O$ and become opaque, but retain their prismatic form. This anhydrous salt may be used as a standard, but the potassium salt seems preferable.

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[1] *Ann.*, **242**, 89.
[2] *Ber.*, **30**, 1496.

## THE INFLUENCE OF HYDROXY ACIDS AND LACTONES UPON DETERMINATIONS OF THE CHEMICAL CONSTANTS OF FATTY ACIDS

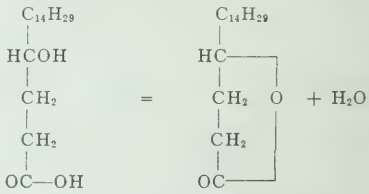
By C. A. BROWNE

Received October 6, 1914

The recent paper by Holland[1] upon "The Determination of the Acetyl Number of Oils, Fats, Etc.," recalls former discussions by Lewkowitsch, Benedikt and others regarding the value of the acetyl figure in the analysis of fatty acids. As the author has recently studied the determination of the acetyl number and other chemical constants in the insoluble acids of several decomposed butter fats, a few observations upon certain analytical data may possibly be of interest.

A serious difficulty, which often confronts the chemist in the analysis of fatty-acid mixtures, is the unstable character of the hydroxy-fatty acids. The latter, from their chemical behavior may be divided into two general classes: (1) the lactone-forming and (2) the non-lactone-forming hydroxy acids.

Lactone-forming hydroxy acids (more especially the $\gamma$ acids) show a pronounced tendency, after being liberated, to form inner anhydrides. Thus $\gamma$-hydroxy-stearic acid, after separation from its salts or esters, passes immediately into stearo-lactone.




Hydroxy-stearic acid Stearo-lactone

The non-lactone-forming hydroxy acids, on the other hand, do not possess the property of yielding inner anhydrides. The hydroxyl group of this class of fatty acids remains unchanged and, in distinction from the hydroxyl group of the lactone-forming acids, is free to react with acetic anhydride during acetylation.

This difference in properties of the two classes of hydroxy-fatty acids has frequently been disregarded by chemists in their treatment of the subject. It is evident, however, that this factor must play at times an important part in the analysis of complex fatty acid mixtures.

### INFLUENCE OF HYDROXY-FATTY ACIDS AND LACTONES ON DETERMINATIONS OF THE ACID, SAPONIFICATION AND ETHER NUMBERS

The insoluble acids prepared from the ordinary normal animal fats show usually but little difference between the acid and saponification numbers, the ether number in such cases being practically zero.

[1] THIS JOURNAL, **6** (1914), 482.

In the case, however, of oxidized and decomposed fats, which contain hydroxy compounds, the formation of lactones in the mixture of fatty acids causes a depression in the acid number and an increase in the saponification and ether numbers. This can best be understood by taking a specific example.

Hydroxy-stearic acid, $C_{17}H_{34}OHCOOH$, of molecular weight 300.288 requires for neutralization and saponification 56.108 molecular parts of KOH. The milligrams of KOH necessary to neutralize and saponify 1 g. of hydroxy-stearic acid are then $56108 \div 300.288 = 186.85$, the acid and saponification number.

If we take a mixture consisting of one molecular part of hydroxy-stearic acid and one molecular part of stearo-lactone the reaction upon neutralization with KOH would be

$$C_{17}H_{34}OHCOOH + C_{17}H_{34}CO_2 + KOH$$
Hydroxy-stearic acid Stearo-lactone
$$= C_{17}H_{34}OHCOOK + C_{17}H_{34}CO_2 + H_2O$$
Potassium hydroxy-stearate Stearo-lactone

In other words 582.560 molecular parts of the mixture would require for neutralization 56.108 molecular parts of KOH. The acid number of the mixture is then $56108 \div 582.560 = 96.31$.

If we saponify the same mixture with KOH, the formula for the reaction would be

$$C_{17}H_{34}OHCOOH + C_{17}H_{34}CO_2 + 2KOH$$
Hydroxy-stearic acid Stearo-lactone
$$= 2C_{17}H_{34}OHCOOK + H_2O$$
Potassium hydroxy-stearate

That is, 582.560 molecular parts of mixture would require for saponification 112.216 molecular parts of KOH. The saponification number of the mixture is then $112216 \div 582.560 = 192.62$.

It is thus seen that if one-half of a sample of hydroxy-stearic acid should undergo lactonization the acid number would be depressed from 186.85 to 96.31 and the saponification number increased from 186.85 to 192.62. The original ether number of zero would become $192.62 - 96.31 = 96.31$.

The occurrence of fatty acids which show a higher saponification than neutralization value has been frequently reported. Tortelli and Pergami[1] give a long list of fatty acids from various sources which show striking differences of this kind, these differences being usually found to increase with the age of the sample. Obviously with these differences in the acid and saponification numbers similar differences will be produced in the calculations of the mean molecular weights of the fatty acids.

Lewkowitsch[2] has also determined the acid and saponification numbers of mixed fatty acids and his results in general confirm the figures of Tortelli and Pergami. The general explanation of the differences, according to Lewkowitsch, is the occurrence of hydroxylated fatty acids which subsequently undergo dehydration with formation of lactones.

A few of the results obtained by Tortelli and Pergami and by Lewkowitsch are given in Columns I to V of Table I. Two determinations made by the author upon the insoluble acids of decomposed butter fat are also included for comparison.

TABLE I

| Source of insoluble fatty acids | I Acid No. | II Mol. wt. from I | III Sapon. No. | IV Mol. wt. from III | V Diff. II–IV | Mol. wt. original lactone-free acids |
|---|---|---|---|---|---|---|
| TORTELLI AND PERGAMI | | | | | | |
| Linseed oil—3 yrs. | 191.5 | 292.8 | 205.4 | 273.2 | 19.6 | 274.4 |
| Cottonseed oil—2½ yrs. | 194.3 | 288.7 | 204.5 | 274.3 | 14.4 | 275.3 |
| Cherry kernel oil | 191.3 | 293.2 | 213.7 | 262.5 | 31.7 | 264.4 |
| Olive oil—3 yrs. | 194.5 | 288.4 | 200.9 | 279.1 | 9.3 | 279.9 |
| LEWKOWITSCH | | | | | | |
| Tung oil | 181.3 | 309.5 | 198.7 | 282.3 | 27.2 | 284.0 |
| Peach kernel oil | 196.8 | 285.0 | 205.0 | 273.6 | 11.4 | 274.4 |
| Olive oil | 200.9 | 279.2 | 200.9 | 279.2 | 0.0 | 279.2 |
| Lard | 196.0 | 286.2 | 205.1 | 273.5 | 12.7 | 274.4 |
| BROWNE | | | | | | |
| Butter fat—17 yrs. | 211.3 | 265.5 | 219.6 | 255.5 | 10.0 | 256.3 |
| Butter fat—17 yrs. | 209.4 | 267.9 | 218.0 | 257.3 | 10.6 | 258.1 |

## CALCULATION OF THE MEAN MOLECULAR WEIGHT OF INSOLUBLE FATTY ACIDS

The customary method of calculating the mean molecular weight of insoluble fatty acids by dividing 56108 by the acid number has caused many erroneous reports of this constant to appear in the literature. In the case of fatty acids which contain lactones the calculation of the mean molecular weight from the saponification number of the insoluble acids is much more accurate but is still incorrect since the weight of fatty acids taken for analysis has not been corrected for the loss in water which has resulted from formation of lactones. The correction for this loss in weight can be made as follows:

The ratio between the weight of water lost by formation of lactones and the weight of KOH required to saponify lactones is represented by

$$\frac{H_2O}{KOH} = \frac{18.016}{56.108} = 0.3211.$$

Let $a$ be the acid number and $s$ the saponification of a mixture of fatty acids; then the grams of KOH required to saponify the lactones in 1 g. of fatty acids equal $0.001\,(s - a)$ and the weight of water lost by dehydration is $0.0003211\,(s - a)$. The saponification number of the fatty acids before lactone formation would then be $\frac{s}{1 + 0.0003211\,(s - a)}$ which divided into 56108 would give the mean molecular weight ($m$) or

$$m = \frac{56108 + 18.016\,(s - a)}{s}$$

It was by this formula that the molecular weights of the original lactone-free acids in Table I were calculated. While the values thus found do not greatly differ from those calculated from the saponification numbers there might arise instances where the errors by the latter method would be of considerable importance.

## INFLUENCE OF HYDROXY ACIDS AND LACTONES ON DETERMINATION OF THE ACETYL NUMBER

It was one of the services of Lewkowitsch to call the attention of chemists to the necessity of determining the acetyl constant of fatty acids by a direct estimation of the acetic acid. He showed that the original method of Benedikt and Ulzer, by which the acetyl number was estimated by taking the difference

[1] L'Orosi, **1901**, 1; Lewkowitsch, "Oils, Fats and Waxes," 4th Ed., Vol. **1**, pp. 419–421.

[2] Lewkowitsch, "Oils, Fats and Waxes," 4th Ed., Vol. **1**, p. 421.

between the acid and saponification numbers of the acetylated fatty acids, usually gave too high results. This error was explained by Lewkowitsch as being due to the conversion of a part of the fatty acids during acetylation into anhydrides of the general formula $(RCO)_2O$: the latter by not becoming completely hydrolyzed during the subsequent washing cause a depression in the acetyl-acid number with a consequent increase in the acetyl-ether number. As examples of the effects of anhydride formation Lewkowitsch[1] states that he obtained the following acetyl values: palmitic acid 82.6, stearic acid 82.29, capric acid 174.00, lauric acid 132.49. These high results, however, must have been due to some unusual condition of acetylation as no such values are obtained under the conditions described by Benekidt and Ulzer for their method.

The errors of estimating the acetyl constant of fatty acids by taking the difference between the acid and saponification numbers of the acetylated acids were also recognized by Benedikt and Ulzer.[2] These authorities took the view, however, that, since fatty acids which contained no hydroxyl groups showed practically the same acid number before and after acetylation, the formation of fatty anhydrides of the formula $(RCO)_2O$ was not the real cause of the error. Benedikt and Ulzer attributed the discrepancies rather to the formation during acetylation of inner anhydrides or lactones of the general formula $R\begin{cases} O \\ | \\ CO \end{cases}$, which would cause a decrease in the acetyl-acid number and an increase in the acetyl-ether number. Since, however, this increase in the acetyl-ether number is due primarily to hydroxy acids which have undergone lactonization, the acetyl-ether number would still remain a fairly accurate measure of the hydroxy acids which were originally present.

As for the lactones which might occur in the mixed fatty acids and would also cause an increase in the acetyl-ether number, Benedikt and Ulzer[3] subtract the ether number due to such lactones from the acetyl-ether number and call the remainder the true acetyl number (Reine Acetylzahl).

A clearer idea of the various questions involved may be secured if we take again the previous example of an equimolecular mixture of hydroxy-stearic acid and stearo-lactone. The action of acetic anhydride upon such a mixture would be

$$\underset{\text{Hydroxy-stearic acid}}{C_{17}H_{34}OHCOOH} + \underset{\text{Stearo-lactone}}{C_{17}H_{34}CO_2} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

$$= \underset{\text{Acetoxy-stearic acid}}{C_{17}H_{34}OCH_3COCOOH} + \underset{\text{Stearo-lactone}}{C_{17}H_{34}CO_2} + \underset{\text{Acetic acid}}{CH_3COOH}$$

When the acetylated acids are neutralized with KOH, as in the determination of the acetyl acid number, the reaction proceeds as follows:

$$\underset{\text{Acetoxy-stearic acid}}{C_{17}H_{34}OCH_3COCOOH} + \underset{\text{Stearo-lactone}}{C_{17}H_{34}CO_2} + KOH$$

$$= \underset{\text{Potassium acetoxy-stearate}}{C_{17}H_{34}OCH_3COCOOK} + \underset{\text{Stearo-lactone}}{C_{17}H_{34}CO_2} + H_2O$$

624.576 molecular parts of acetylated mixture require for neutralization 56.108 parts of KOH. The acetyl-acid number of the mixture would then be $56108 \div 624.576 = 89.83$.

In case the acetylated mixture be saponified with an excess of KOH the reaction would be

$$\underset{\text{Acetoxy-stearic acid}}{C_{17}H_{34}OCH_3COCOOH} + \underset{\text{Stearo-lactone}}{C_{17}H_{34}CO_2} + 3KOH$$

$$= 2\underset{\text{Potassium hydroxy-stearate}}{C_{17}H_{34}OHCOOK} + \underset{\text{Potassium acetate}}{CH_3COOK} + H_2O$$

The acetyl-saponification number of the acetylated mixture would then be $168324 \div 624.576 = 269.50$.

The acetyl-ether number (acetyl number of Benedikt and Ulzer) is then $269.50 - 89.83 = 179.67$.

The acetyl number of Lewkowitsch, *i. e.*, the mg. of KOH necessary to saponify the combined acetyl would be $56108 \div 624.576 = 89.83$.

The relationship of the theoretical constants for the non-acetylated and acetylated mixture of hydroxy-stearic acid and stearo-lactone is shown in Table II:

TABLE II

| Hydroxy-stearic acid and stearo-lactone | Acid No. | Sapon. No. | Ether No. | Acetyl No. | Lactone No. |
|---|---|---|---|---|---|
| Non-acetylated | 96.31 | 192.62 | 96.31 | ... | 96.31 |
| Acetylated | 89.83 | 269.50 | 179.67 | 89.83 | 89.83 |

The acid number of the acetylated mixture is lower and the ether and saponification numbers are higher than the similar constants of the non-acetylated product.

The lactone number, *i. e.*, the mg. of KOH necessary to saponify the lactones in 1 g. of acids is lower in the acetylated mixture.

If we subtract the ether number of the non-acetylated from the ether number of the acetylated mixture we obtain 83.36—the so-called "Reine Acetylzahl" of Benedikt and Ulzer; this value, owing to the non-correction for increase in weight of the fatty acids during acetylation, is less than 89.83—the true acetyl number of Lewkowitsch.

Theoretically, the increase in weight of fatty acids during acetylation is expressed by the ratio of the acid number of the non-acetylated divided by the acid number of the acetylated acids.

Let $a$ be the acid no. of the non-acetylated acid.

Let $\alpha$ be the acid no. of the acetylated acid.

Let $s$ be the saponification no. of the non-acetylated acid.

Let $\sigma$ be the saponification no. of the acetylated acid.

Let $e$ be the ether no. of the non-acetylated acid.

Let $\epsilon$ be the ether no. of the acetylated acid.

Let $x$ be the acetyl no. on basis of non-acetylated acid.

Let $\xi$ be the acetyl no. of the acetylated acid.

The ratio of KOH used in saponifying acetyl to the increase in weight of fatty acids during acetylation is expressed by:

$$\frac{C_2H_2O}{KOH} = \frac{42.016}{56.108} = 0.7488$$

[1] Lewkowitsch, *J. Soc. Chem. Ind.* (1890), p. 660.

[2] Benedikt-Ulzer, "Analyse der Fette," 3rd Ed. (1897), p. 179.

[3] Benedikt and Ulzer, "Analyse der Fette," 3rd Ed. (1897), p. 650. In the sentence "Davon ist die constante Verseifungszahl in Abzug zu bringen" Verseifungszahl is obviously a misprint for Aetherzahl.

If $x$ be the true acetyl number on the basis of the non-acetylated acids, the g. of KOH necessary to saponify the acetyl after acetylating 1 g. of mixed acids would be $0.001x$. The weight of the 1 g. of acids after acetylating would then be $1 + 0.0007488x$.

Then

$$\frac{x}{1 + 0.0007488x} = \xi$$

$$\text{and } x = \frac{\xi}{1 - 0.0007488\,\xi} \qquad \text{I}$$

$$\frac{a}{1 + 0.0007488\,x} = \alpha \qquad \text{II}$$

Substituting I in II we obtain

$$\xi = \frac{a - \alpha}{0.0007488\,a} \qquad \text{III}$$

The small denominator in Formula III causes a very great multiplication of any experimental errors. The following methods of calculation are less objectionable.

Theoretically, the lactone number of the acetylated acids equals $\frac{e\alpha}{a}$, then the acetyl number of the acetylated acids is found by the equation

$$\xi = \epsilon - \frac{e\alpha}{a} \qquad \text{IV}$$

Since $e = s - a$ and $\epsilon = \sigma - \alpha$, we obtain by substituting these values for $e$ and $\epsilon$ in Equation IV

$$\xi = \sigma - \frac{s\alpha}{a} \qquad \text{V}$$

The determination of the acetyl number in the insoluble acids of two decomposed butter fats was carried out by the author both according to the original Benedikt-Ulzer method and the improved method of Lewkowitsch. The determinations were all made upon the same weighed sample of acetylated acids.

After determining the acetyl acid and acetyl-saponification numbers, the calculated amount of standard acid was added to unite with all the alkali combined as potassium soaps. The insoluble acids were filtered off and the free acetic acid in the filtrate determined by titration.

The insoluble acids from the determination of the acetyl numbers were washed with boiling water, dried, and the acid and saponification numbers of the de-acetylated product determined. A summary of the results is given in Table III.

TABLE III—INSOLUBLE FATTY ACIDS FROM BUTTER FATS

| No. | | Acid No. | Sapon. No. | Ether No. | Acetyl No. | Lactone No. |
|---|---|---|---|---|---|---|
| 1 | Non-acetylated | 211.32 | 219.59 | 8.27 | ... | 8.27 |
| 1 | Acetylated | 194.71 | 238.88 | 44.17 | 37.04 | 7.13 |
| 1 | De-acetylated | 201.52 | 209.13 | 7.61 | ... | 7.61 |
| 2 | Non-acetylated | 209.45 | 218.02 | 8.57 | ... | 8.57 |
| 2 | Acetylated | 196.21 | 238.65 | 42.44 | 35.72 | 6.72 |
| 2 | De-acetylated | 205.00 | 212.35 | 7.35 | ... | 7.35 |

The same relationship is noted between the constants of the non-acetylated and acetylated acids as between the theoretical constants of Table II.

It will be instructive to compare the acetyl numbers actually determined with the numbers calculated by Formulas III and IV.

The calculation from the acid numbers of the non-acetylated and acetylated acids, using Formula III, gives for Sample 1 an acetyl number of 105.00 and for Sample 2 an acetyl number of 84.40. These calculated values, which are several times those actually found, show a depression in the acid number of the acetylated acids greater than that, due to the increase in weight from acetylation, a depression of 1 in the acid number making a difference of about 7 in the acetyl number as thus calculated.

This excessive depression of the acid number of the acetylated acids, as already stated, was explained by Lewkowitsch as being due to the formation of fatty anhydrides, and by Benedikt and Ulzer as being due to the formation of lactones. There is, however, one other possibility, and that is the decomposition of some of the fatty acids during acetylation. Table III shows that the constants of the de-acetylated acids are uniformly lower than those of the acids before acetylating and this would indicate the formation of small amounts of decomposition products by the boiling acetic anhydride. The much darker color of the de-acetylated acids is an additional indication of such decomposition. If the formation of fatty anhydrides or lactones were the sole cause of the depression in the acetyl-acid number, the constants of the de-acetylated and non-acetylated acids should agree.

If the calculation of the acetyl number be based upon the acid numbers of the de-acetylated and acetylated acids we obtain, using Formula III, for Sample 1 an acetyl number of 45.06 and for Sample 2 an acetyl number of 57.26. The values thus calculated approach much nearer those actually found; there still remains, however, a marked discrepancy which may be due to the dehydration of a small amount of fatty acids during acetylation with formation of anhydrides or lactones.

If the calculation of the acetyl number be based upon the ether or saponification numbers, using Formulas IV or V, experimental errors are less magnified than by use of Formula III and a much closer agreement in the results is obtained.

| | Lactone No. | | Acetyl No. | |
|---|---|---|---|---|
| | 1 | 2 | 1 | 2 |
| From ether no. of non-acetylated acids | 7.62 | 8.03 | 36.55 | 34.41 |
| From ether no. of de-acetylated acids | 7.36 | 7.03 | 36.81 | 35.41 |
| Direct determination | 7.13 | 6.72 | 37.04 | 35.72 |

As was the case with Formula III, the calculations from the constants of the de-acetylated acids agree more closely with the actual determinations than the calculations from the constants of the non-acetylated acids.

A comparison of the lactone numbers shows the determined values to be lower than those calculated, whereas if lactones or anhydrides were formed during acetylation the determined lactone values might be expected to be higher. The contradiction may perhaps be due to the fact that some of the lactones in the fatty acids exist in an unstable $\delta$ or other form, and by the action of the acetic anhydride become acetylated with the hydroxy acids; these decomposed lactones during the drying of the de-acetylated acids

might again be reformed in whole or in part. In confirmation of this view it might be mentioned that Lewkowitsch[1] obtained pronounced acetyl values with certain substances of a lactonic nature. The discrepancies, however, in view of the limitations which attend an indirect method of calculation, are not great enough to warrant making any sweeping conclusions. Further investigations upon the fatty acids from other sources are needed before this and other doubtful points can be decided. Changes during acetylation through the partial destruction of fatty acids, through the formation of small amounts of fatty anhydrides or lactones, and through the slight acetylation of preexisting lactones, may, however, be considered as among the possible causes of disturbances in the normal process of acetylation.

Finally, it must be admitted that there is much truth in the argument that, since the lactones in a mixture of fatty acids are derived from preexisting hydroxy acids, the acetyl number of Benedikt-Ulzer is a truer measure of the original hydroxyl content of fatty acids than the acetyl number of Lewkowitsch. Thus γ-hydroxy-stearic acid in the glyceride molecule can be acetylated and would show an acetyl number by the method of Lewkowitsch, whereas, the separated fatty acids would show no acetyl number on account of the formation of stearo-lactone.

The acetyl value of a mixture of fatty acids may be calculated back to the condition preceding lactone formation in the following way:

The ratio between KOH used to saponify lactones and the increase in weight which the acids would undergo from acetylation of lactones is represented by

$$\frac{C_2H_4O_2}{KOH} = \frac{60.032}{56.108} = 1.07$$

Let $\epsilon$ and $\xi$ be respectively the acetyl-ether and true acetyl numbers, then $\epsilon - \xi$ = the lactone number and 0.001 $(\epsilon - \xi)$ = the g. of KOH required to saponify the lactones in 1 g. of acetylated acids. $1.07 \times 0.001$ $(\epsilon - \xi) = 0.00107$ $(\epsilon - \xi)$ = the increase in weight of 1 g. of acetylated acids if the lactones present were also acetylated.

The original acetyl number, calculated to the acetylated hydroxy acids before lactone formation, then

$$= \frac{\epsilon}{1 + 0.00107\ (\epsilon - \xi)}.$$

In the author's experience a combination of the Benedikt-Ulzer and Lewkowitsch methods for determining the acetyl number has been found to throw most light upon the chemical changes which have taken place in insoluble fatty acids as a result of oxidation. The determinations of acid, saponification, ether, acetyl and lactone numbers can all be performed upon one weighed sample of acetylated acids and the results enable the chemist to estimate the relative distribution of the free and lactonized hydroxy acids.

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[1] Lewkowitsch, *Analyst* (1899), 339.

## A NEW METHOD FOR THE DETERMINATION OF UNSAPONIFIABLE MATTER APPLICABLE TO ETHER EXTRACTS, FATS, OILS AND WAXES[1]

By J. B. RATHER[2]

Received October 27, 1914

Methods for the removal of unsaponifiable matter from fats and oils fall into two divisions:[3] (1) Extraction of the soap solution with solvents, and (2) the extraction of the dried soap with solvents. The method here proposed differs from both of these general processes in that the fatty acids are removed from the unsaponified material by precipitation from ethereal solution.

Stellwaag[4] in his work on the unsaponifiable matter in concentrated feeding stuffs and Fraps and Rather[5] in their investigation on the unsaponifiable matter in hays have shown the need of a rapid and reasonably accurate method for the systematic removal of unsaponified matter in the determination of fats.

### PRECIPITATION METHOD

The method used for the determination of unsaponifiable matter in ether extracts was adopted after considerable experimental work. The data on which it is based will be published in another place.[6] The process, designated as the Precipitation Method, is as follows: Add 20 cc. of approximately 2 *N* alcoholic sodium hydroxide to a known amount of the sample (about 0.4 g.), and boil under a reflux condenser for one hour. Evaporate nearly to dryness and add 3.5 cc. glacial acetic acid, or its equivalent in weaker acetic acid. Add 50 cc. of redistilled ether and warm to dissolve the extract. Add 25 cc. water and warm a minute more. Transfer to a 500 cc. pear-shaped separatory funnel with a short neck and wash out the flask with 5 successive 20 cc. portions of ether, pouring the washings in the funnel. Turn the funnel on its side and shake gently. The two layers should now be clear and the aqueous layer nearly colorless. Draw off the lower layer into a 500 cc. Erlenmeyer flask. Add to the ethereal solution 10 cc. of warm 1 : 2 aqueous sodium hydroxide solution, turn the funnel on its side and shake gently. Allow the precipitate to settle, add 25 cc. warm water, hold funnel in vertical position and give rotary motion. Allow the two layers to separate, and draw off the clear aqueous solution into the Erlenmeyer flask, leaving any emulsion in the funnel. Repeat and then shake gently as above with 5 successive 30 cc. portions of cold water, allowing a short time for the two solutions to separate, and add the washings to the soap solution in the Erlenmeyer flask. Transfer the ethereal solution to a tared 200 cc. flask, evaporate or distil off the ether, and dry to constant weight in a steam oven at 100° C.

The following correction for fatty acids in unsaponified should be used for material high in fatty acids and low in unsaponified. Add 20 cc. of 0.2 *N* hydrochloric

[1] Abstracted by the author from Texas Experiment Station, *Bull.* **169.**

[2] Under the general direction of G. S. Fraps, Chemist.

[3] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., Vol. I, p. 456–60.

[4] *Landw. Versuch. Stat.*, **37**, 148.

[5] Texas Exp. Sta., *Bull.* **150.**

[6] *Loc. cit.*

acid to the ethereal solution of the unsaponified matter in the separatory funnel before evaporation, stopper and shake vigorously. Draw off the aqueous layer and discard. Evaporate the ethereal solution, dry and weigh. Heat to boiling with 20 cc. alcohol, titrate with $N/10$ sodium hydroxide and phenolphthalein, running a blank on the alcohol. Multiply the corrected reading by 0.028. The result is grams fatty acids in the unsaponified matter. Subtract this from the unsaponified matter. The amount of fatty acids dissolved in the ethereal solution of unsaponified matter is, on an average, 16 mg. for substances very low in unsaponified matter and this figure may be used if very accurate results are not desired. The amount of fatty acids in unsaponified fractions from samples containing 25 per cent or more of unsaponified may be disregarded. It amounts to about 2 mg. on an average and is balanced by a corresponding amount of unsaponified matter in the soap solution.

The results on a number of ether extracts from plant and animal products are given in Table I, together with results by the method of Fraps and Rather[1] (Digestion Method).

Table I—Unsaponified Matter in Ether Extracts

| | Method | Precipitation | | Digestion | |
|---|---|---|---|---|---|
| No. | Percentage of | Extract | Sample | Extract | Sample |
| 1 | Wheat shorts | 6 | 0.23 | 6 | 0.23 |
| 2 | Corn chops | 4 | 0.16 | 6 | 0.25 |
| 3 | Cottonseed meal | 3 | 0.47 | 2 | 0.28 |
| 4 | Rice bran | 8 | 0.60 | 2 | 0.18 |
| 5 | Milo maize chops | 7 | 0.21 | 4 | 0.13 |
| 6 | Cold pressed cottonseed | 4 | 0.29 | 2 | 0.16 |
| 7 | Kafir chops | 8 | 0.26 | 17 | 0.56 |
| 8 | Corn bran | 3 | 0.29 | . | .... |
| 9 | Red rice | 9 | 0.15 | 9 | 0.14 |
| 10 | Wheat bran | 6 | 0.25 | 4 | 0.18 |
| 11 | Wheat shorts | 6 | 0.17 | 3 | 0.07 |
| 12 | Rice polish | 0.5 | 0.51 | 0.5 | 0.19 |
| 13 | Tobasa grass | 61 | 0.56 | 36 | 0.33 |
| 14 | Sheep excrement from No. 13 | 66 | 0.70 | 47 | 0.50 |
| 15 | Prairie hay | 37 | 0.84 | 46 | 1.05 |
| 16 | Sudan grass | 38 | 0.55 | 36 | 0.53 |
| 17 | Excrement from No. 15 | 59 | 1.68 | 63 | 1.78 |
| 18 | Excrement from No. 16 | 74 | 1.41 | 69 | 1.32 |
| 19 | Sudan straw | 38 | 0.55 | 30 | 0.43 |
| 20 | Sorghum hay | 27 | 0.49 | 32 | 0.58 |
| 21 | Excrement from No. 19 | 64 | 1.09 | 69 | 1.18 |
| 22 | Moth bean hay | 43 | 0.66 | 47 | 0.73 |
| 23 | Excrement from No. 20 | 61 | 1.08 | 45 | 0.80 |
| 24 | Excrement from No. 22 | 66 | 1.99 | 58 | 1.76 |
| | Average concentrates | 5 | 0.30 | 5 | 0.22 |
| | Average, hays and excrements | 53 | 0.97 | 50 | 0.92 |

The results are expressed in percentage of extract and in percentage of sample. The digestion method, as already reported,[2] was devised because the ordinary methods for the removal of unsaponified material from ether extracts very rich in that substance proved inadequate. The method is very long, but it gave satisfactory results with hays and fodders. On applying it to extracts consisting almost entirely of fats, the method was found to be very tedious. The precipitation method described herein was found to be equally as applicable to extracts rich in fat as to those poor in fat. It is a very rapid method and the process is not attended with any difficulty. The results obtained by this method were, as a rule, about the same as by the digestion method.

The ether extracts of the concentrated feed-stuffs examined contained an average of 5 per cent unsaponifiable matter in percentage of extract and 0.30 per cent in percentage of sample. The error introduced by estimating this material as fat amounts to 0.50 per cent (on sample) or more in the cottonseed meal, rice bran and rice polish. With the hays and excrements the great need of a more reliable method for the estimation of fats is shown by the amount of unsaponifiable matter obtained. This varied, in the samples examined, from 27 to 74 per cent of the extract and from 0.49 to 1.99 per cent of the sample. These results confirm those previously reported from this laboratory.

The precipitation method proposed in this article is believed to be very rapid and accurate, and to furnish a very complete separation of the unsaponified matter from the saponified material in ether extracts, fats, oils and waxes.

[1] Texas Exp. Sta., *Bull.* **150.**

[2] *Loc. cit.*

SUMMARY

A method for the removal of unsaponifiable matter from ether extracts has been devised, which is applicable to materials both rich and poor in unsaponifiable matter. The method is believed to have several points of superiority over others which have been proposed.

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## DETERMINATION OF FORMIC ACID IN KETCHUP

By C. A. Peters and L. P. Howard

Received October 24, 1914

This work was undertaken to find out whether formic acid can be determined readily and quantitatively, if present in ordinary ketchup.

The process in brief consisted in passing steam under pressure through a sample of ketchup in a flask, in allowing the material carried from the ketchup to be in contact with a suspension of calcium carbonate in a second flask, and in determining the soluble formate in the filtrate from the calcium carbonate suspension.

The ketchup used was a sample of "Blue Label" purchased at a local store, said to contain 0.1 per cent of sodium benzoate,[1] to which formic acid was added as desired. The method for the estimation of the formic acid was the gravimetric method described by Fincke.[2]

To obtain steam for nearly all the work, a connection was made with a heating radiator. To assure intimate mixing of the distillate in the second flask with the suspension of calcium carbonate, the hydra-headed tube, described by Stolzenberg,[3] was used except that the tube had only six openings, whereas Stolzenberg specifies eight. The openings were of 0.5 to 1.0 mm. in diameter. For both flasks we used long neck 500 cc. Kjeldahl's, those with wide openings being selected to admit the variously bent tubes.

In a few distillations, where the steam supply was taken at some distance from its source, the condensation of water in the flask containing ketchup was so great that a third flask had to be placed between the steam supply and the flask containing the ketchup to catch the condensed water.

Some preliminary experiments were necessary to

[1] *Zeit. Nahr. Genussm.*, **22** (1911), 98. Fincke here states that benzoic acid does not reduce mercuric chlorid.

[2] *Zeit. Nahr. Genussm.* **21** (1911), 5.

[3] *Chem. Ztg.*, **32** (1908), 770.

ascertain the conditions under which the determination could be carried out. To see if the steam or reagents used contained substances that would reduce mercuric chloride, steam was passed through the apparatus for one and one-half hours until 1000 cc. of distillate had collected. The filtrate from the calcium carbonate suspension was evaporated to a small volume, and allowed to act on mercuric chloride with the addition of a few grams of sodium chloride and sodium acetate (the latter to neutralize the hydrochloric acid formed during the reaction). After eliminating several samples of acetate and acetic acid, which contained considerable amounts of reducing substances—Fincke[1] states that most acetic acid contains formic acid—the amounts of reduced mercurous chloride corresponded to only 0.2 to 0.4 mg. of formic acid, an amount which was accepted as a constant error in the process with the reagents at hand.

Experimentation with various amounts of ketchup in the first 500 cc. Kjeldahl flask established the fact that 40 g. of ordinary ketchup in 100 cc. of water could be subjected to a vigorous action of steam without serious danger of spattering. Inclining the flask at an angle of 45°, keeping the outlet tube at the top, reduced this danger. A piece of paraffin, as large as half a pea, also helped to reduce the frothing. Larger amounts of ketchup than 40 g. in 100 cc. of water made spattering a difficulty, some colored material being carried over into the suspension of calcium carbonate.

The time necessary to volatilize formic acid in this apparatus was next subjected to test. An amount of formic acid equal to 0.0405 g. was placed in 100 cc. of water in the first Kjeldahl flask ultimately intended to receive ketchup. One gram of precipitated calcium carbonate in 100 cc. of water was placed in the second flask and steam passed through for various lengths of time, flames under each flask being adjusted so that the volumes remained constant. After 50 minutes, 80 per cent of the formic acid in the first flask was held by the calcium carbonate in the second flask, and in one and one-half hours 91.6 per cent of the formic acid was held by the suspension.

Steam was next passed through 41 g. samples of ketchup acidulated with 0.5 g. of tartaric acid to determine if material capable of reducing mercuric chloride would be caught by the suspension. The filtrates from the calcium carbonate gave at first up to 6 mg. of suspended matter after treatment with mercuric chloride. It was evident at a glance that the light brown flocculent precipitate was not calomel. Filtering the solutions through paper before adding the mercuric chloride reduced the amount of the precipitate subsequently appearing to 0.3 to 0.8 mg. calculated as formic acid. The character of this precipitate was not investigated, and it was considered that the amounts of reducing substances volatilized from ketchup by steam and acting upon calcium carbonate, other than the 0.2 to 0.4 mg. introduced in the reagents, were negligible.

If new rubber stoppers are used in the flasks during the reduction of the mercuric chloride the stoppers should be boiled in caustic soda to remove the loosely adhering sulfur, some of which might otherwise be weighed as mercuric chloride.

The data collected in these preliminary experiments just described enabled us to adapt the method of Fincke to the determination of formic acid in ketchup. The reagents used and details of the process follow.

REAGENTS—Mercuric chloride solution: 100 g. per liter containing 30 g. sodium chloride.[1] Sodium acetate: 300 g. per liter. Acetic acid and acetate should be free from formic acid. Tartaric acid: 100 g. per liter.

PROCESS—About 40 g. of ketchup were weighed out and washed into a 500 cc. wide mouth, long neck Kjeldahl flask to which was added 0.5 g. of tartaric acid. This flask was supported at an angle of 45° and steam passed through it for one and one-half hours. Volatile matter from the flask was forced through a Stolzenberg tube, adjusted in the second Kjeldahl flask of 500 cc. capacity, containing 1.0 g. of precipitated calcium carbonate. Material distilling from the calcium carbonate suspension passed through a Liebig condenser. The volume in both flasks was kept at 100 cc. by regulation of the flame underneath. When 1000 cc. of distillate had been collected (which took one and one-half hours with our apparatus) the steam was shut off—it was found desirable to insert a T-tube, closed with a pinch-cock, in the system to quickly adjust the pressure. The contents of the flask containing the calcium carbonate were then filtered and well washed with hot water, and the filtrate was evaporated on a steam bath to a volume of 20 to 50 cc. If any precipitate appeared in the liquid it was filtered; otherwise it was transferred into a 300 cc. Erlenmeyer flask to which 5 to 20 cc. of mercuric chloride[2] and 5 to 10 cc. of sodium acetate[2] solutions were added. The flask was stoppered with clean rubber stoppers, carrying 2 feet of glass tubing to act as air condensers and was inserted in the hot water of a steam bath. The larger rings of the bath were put over the flask, so that all the liquid was under water and some of the air space above was not exposed to steam. After two hours' heating the precipitate was filtered on weighed Gooch crucibles previously dried at 100°, and washed with hot water, alcohol and ether in the order named, dried at 100° for three-quarters of an hour, cooled and weighed. The weight of calomel multiplied by 0.0975 gave the weight of formic acid.[3] Results obtained by this method are given in the following table:

DISTILLATION OF FORMIC ACID IN KETCHUP

| No. | 1 | 2 | 3 |
|---|---|---|---|
| Formic acid used—grams | 0.0405 | 0.0405 | 0.0405 |
| Time of distillation—minutes | 80 | 90 | 120 |
| Formic acid recovered from calcium carbonate suspension—per cent | 89.5 | 91.6 | 91.9 |

## SUMMARY

It is evident that by applying the Fincke process,

[1] Fincke states that sodium chloride prevents the formation of insoluble compounds between mercuric chloride and salicylic acid.

[2] The amount of mercuric chloride is 15 times the amount of formic acid present, while 3 g. of sodium acetate are necessary when the largest amounts (125 mg.) of formic acid are present.

[3] *Z. Nahr. Genussm.*, **25**, 386.

[1] *Loc. cit.*, p. 2.

with the apparatus described above, 91 to 92 per cent of the total formic acid added to ketchup can be collected in an hour and a half, when the amount of distillate that has passed through the apparatus is about 1000 cc.

Thanks are due Mr. H. C. Lythgoe, chemist of the State Board of Health Laboratory of Massachusetts, for the suggestion which led to this work.

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## THE VOLUMETRIC FEHLING METHOD USING A NEW INDICATOR

By A. M. Breckler

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The volumetric Fehling method has been looked on very unjustly as inaccurate and unreliable. An inspection of the work of A. W. Peters[1] shows that under the most carefully controlled conditions of the gravimetric method, the ability to duplicate reducing sugar determinations is limited to an accuracy of about one part in 200. His dextrose copper ratios fluctuate about a mean value of 0.522 in the range of 25 to 100 mg. of dextrose. The highest value is 525 and the lowest is 520, the value in each case being a mean of 4 to 6 determinations. The work of Munson and Walker[2] at times shows departures from the average which are fully as great. In seeking a method of reducing sugar estimation, therefore, an accuracy of one part in 200 is as great as can be expected.

The method here described is dependent on a constant volume at the close of the titration, a constant time of boiling, and the use of sodium monosulfide solution as indicator.

### DESCRIPTION OF METHOD

The Fehling solution used is made up as follows:

A. FEHLING'S COPPER SOLUTION[3]—34.639 g. of carefully selected crystals of pure copper sulfate dissolved in water and diluted to exactly 500 cc.

B. FEHLING'S ALKALINE TARTRATE SOLUTION—173 g. of Rochelle salts and 50 g. of sodium hydroxide are dissolved in water and diluted to exactly 500 cc. The solution of sodium monosulfide is made up by dissolving 4 g. of crystalline sodium monosulfide in 100 cc. of water. It should be made fresh every day. The test is conducted in a test tube $8^1/_2 \times {}^3/_4$ in. A wooden clamp for holding this tube should be provided. A spot tile with six or more cavities, a 10 cc. pipette, some straight pipettes, and a burette for the sugar solution completes the outfit.

To make a determination, 10 cc. of the mixed Fehling solution are pipetted into the test tube. The sugar solution, which should contain between 200 and 400 mg. of dextrose or an amount of other sugar equivalent in reducing value to these amounts, is then run in, starting with 8.5 cc. The solution is then boiled one minute, counting from the time a bubble of steam first traverses the entire length of liquid. After the addition of 8.5 cc. and boiling, the color is noted. If the solution is very blue, the sugar solution may be added 2 cc. at a time, boiling 15 seconds after each addition. When the solution in the tube is only a faint blue, a drop of it is added to two drops of sulfide solution on the tile. The tile is given a slight rotary shake and the color of the spot noted. It will be seen that the suspended cuprous oxide turns black and settles at once, while the supernatant liquid turns a more or less intense yellow. The sugar solution is now added to the test tube in smaller portions, depending on the intensity of the yellow coloration, boiling 15 seconds after each addition. It is usual in this laboratory to use 0.4 cc. at this point. As the color becomes fainter, less is added each time, until finally successive additions are only 0.1 cc. each. As soon as no color is perceived immediately upon the settling of the cuprous compound, the result is read from the burette and the mean of this reading and the previous one taken as the number of cubic centimeters required to reduce the ten cc. taken. The experiment is then repeated, adding enough water to make the final volume up to 30 cc., and 97 to 98 per cent of the sugar solution required in the previous trial. This is then boiled $1^1/_2$ minutes and the exact amount adjusted, which can usually be done in two additions. This final determination should require from four to six minutes from the time the solutions are mixed until the estimation is finished. It will rarely be found that these two determinations differ more than 1 per cent in value from each other. The second determination is the one to be used.

When the approximate amount of sugar is known, as it is in most cases, the first approximation can be made much closer and the two titrations given equal weight.

### NOTES ON THE METHOD

The time of boiling after $^1/_2$ minute seems to play a comparatively unimportant part. In a series of experiments 99 per cent of the sugar (dextrose) required to reduce a solution was added and the mixture boiled different lengths of time. The amount required for complete reduction was the same whether the first portion was boiled $^1/_2$ minute or $1^1/_2$ minutes. Too protracted boiling, however, is undesirable on account of evaporation and exposure to air. Hence the total time of boiling should be kept within $1^3/_4$ to $2^1/_4$ minutes.

The desirability of a constant volume in the gravimetric method during the reduction is well known; preliminary experiments showed this plainly. Under the conditions of this method 10 cc. of Fehling solution with a final volume of 50 cc. required as a mean of several determinations 49.3 mg. of dextrose for reduction; 10 cc. with a final volume of 30 cc. required 47.6 mg. for reduction. By making a preliminary titration, bringing the volume up to a constant amount, and adding most of the sugar at once, its reducing values become constant. Even if the reducing values of the 2 or 3 per cent subsequently added vary 20 per cent, the results are still within the limits of the method. As can be seen from the difference shown above, a variation of 2 or 3 cc. in the final volume may be con-

[1] *J. A. C. S.*, **34**, 928.
[2] *Ibid.*, **38**, 663.
[3] Leach, "Food Inspection and Analysis," p. 591.

sidered negligible. The final volume was arbitrarily selected, as it was the greatest volume at which 0.1 cc. of 0.2 per cent dextrose solution would make a distinct change in color.

A test tube of the size given prevents much exposure to the air, and its liability to boil over when heated too rapidly, prevents excessive evaporation.

Numerous trials were at first made with ferrous sulfocyanide[1] and iodide starch mixture,[2] but it was found that both have a common defect; namely, they become colored on exposure to air without addition of Fehling solution. Attempts to obviate this destroy their sensibility to a large extent. The writer had used sodium monosulfide for some time for colorimetric copper estimations and was impressed by its sensitiveness. Furthermore, there ought to be no tendency for the reoxidation of the copper on mixing with the indicator, as the medium is a reducing one. After a few minutes a yellow color will appear, owing probably to solution of some of the copper sulfide. The absence of color, however, is permanent for sufficient time for an observation to be made, while when copper is unreduced, the appearance of the color is immediate. After the operator has become familiar with the end point, it can be judged very closely by the appearance immediately on addition of the drop. As long as unreduced copper is present, a yellowish color is perceptible without agitation, while when all the copper is reduced, the only shade is the reddish brown of the cuprous oxide.

Proteins, and metals which give colored sulfides interfere with the end point. For the former, the writer boils a measured volume and adds alumina cream while still hot, then cools and makes up to a convenient volume, adding sufficient water to correct for the volume occupied by the alumina. The solution can then be allowed to settle and the clear supernatant liquid used, or if time is an object, it may be filtered. This method works very well on most urines and colored solutions. For removing the metals, methods will doubtless suggest themselves.

### RESULTS OBTAINED

Various dilutions of a sugar solution were made up and given to a member of the staff (without information as to their sugar content), who obtained the following figures.

| No. of cc. used in titration | Mg. total dextrose present |
|---|---|
| 23.30 | 47.60 |
| 15.65 | 47.75 |
| 11.70 | 47.60 |
| 9.35 | 47.75 |

It must be understood that this was not pure dextrose, as the purpose was only to see whether results were constant and independent of the concentration of the titrating solution over comparatively wide limits. The above results were each obtained with one titration besides the preliminary one.

Impure maltose solutions were titrated in a similar manner.

[1] Ling Rendle and Jones, Allen's "Commercial Organic Analysis," 4th edition.

[2] F. F. Harrison, Sutton's "Volumetric Analysis," 10th edition.

| No. of cc. used in titration | Mg. total maltose present |
|---|---|
| 23.2 | 92.8 |
| 15.5 | 93.0 |
| 11.6 | 92.4 |
| 9.25 | 92.5 |

The following results show the remarkable constancy of results over long periods. The titrations are on 5 cc. of mixed Fehling solution, which was the original manner of using the method, but it was changed to increase the accuracy of the end point.

6/11/1914 5 cc. Fehling reduced by 44.43 mg. crude maltose
8/26/1914 5 cc. Fehling reduced by 44.47 mg. crude maltose

For each value four concentrations were titrated. This constancy is not confined to maltose, but is also true of dextrose. The dextrose factor for 5 cc. in May was 23.6 mg. and in August 23.8 mg.

The writer advises the standardization of the Fehling solution by each user, and hence his factor should not be accepted as final. A mean of four determinations on pure glucose from two different sources in which the maximum variation from the average was ±0.15 mg., gave 47.5 mg. dextrose as the value of 10 cc. of a Fehling solution whose copper content had been accurately adjusted by a sodium thiosulfate solution standardized with pure copper. As can be seen, the factors, once obtained, need be determined only at rare intervals. Pure dextrose, prepared by the Bureau of Standards, is now available for this purpose.

### SUMMARY

The writer describes a modification of Fehling's volumetric method designed to do away with some of its sources of error.

The use of a new indicator is described which, so far as is known, is here first used for that purpose.

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## A COMPARISON OF THE GUNNING-COPPER METHOD WITH THE KJELDAHL-GUNNING-ARNOLD METHOD FOR THE DETERMINATION OF NITROGEN

By OVE F. JENSEN

Received June 3, 1914

In 1908 the Association of Official Agricultural Chemists officially adopted[1] a modification of the Gunning method for the determination of nitrogen which prescribes the use of 0.1 to 0.3 g. of crystallized copper sulfate in addition to the potassium sulfate. Penny,[2] in his report on the determination of nitrogen in 1907, says of this modification: "The claims made for the catalytic action of copper sulfate seem to be justified by experience, and there is reason to suppose that this reagent will do much to shorten the time of digestion." Although possessing many advantages over the other methods in use at that time, it was not generally adopted. More recently another modification known as the Kjeldahl-Gunning-Arnold[3] method has been proposed. This method differs from the Gunning-Copper method, only in the use of metallic mercury instead of copper sulfate. In a recent number of THIS JOURNAL,[4] Trescot shows, very conclusively,

[1] U. S. Dept. Agr., Bureau of Chemistry, *Bull.* **122**, p. 183.

[2] *Ibid.*, **116**, p. 43.

[3] *Ibid.*, **108**, p. 15.

[4] Vol. **5** (1913), 914.

that the Kjeldahl-Gunning-Arnold method reduces the time of digestion over the original Kjeldahl or Gunning methods from four hours to one and one-half hours. This is a very important item in laboratories where a large number of nitrogen determinations are being made. The Gunning-Copper method has been in use in this laboratory for the past nine years, and the general practice has been to digest from two to three hours after the solution becomes clear.

Since this method possesses several advantages in manipulation over the Kjeldahl-Gunning-Arnold method, a comparison of the two methods with different periods of digestion was undertaken, using bone meal, dried blood, cyanamide, and linseed meal as representative substances. In Table I, the period of

TABLE I—EFFECT OF DIFFERENT PERIODS OF DIGESTION ON PERCENTAGES OF NITROGEN FOUND

| Period of digestion after solutions became clear | 1 hour | | | | 1½ hours | | | | 2 hours | | | | 3 hours | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Method | No. of analyses | Max. | Min. | Av. | No. of analyses | Max. | Min. | Av. | No. of analyses | Max. | Min. | Av. | No. of analyses | Max. | Min. | Av. |
| BONE MEAL: | | | | | | | | | | | | | | | | |
| Gunning-Copper | 6 | 2.18 | 2.16 | 2.16 | 4 | 2.20 | 2.18 | 2.19 | 6 | 2.20 | 2.18 | 2.19 | 6 | 2.23 | 2.20 | 2.20 |
| Kjeldahl-Gunning-Arnold | 6 | 2.25 | 2.19 | 2.20 | 4 | 2.20 | 2.18 | 2.19 | 6 | 2.23 | 2.19 | 2.20 | 6 | 2.22 | 2.20 | 2.20 |
| DRIED BLOOD: | | | | | | | | | | | | | | | | |
| Gunning-Copper | 6 | 14.11 | 14.03 | 14.07 | 6 | 14.24 | 14.07 | 14.13 | 6 | 14.32 | 14.15 | 14.22 | 6 | 14.40 | 14.23 | 14.29 |
| Kjeldahl-Gunning-Arnold | 6 | 14.32 | 14.11 | 14.24 | 6 | 14.32 | 14.19 | 14.29 | 6 | 14.30 | 14.19 | 14.25 | 6 | 14.34 | 14.15 | 14.26 |
| CYANAMIDE: | | | | | | | | | | | | | | | | |
| Gunning-Copper | 6 | 15.75 | 15.37 | 15.52 | 6 | 15.62 | 15.50 | 15.53 | 6 | 15.67 | 15.46 | 15.55 | 6 | 15.58 | 15.50 | 15.53 |
| Kjeldahl-Gunning-Arnold | 6 | 15.62 | 15.46 | 15.55 | 6 | 15.54 | 15.41 | 15.49 | 5 | 15.62 | 15.50 | 15.55 | 6 | 15.62 | 15.50 | 15.55 |
| LINSEED MEAL: | | | | | | | | | | | | | | | | |
| Gunning-Copper | 6 | 5.53 | 5.45 | 5.49 | 5 | 5.62 | 5.50 | 5.57 | 6 | 5.62 | 5.50 | 5.55 | 6 | 5.64 | 5.56 | 5.62 |
| Kjeldahl-Gunning-Arnold | 6 | 5.62 | 5.53 | 5.56 | 4 | 5.62 | 5.59 | 5.61 | 6 | 5.59 | 5.53 | 5.58 | 6 | 5.62 | 5.56 | 5.58 |

digestion in all cases refers to the length of time after the solutions became clear. In the length of time required to become clear, no difference was noted in the two methods. Using a moderate flame, the time required for the sulfuric acid solution to become clear was as follows:

| | | | |
|---|---|---|---|
| Bone meal | 25 min. | Cyanamide | 20 min. |
| Dried blood | 25 min. | Linseed meal | 35 min. |

The results seem to indicate that a digestion of one and one-half hours is sufficient to produce a quantitative yield of ammonia in either method, except in the dried blood, where from two to three hours are necessary in the Gunning-Copper method. Hibbard[1] found three hours to be necessary, using this method. On the whole, the results are slightly in favor of the Kjeldahl-Gunning-Arnold method, as a quantitative yield of ammonia is produced after a digestion of from one to one and one-half hours. However, it is doubtful if there are many substances for which the Gunning-Copper method will not give an equally high yield with the same length of digestion. In order to test this point, determinations were made on a number of substances such as are encountered in a fertilizer or food laboratory. Three determinations were made on each substance by each method. The data are given in Table II.

TABLE II—DETERMINATIONS OF NITROGEN ON VARIOUS SUBSTANCES

| Method | Gunning-Copper | | | Kjeldahl-Gunning-Arnold | | |
|---|---|---|---|---|---|---|
| Period of digestion | 1½ hours | | | 1½ hours | | |
| Substance | Max. | Min. | Av. | Max. | Min. | Av. |
| Gelatin | 15.14 | 15.12 | 15.13 | 15.16 | 15.04 | 15.09 |
| Egg albumin (dried) | 12.86 | 12.75 | 12.80 | 12.86 | 12.80 | 12.83 |
| Peptone | 14.49 | 14.38 | 14.45 | 14.49 | 14.38 | 14.43 |
| Casein | 13.87 | 13.81 | 13.83 | 13.92 | 13.81 | 13.85 |
| Feathers | 14.49 | 14.43 | 14.47 | 14.54 | 14.38 | 14.46 |
| Leather | 4.83 | 4.72 | 4.76 | 4.80 | 4.75 | 4.78 |
| Fish scrap | 6.48 | 6.35 | 6.43 | 6.51 | 6.43 | 6.47 |
| Animal tankage | 6.32 | 6.26 | 6.31 | 6.35 | 6.29 | 6.33 |
| Garbage tankage | 2.99 | 2.96 | 2.98 | 3.00 | 2.96 | 2.99 |
| Beef scraps | 9.14 | 8.97 | 9.04 | 9.05 | 8.97 | 8.99 |
| Castor bean pomace | 4.66 | 4.55 | 4.59 | 4.55 | 4.52 | 4.53 |
| Cocoa | 4.01 | 3.94 | 3.97 | 3.97 | 3.90 | 3.93 |
| Cottonseed meal | 7.33 | 7.30 | 7.31 | 7.29 | 7.24 | 7.26 |
| Cottonseed meal | 6.43 | 6.40 | 6.42 | 6.37 | 6.32 | 6.35 |
| Silage (dried) | 1.30 | 1.26 | 1.28 | 1.29 | 1.26 | 1.27 |
| Flour | 2.43 | 2.41 | 2.42 | 2.44 | 2.43 | 2.43 |
| Bran | 2.60 | 2.55 | 2.58 | 2.58 | 2.58 | 2.58 |
| Bone meal | 3.06 | 3.02 | 3.04 | 3.11 | 3.02 | 3.07 |
| Peat | 2.41 | 2.37 | 2.38 | 2.37 | 2.36 | 2.37 |

The results obtained for these substances by the two methods show a very close agreement, and in point of accuracy there is no choice between them. The Gunning-Copper method possesses several distinct advantages over the other which may be enumerated as follows:

I—The use of potassium sulfide is unnecessary, and thus one detail of manipulation (addition of $K_2S$) is eliminated, slightly shortening the time required for the determination. Also the presence of hydrogen sulfide in the laboratory from this source is avoided.

II—In adding the sodium hydroxide before distilling, the copper sulfate acts as an indicator, so that a large excess of alkali is easily avoided, and the bumping during distillation is much lessened.

III—The difference between the price of copper sulfate and metallic mercury, and the elimination of potassium sulfide, makes the Gunning-copper method somewhat cheaper.

SUMMARY

A quantitative yield of ammonia in dried blood is produced sooner in the Kjeldahl-Gunning-Arnold method than in the Gunning-Copper method. In the case of all the other substances studied, a digestion of one and one-half hours proved equally efficacious for either method.

The Gunning-Copper method possesses advantages in manipulation which make it preferable to the Kjeldahl-Gunning-Arnold method, especially where a large number of determinations are to be made.

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[1] THIS JOURNAL, 2, 464.

## COMPARISON OF A FEW METHODS FOR TOTAL PHOSPHORIC ACID IN SUPERPHOSPHATE[1]

By C. A. PETERS

Received October 5, 1914

A comparison of several methods for the determination of total phosphoric acid in superphosphate has been made, emphasizing the interference of silica in the gravimetric method, and showing that shorter methods give as accurate results as the customary double precipitation as phosphomolybdate and ammonium

[1] Taken from a thesis by Arthur G. Weigel, optionally presented for the degree of B.S. at the Massachusetts Agricultural College at Amherst.

magnesium phosphate. Nothing new is claimed for the work.

The superphosphate used was home-made from ground rock. All but about three-quarters of one per cent of the phosphoric acid was water-soluble. Aqua regia was used to dissolve the phosphoric acid.

For the determination of the phosphoric acid various procedures were carried out as follows:

A—The Official Method.[1]

B—The Official Method modified by evaporating the liquid on a water bath, taking up with dilute nitric acid and filtering through paper to remove silica before precipitation.

C—Direct weighing of the yellow precipitate as outlined by Baxter.[2]

D—The volumetric process of Pemberton as described by Wiley.[3]

E—The direct precipitation of ammonium magnesium phosphate in the presence of ammonium citrate.[4]

F—Same as E, substituting citric acid for ammonium citrate.[5]

None of these methods require description. However, the apparatus used for heating the yellow precipitate to 290°–300°, as outlined by Baxter, will be described. This consisted of two 6-in. iron dishes, deep form, such as are used for sand baths. The edges of one dish were cut back $^3/_4$ in. every half inch and bent in so as to make a cover for the uncut dish. A hole in the top of the cover held a cork and thermometer. Triangles inside were arranged to hold two or three crucibles, each covered with a small watch glass. An asbestos jacket consisting of a side and top prevented the radiation of heat. The whole was heated with a Bunsen burner, the flame being protected from draft by an iron conical shield 8 in. high.

The results obtained by the different methods are given in Table I, each determination made being listed.

TABLE I—TOTAL PHOSPHORIC ACID IN SUPERPHOSPHATE

| METHOD | DUPLICATES Per cent | | Average Per cent | Variation from B Per cent | REMARKS |
|---|---|---|---|---|---|
| A—Official Method | 15.30 | 15.25 | 15.28 | +0.26 | No silica removed |
| B—Official Method (modified) | 15.07 | 14.97 | 15.02 | 0.00 | Silica removed |
| C—Direct weight of yellow ppt. | 14.81 | 14.81 | | | |
| | 14.82 | 14.85 | 14.82 | —0.20 | Temp. 290°–300° |
| $C_1$—Same as C but overheated | 14.53 | 14.54 | 14.54 | —0.48 | Temp. 300°–330° |
| D—Volumetric method | 14.80 | 14.86 | 14.83 | —0.19 | KOH : $HNO_3$ |
| E—Pptd. as $NH_4Mg$-$PO_4$ | 14.85 | 14.94 | | | |
| | 14.85 | 14.87 | 14.88 | —0.14 | In am. citrate |
| F—Pptd. as $NH_4Mg$-$PO_4$ | 16.50 | 16.29 | 16.39 | +1.37 | In citric acid |

From the comparison of the results given under A and B in Table I it would be inferred that there was 0.26 per cent of silica in the pyrophosphate when the solution of total phosphoric acid before precipitation with molybdate was not evaporated to dryness. The results indicated under C, D and E, which were obtained by direct weighing of the yellow precipitate by the volumetric method and by precipitation in ammonium citrate, are, on the average, 0.17 per cent less than those listed under B. If the results obtained under B—silica-free—are taken as standard, then it is apparent that either of three more rapid methods (C, D or E) give as accurate results as the Official Gravimetric Method. No attempt was made to find silica in any of the precipitates as its presence is generally acknowledged.[1] The results given under $C_1$ show the decomposition of ammonium molybdate by temperature over 300° and the resulting negative error.

[1] *Bull.* **107**, p. 2.
[2] *Am. Chem. J.*, **39** (1902), 298.
[3] Wiley, "Principles and Practice of Agricultural Chemistry," II (1908), p. 160.
[4] Wiley, *Ibid.*, II (1908), p. 88.
[5] Wiley, *Ibid.*, II (1908), p. 98.

### CONCLUSION

The above work emphasizes what is already known:

I—That the Official Gravimetric Method of determining total phosphoric acid gives high results when phosphoric acid is determined in superphosphate without evaporation of the solution to dryness on a steam bath to remove silica.

II—That several methods other than the Official Gravimetric give equally good results in half the time.

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## CLEANING SOILS FOR MICROSCOPIC EXAMINATION

By W. H. FRY AND JOHN A. CULLEN

Received Oct. 22, 1914

In microscopic mineralogical work on soils it is necessary that the grains be transparent or at least strongly translucent and that the grain-surfaces be free from all coatings and adhering material. Where light is not transmitted, the optical properties of the minerals cannot be determined in soil preparations; and where the material carries an appreciable coating of some foreign substance the refractive index determined will be that of the coating instead of the mineral, even though the determination of other optical properties of the grain under examination may remain unaffected.

Many soils have their constituent grains more or less stained and coated by various substances. Often simple washing and drying serve to render them adaptable to microscopic examination. But in a great number of cases the grains are so coated with iron oxides, hydroxides, or both, that other means of cleansing have to be resorted to. That cleansing agent would be most efficient which, while entirely removing the iron and other stains, at the same time had the least decomposing action on the minerals themselves.

Hydrochloric and nitric acids act very energetically upon apatite, the determination of the presence of which is sometimes the primary object of the examination. Sulfuric acid cannot be used for the same reason, and in addition has the disadvantage of decomposing biotite, a common soil constituent.

Several readily available organic acids were tested on various soils, different concentrations of the various acids being used in order to ascertain the most efficient

[1] Wiley, *loc. cit.*, p. 78.

strength. It has been found that, in general, 10 per cent oxalic acid best serves the purpose. In about 30 minutes it removes the iron stains satisfactorily. Tests upon various soil minerals showed that, with the exception of apatite, it did not affect them appreciably; and in the case of apatite, although there is undoubtedly some effect, it leaves that mineral in a determinable state. Of course, in any case calcite would be removed—a fact which renders very difficult the determination of small quantities of this mineral in discolored soils.

Bureau of Soils
U. S. Department of Agriculture
Washington

# LABORATORY AND PLANT

## REPORT OF THE SELBY SMELTER COMMISSION

Received December 8, 1914

The filing of the report, findings and recommendations of the Selby Smelter Commission with the Superior Court of Solano County settles finally and conclusively the long continued controversy between the residents of Benicia and the adjacent agricultural country and the Selby Smelting and Lead Company concerning the alleged disagreeable and injurious effects produced by the smoke from the Selby Smelter.

The smelter operated by the Selby Smelting and Lead Company is situated near Vallejo Junction in Contra Costa County, California, at the western end of the Carquinez Straits. The City of Benicia is situated in Solano County at the eastern end of the Straits, about five miles from the smelter. During nine months of the year the prevalent trade winds blow the smoke from the Selby Smelter over and into the City of Benicia and the agricultural area lying between Benicia and Vallejo.

On March 14, 1905, action was brought by the District Attorney of Solano County, California, in the Superior Court of Solano County, praying for an injunction which would restrain and enjoin the Selby Smelting and Lead Company from permitting injurious smoke and gas from the Selby Smelter to blow over and upon the City of Benicia and the tributary country. The case was brought to trial on August 7, 1906, and judgment of the Court in favor of the Plaintiff was rendered on July 16, 1908. The decree of the Court was to the effect that during eight months of each year between the 15th of March and the 15th of November, the Selby Company was enjoined from discharging noxious gases and fumes into the open air in such a manner that the same would be carried into and upon the City of Benicia and the tributary country in Solano County in such quantities as to be offensive to the senses and to interfere with the comfortable enjoyment of life and property.

After motion for a new trial was made by the Defendant and denied by the Court, an appeal was thereupon taken to the Supreme Court of the State. On June 12, 1912, the judgment of the trial court was affirmed by the Supreme Court.

During the period covered by this litigation the Selby Company had been making efforts toward the elimination of some of the objectionable constituents of the smoke, these efforts having resulted in the removal of the major portion of lead, arsenic and sulfur trioxide from the smelter smoke.

In the spring of 1913, although the Selby Company maintained that they had abated the nuisance, complaints were made by the residents of the area that a nuisance still existed, and that the decree of the Court was, therefore, being violated by the Smelting Company.

Various considerations, among them the prospective heavy expense which would accrue to both parties to the litigation as a result of a trial of the Smelter Company for contempt of Court, led to conferences of the attorneys representing both sides, which resulted in an agreement to submit the question of fact as to the violation of the decree of injunction to a board of technically trained men, deemed by both sides to be qualified to act in such a capacity, and equal financial responsibility of the parties in the expense of the Commission's activities. The result of the agreement was the filing of a stipulation in the record of the cause providing for such a board.

### ORGANIZATION OF COMMISSION

On May 22, 1913, this board was organized as the Selby Smelter Commission, with the following personnel:

J. A. Holmes, Director U. S. Bureau of Mines.

E. C. Franklin (at the time of appointment Chief of the Chemical Division of the Hygienic Laboratory of the U. S. Public Health Service), Professor of Organic Chemistry, Leland Stanford, Jr., University.

Ralph A. Gould, Chemical Engineer, San Francisco, Secretary of the Commission.

The function of the Selby Smelter Commission was to determine the facts and report its findings on the following:

1—Is the Selby Smelter operating in such a manner as to violate the decree of the Court dated July 16, 1908?

2—If the Defendant Company is violating the decree, what is the extent of the violation?

3—If the Defendant Company is violating the decree, what steps must be taken by the Defendant to avoid a violation of the decree?

For the determination of facts, the Commission and its staff have carried on very careful and complete investigations of all matters which in the opinion of the Commission could have any bearing on the questions at issue and to be answered. These investigations were made by the following staff of trained scientific and technical men, no one of whom, otherwise than in arriving at the truth, was directly or indirectly interested in the findings of the Commission:

A. E. Wells, Metallurgist and Chief Chemist, in charge of Smelter Investigations and Field Work.

C. B. Dutton, Special Legal Agent, U. S. Bureau of Mines.

CHARLES F. SHAW, Professor of Agronomy, College of Agriculture, University of California.

E. E. FREE, Soil Expert and Agronomist.

J. W. BLANKINSHIP, Ph.D., Plant Pathologist.

WYATT W. JONES, Plant Pathologist.

R. W. DOANE, Professor of Entomology, Leland Stanford, Jr., University.

C. M. HARING, D.V.M., Professor Veterinary Science, College of Agriculture, University of California.

K. F. MEYER, D.V.M., Professor Bacteriology and Protozoölogy, University of California.

Through the courtesy of Dean Thomas Forsyth Hunt, of the College of Agriculture, and Professor F. T. Gay, of the Department of Pathology, the Commission had the valued coöperation of several of the staff of the University of California. The facilities of the U. S. Bureau of Mines also were placed at the disposal of the Commission and much assistance was rendered by its staff of experts, especially by Dr. F. C. Cottrell and Dr. L. H. Duschak.

The results of the investigations of the several experts were presented to the Commission in the form of reports, as given below:

1—A Detailed Study of Statements of Residents of the Selby "Smoke Zone" as regards the Presence of a Nuisance in the Area, by C. B. Dutton.

2—Conditions in and around the Selby Smelter and the Selby "Smoke Zone," by A. E. Wells.

3—Investigations to Determine the Extent of the Contamination of the Atmosphere in the Selby "Smoke Zone" by the Smelter Emanations, by A. E. Wells.

4—Investigations to Determine the Sulfur Dioxide Present in the Atmosphere in Places Outside the Selby "Smoke Zone," by A. E. Wells.

5—Conditions of Plant Life in the Selby "Smoke Zone," by J. W. Blankinship.

6—The Occurrence of Sulfur Dioxide Injury to Plants in the Selby "Smoke Zone," by Wyatt W. Jones.

7—Insect Pests in the Selby "Smoke Zone," by R. W. Doane.

8—Agronomic and Soil Conditions in the Selby "Smoke Zone," by Charles F. Shaw.

9—Investigations of Live Stock Conditions and Losses in the Selby "Smoke Zone," by C. M. Haring and K. F. Meyer.

10—Fumigation Experiments to Determine the Effect of Highly Diluted Sulfur Dioxide upon a Growing Grain Crop, by A. E. Wells.

11—Investigations to Determine the Effects of Sulfur Dioxide on Man, by A. E. Wells.

12—The Possibility of Reducing the Sulfur Dioxide Output from the Selby Smelter, by A. E. Wells.

(*a*)—Investigations on the Gases from the Dwight and Lloyd Sintering Machines of the Selby Smelter.

(*b*)—Studies in the Commercial Utilization of the Sulfur Dioxide Produced by the Selby Smelter.

13—Bibliography: The Effect of Sulfur Dioxide on Vegetation and Animal Life, The Chemists' Club Library, New York.

The field investigations upon which these reports are based were conducted between June, 1913, and September, 1914.

In collecting the data for his report, Mr. Dutton interviewed the residents of the "Smoke Zone" in as thorough and as representative a manner as possible, and sought to obtain directly their ideas concerning the existence of a nuisance. The opinion expressed as to the existence of the nuisance and injury from the smelter smoke varied from the extreme of unreasoning radicalism to entire indifference.

A study of Mr. Dutton's report reveals the fact that two classes of odors have been described by the residents of the "Smoke Zone" as "smelter smoke;" one is undoubtedly that due to sulfur dioxide, and the other is that of certain products from the refining of petroleum, the so-called "oil smell." Judging from the statements of these residents, there can be no doubt that in the past, up until 1910 or 1911, there were present at times in the "Smoke Zone" fumes and gases possessing very disagreeable odors, the "oil smell," which could not possibly have been due to smelter emanations. Subsequent to 1911, "oil fumes" have not been so prevalent, but occasionally the odor of sulfur dioxide has been detected.

The conclusions derived from Mr. Dutton's report are that among the greater proportion of the residents there is at the present time only slight, if any, legitimate objection to the presence of "smelter smoke" in the atmosphere of the "Smoke Zone." Under extremely unfavorable conditions and to supersensitive persons, "smelter smoke" may occasionally be smelled in the area, but to the fair-minded person such occurrences do not prevent the enjoyment of life nor are they detrimental to the health of the community.

The Commission considers that one of the most important phases of its investigations has been the direct determination by chemical analyses of the sulfur dioxide contained in the atmosphere of the "Smoke Zone."

This work was conducted under the superintendence of Mr. A. E. Wells, the Metallurgist and Chief Chemist of the Commission, with the assistance of eight trained chemists and six helpers, and is believed by the Commission to be the most extensive and exhaustive of its kind heretofore.

### SULFUR DIOXIDE DETERMINATIONS

For the determination of sulfur dioxide, a method has been developed which is believed to be by far the best yet used in work of this character, in that it combines in a most satisfactory manner those characteristics which permit "instantaneous sampling," rapidity of execution, easy field manipulation, and a high degree of accuracy. Concentrations of sulfur dioxide as low as 0.2 part per million of air are rapidly and easily determined by the method as developed and finally adopted by the Commission. For the essential features of the method, the Commission is indebted to Mr. J. R. Marsden, Chief Chemist of the Selby Smelter.

For making observations in the field, two permanent laboratories were established, where sulfur dioxide determinations were made at brief intervals daily, and an automobile was equipped as a portable laboratory, by means of which determinations were made in all parts of the Selby "Smoke Zone," as well as in many places outside the Selby "Smoke Zone."

The field investigations to determine the sulfur dioxide content of the atmosphere in the Selby "Smoke Zone" extended from September 17 to December

15, 1913, and from March 1 to April 15, 1914, during which time 4862 determinations were made. During the same period about 700 determinations were made in places outside the Selby "Smoke Zone."

During the entire course of the investigations, special attention was given to the metallurgical processes going on at the smelter and the amount of sulfur dioxide eliminated from the smelter during the tests in the "Smoke Zone" has been checked by the staff of the Commission. Determinations were made when the wind conditions were the worst possible for the area, and when, at the request of the Commission and under its supervision, the output of sulfur dioxide from the smelter was the highest possible. Other tests have been made with the smelter entirely closed down and with the wind conditions favorable and unfavorable to the "Smoke Zone." Every attempt has been made to obtain these data under all possible conditions, in order that maximum, average and minimum figure might be obtained as to the sulfur dioxide content of the atmosphere of the "Smoke Zone."

Of the total number of "instantaneous" samples (4862) taken in the Selby "Smoke Zone" during the period of field work, 75 per cent contained less than 0.2 part $SO_2$ per million of air; 86 per cent contained less than 0.4 part $SO_2$ per million; and over 97 per cent contained less than 1.0 part $SO_2$ per million parts of air. Only 21 samples, or 0.43 per cent of the total, contained more than 2.0 parts $SO_2$, and no sample analyzed more than 7.1 parts $SO_2$ per million.

The higher concentrations were found only when puffs of the smoke from the Selby Smelter were drifted by a gentle breeze over the most exposed portions of the "Smoke Zone," and at no time did a concentration greater than 2.0 parts $SO_2$ per million persist for a continuous period of more than thirty minutes. The total time during the whole period of the Commission's investigation that the concentration of sulfur dioxide was more than 2.0 parts per million at any part of the "Smoke Zone" was 220 minutes, or 3 hours and 40 minutes.

Only on six occasions was the concentration above 3.0 parts $SO_2$ per million, and the total time that the concentration was above that amount was 65 minutes. Within the city limits of Benicia itself, the maximum concentration of sulfur dioxide found was 2.4 parts per million, and only 21 out of the 2840 samples taken in this portion of the "Smoke Zone" contained more than 1.0 part $SO_2$ per million.

In the business section of San Francisco during calm mornings, the concentration of sulfur dioxide was found to be as high as 1.8 parts $SO_2$ per million. Under brisk wind conditions such as are prevalent during the late morning and early afternoon during the period of trade winds, the sulfur dioxide content was seldom over 0.2 part $SO_2$ per million. On the Ocean Beach no determinable quantity of sulfur dioxide was found. In Oakland and Berkeley, of the 148 determinations made, none showed a concentration of sulfur dioxide higher than 1.0 part per million. One hundred and three determinations were also made in the vicinity of Richmond, which showed an average value of 1.1 parts $SO_2$ per million, and a maximum content of 4.5 parts $SO_2$ per million. In Martinez and vicinity, 168 determinations were made. The average of these determinations was 0.23 part $SO_2$ per million, and the maximum 1.7 parts $SO_2$ per million.

The results of these investigations show that, on the one hand, although the atmosphere of other areas investigated show a higher constant concentration of sulfur dioxide than the Selby "Smoke Zone," the maximum concentrations in the Selby "Smoke Zone," on the other hand, are higher than those of any of the other areas investigated. These higher concentrations, however, never persist for more than a few minutes.

### SENSITIVENESS OF HUMAN BEINGS TO SULFUR DIOXIDE

In order to determine whether the concentration of sulfur dioxide found in the "Smoke Zone" could be considered sufficient cause for a nuisance complaint, or could be injurious to the health of people residing in the Zone, it became necessary to study the effects of high dilutions of sulfur dioxide upon man and to determine the sensitiveness of various persons to the gas. The following is a brief summary of the results of these investigations:

Of the 60 subjects experimented upon, 32 of whom were previously acquainted with the gas, no one was able to detect the presence of 1.0 part $SO_2$ per million of air. With concentrations of 2.0 parts $SO_2$ per million several of the subjects detected the presence of something foreign in the air, but could not identify it, and 2 identified the gas by taste. With concentrations of 3.0 parts $SO_2$ per million, the greater proportion of the subjects acquainted with the gas were able to identify it, and at 4.0 parts practically all were able to do so. The greater proportion of the subjects not previously acquainted with sulfur dioxide did not identify the gas until the concentration was greater than 4.0 parts per million.

In the investigations to determine what concentration of sulfur dioxide would be considered a nuisance to all persons, very little agreement was found between the ideas expressed as to what was a nuisance. As a general statement, it may be said that concentrations of 3.0, 4.0 and even 5.0 parts $SO_2$ per million were not considered to be a nuisance even if continued for considerable periods of time; concentrations of from 5.0 to 10.0 parts $SO_2$ per million if continued for 10 to 15 minutes would be considered a nuisance; concentrations above 10.0 parts $SO_2$ per million if existing for only a few minutes would certainly be called a nuisance. It was definitely determined that concentrations below that at which the sulfur dioxide can be smelled, that is, below about 3.0 parts $SO_2$ per million, cannot possibly be considered a nuisance or cause for discomfort.

It will be recalled that in the atmosphere of the city of Benicia the sulfur dioxide concentration never reached 2.5 parts per million during the whole period of the Commission's investigations, and that at one of the most exposed spots in the "Smoke Zone" there were but six short periods when it was above 3 parts, reaching a maximum of 7 parts on one occasion only.

In view of the established facts therefore, it is quite

impossible to maintain that during the period of investigations by the Commission the residents of the City of Benicia or of any other part of the "Smoke Zone" have been subjected to a nuisance as the result of discharge of sulfur dioxide from the Selby Smelter.

### EFFECT OF SULFUR DIOXIDE ON VEGETATION

Extended experiments were conducted to determine whether such concentrations of sulfur dioxide as are found in the Selby "Smoke Zone" are capable of doing any injury to crops or other vegetation growing in the Zone.

The plan of these experiments was to allow barley plants to grow normally in an open field, and occasionally and for definite periods of time to subject the plants to definite concentrations of sulfur dioxide. These experiments were carried out with the following object in mind:

1—To determine the visible injury produced by definite concentrations of sulfur dioxide applied for definite periods of time

2—To determine the economic injury or decrease in yield resulting from the visible injury produced.

3—To determine the possibility of "invisible injury" to a growing grain crop and the extent to which this may take place.

In a field of growing barley, experimental plots four feet by twenty feet in area were laid out, and covered during periods of fumigation with a cabinet designed so as to interfere as little as possible with the illumination of the plot. The sulfur-dioxide-air-mixture was blown in at one end and allowed to escape at the other, in such a way as to maintain a steady stream of air containing sulfur dioxide through the cabinet during the fumigation periods. The length of time of each fumigation varied between two minutes and one hour.

Experiments were carried on simultaneously on a farm near Vallejo and at the University farm at Davis. At Vallejo, 106 plots, and at Davis 35 plots were experimented upon, with results which were concordant in every respect.

A concentration of 5.0 parts sulfur dioxide applied for an hour under ordinary humidity conditions produced considerable visible injury. Visible injury is produced on growing barley by concentrations of 1.0 part $SO_2$ per million of air if the length of time of application is sufficiently great. Thus, 3 fumigations of 7 hrs. each produced slight visible injury and no reduction in yield, with air containing 1.0 part sulfur dioxide per million. Sixty-two fumigations of one hour each, with 0.5 part $SO_2$ per million, irregularly continued through the growing period, produced very slight visible injury and no reduction in yield.

From a study of the results of these experiments in connection with the information gained from the investigations upon the sulfur dioxide content of the atmosphere of the "Smoke Zone," the Commission has found that from time to time conditions may arise under which slight visible injury will be visited upon susceptible plants growing on the more exposed portions of the "Smoke Zone." Since, however, plants will endure a considerable amount of visible injury without any diminution of crop yield, the Commission concludes that within the "Smoke Zone" no economic damage results from the smoke of the Selby Smelter. This conclusion receives convincing confirmation from the observations of the Commission's plant pathologists, who have found no indications whatever of economic sulfur dioxide damage within the area of the "Smoke Zone." It was found that when the plants were at one time badly bleached this fact did not necessarily mean a decrease in the yield. A number of plots badly bleached in the early stages of growth were observed to recover rapidly, and it was found that their yield at maturity averaged within three per cent of the yield from the check plots. Short time fumigations repeated a great many times, and of sufficient intensity to keep the foliage bleached throughout the season, were much more effective in reducing the yield than were one or two very strong fumigations.

No economic damage or loss as expressed in decreased yield of crops or decrease in the fertility of the seed resulted from the treatment of barley plants with quantities of sulfur dioxide insufficient to produce marked visible injury. Thus, there was no indication of an economic "invisible injury."

### AGRICULTURAL CONDITIONS IN "SMOKE ZONE"

For the determination of the condition existing in the "Smoke Zone" as regards the crops of various kinds and the many kinds of plant life found therein the Commission engaged two plant pathologists of a high degree of training and of extensive experience in the study of plants in relation to smelter smoke injury. Each was commissioned to make a complete plant pathological survey of the area, reporting all abnormal conditions which exist and to trace, wherever possible, the actual cause of such conditions. The only conclusions which can be drawn from the work done in the plant pathological survey are that such poor conditions of plant growth as exist in the "Smoke Zone" are directly traceable to one or more of the following causes: plant diseases, predacious insects, poor soil, poor cultivation, lack of water and indifference to all of those conditions by the farmers of the area. None of the conditions existing so far as vegetation is concerned can be attributed to the effects of the smoke from the Selby Smelter.

From a consideration of the data collected during the entomological survey, the general conclusion reached is that lack of cultivation, lack of proper pruning, absence of spraying and fumigation with insecticides are mainly responsible for the unusually bad condition which exists among the trees, vines and shrubs in the Selby "Smoke Zone." The indifference of certain farmers to these conditions is illustrated by the fact that, during his investigations, Professor Doane volunteered to advise the farmers free of charge as to the proper methods for combating insects and to supervise their attempts, yet none of them accepted his services or took advantage of the opportunity to improve existing conditions.

### SOIL INVESTIGATIONS

The problems presented to the agronomic soil experts were:

1—Are the agronomic conditions of the "Smoke Zone" such as to conduce to high agricultural development?

2—Does there exist in the "Smoke Zone" any soil trouble which is responsible for any poor condition of plant growth which may exist?

3—Has the soil of the "Smoke Zone" been polluted by materials deposited therein from smelter smoke?

4—If such pollution exists, is it of economic importance? May it influence the growth of crops or plants for good or for ill?

The yield of crops in the area are below the average for areas in other sections of the state having the same climate. The poor quality of the soil and the poor agricultural practices are sufficient to account for the existing bad conditions as to crops and crop yields. No soil trouble exists, other than the poor quality of the soil, to which the existing conditions of plant growth can be traced.

In the matter of soil pollution, an extensive investigation was conducted. Samples of soil were taken from various portions of the area and subjected to examination to determine the presence of lead and arsenic. These metals were found to be natural constituents of the soils of the "Smoke Zone" and the country surrounding the "Smoke Zone." A slight increase in the lead and arsenic present in the soil was found in the area nearest the smelter, but this increase was shown to be of no economic importance.

Supplementing this work, the data collected by Mr. Wells on the presence of lead and arsenic in the air before the installation of the roaster baghouse proved that although lead and arsenic were present, the amount was unimportant from the point of view of soil contamination.

### EFFECT OF SMELTER FUMES ON HORSES

The veterinary survey included the identification of every horse and the enumeration of all the other important domestic animals within the Zone. The listing of the horses developed the fact that 31 horses out of a total of 308 within the "Smoke Zone" were suspected as being of the type known as "roarers;" 12 of these 31 were diagnosed as "roarers," the "roaring" condition being brought about directly by the paralysis, either partial or complete, of certain muscles of the throat and neck, which causes improper functioning of the respiratory system, so that under exercise the animal so affected breathes with a peculiar roaring sound.

It was the opinion of the experts that the condition of these roarers was due to chronic lead poisoning and that the animals had been injured by smelter smoke.

### INSTALLATION OF BAGHOUSE FOR ELIMINATION OF VISIBLE SMOKE

Soon after beginning its investigations, the Commission came to the conclusion that a study of the atmosphere of the "Smoke Zone" uncontaminated by the visible element of the smoke of the Selby Smelter would be highly desirable. The Selby Smelting and Lead Co. were, thereupon, requested by the Commission to take steps to remove all solids from the smoke that was being discharged from the plant. The Selby Company, with commendable promptness, began the erection of a baghouse, by means of which the visible smoke from the roaster stack (the only source of visible smoke) could be eliminated. The Commission's request was made October 25, 1913, and the installation of the baghouse was completed April 1, 1914, at an expense to the Selby Smelting and Lead Co. of approximately $35,000.

In order that full information might be at hand upon which to base recommendations for the subsequent operation of the smelter, in the event that a nuisance was found to exist within the "Smoke Zone," the Commission early undertook certain studies to determine the possibility of eliminating the sulfur dioxide from the smoke of the plant before the latter is sent into the atmosphere.

An investigation was conducted to determine the possibility of operating the Dwight and Lloyd Sintering machines of the plant in such a manner as would allow the production of a gas with a sulfur dioxide content sufficiently high for its recovery as a by-product. As a result of this investigation, it was found that by a proper preparation of the charge and the recirculation of a part of the gases, that 80 per cent of the total sulfur dioxide eliminated by the machines can be concentrated in a volume containing 7.5 per cent sulfur dioxide. With this concentration it is possible to apply a commercial scheme for recovery by the production of sulfuric acid, liquid sulfur dioxide or sulfur.

### FINDINGS OF COMMISSION

From the personal investigations by the Commission and from a study of the various reports presented, the Commission finds that:

I—The Smelter Company violated the injunction up to April, 1914, with respect to damage to certain horses in the "Smoke Zone," and that this violation ceased when the roaster stack baghouse was installed.

II—The Smelter Company has not violated the injunction with respect to disagreeable odor maintained in the "Smoke Zone," nor with respect to injury produced on crops or vegetation or on domestic animals through emitting sulfur dioxide into the atmosphere.

III—The Smelter Company will not violate the injunction if it discharges less than 80 tons of sulfur dioxide per 24 hours into the atmosphere, and cleans the smoke of its visible element.

IV—The Smelter Company will not violate the injunction, if for purposes of cleaning or repairing the baghouse, visible smoke is discharged for periods not to exceed a total of 48 hours in any one month.

SELBY SMELTER COMMISSION
325 MONADNOCK BUILDING, SAN FRANCISCO

## A TITRATION TABLE

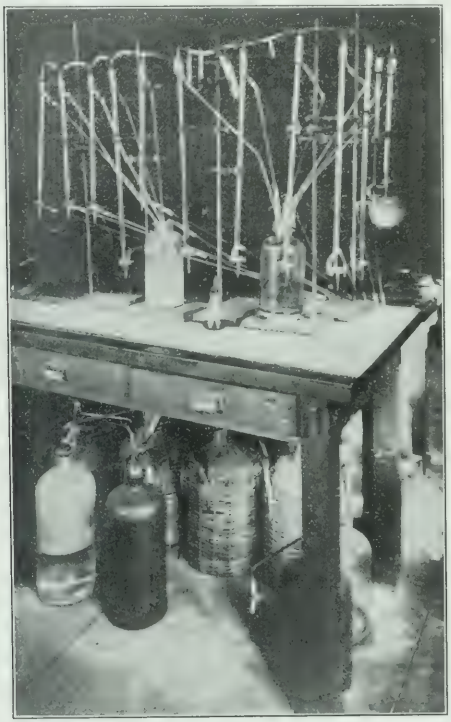
By R. S. POTTER AND R. S. SNYDER

Received October 17, 1914

In the course of some work which was being carried on here at one time, twelve different standard solutions were required and a space-saving disposition of these was necessary. The arrangement which has been found very practicable is shown in the accompanying illustration. Others might find something similar

of some use, so a brief description of the apparatus shown will be given.

From the large bottles which are kept on the floor under the table and which contain the various solu-



Titration Table

tions, delivery tubes run up through suitable holes in the back of the table to their respective burettes. The burettes used are of the three-way stopcock, overflow, zero point type. Tubes from the overflows of the six burettes at the right, which do not need to be protected from the air, lead to the large waste bottle at the right as shown. Entering this bottle is a tube connected to an ordinary air pump. The disposition of the burettes which are used for solutions to be protected from carbon dioxide is somewhat different. The tubes from the overflows lead to the large, open waste jar as shown. At the rubber connection of each of these overflows is a pinch-cock, which is kept closed, except as will be pointed out below. The upper openings of all the burettes are connected as shown, and a soda lime tube placed next the first burette, whose solution is to be protected from carbon dioxide. An open T tube is placed in the series of connections as shown.

The operation of the apparatus is as follows: The pump is turned on; the open end of the glass T is closed with the finger and if it is desired to use one of the six solutions to the right, the respective stopcock in the burette is opened; the solution is drawn up and the excess runs into the waste jar. If a solution which is to be protected from the carbon dioxide is to be used, the operation is just the same, except that any excess solution in the overflow cup must be gotten rid of by opening the corresponding pinch-cock in the overflow tube. Siphon tubes are kept in the two waste jars to draw off the waste solutions as they accumulate. As the rapidity with which the solutions are drawn up depends upon the rapidity with which a partial vacuum is created, it is better either to have the waste jar to the right small, or as we have done, keep a large one nearly full of water. It is scarcely necessary to state that all the overflow tubes might have been connected to the one bottle shown at the right, but space in the rubber stopper prohibited. The apparatus here shown was set up eight months ago and no changes nor repairs have been necessary during that time.

This scheme has the following advantages:

I—The minimum table space is taken up.

II—The solutions left in the burettes and delivery tubes can be automatically returned to the respective stock bottles whenever that is desirable.

III—A leak will not cause a loss of solution and a sometimes disastrous flood, as is the case when the stock solution is kept on a shelf above the burette.

Soil Chemistry Laboratory
State College Experiment Station
Ames, Iowa

## A BLAST LAMP FOR NATURAL GAS

By Harold Canning Chapin

Received December 7, 1914

The simple arrangements here illustrated, having served this laboratory for a year, may be of interest to others using natural gas. For complete combustion methane requires four times as much oxygen as does either hydrogen or carbon monoxide. Hence natural gas, which averages over 90 per cent methane and related hydrocarbons, will not burn completely

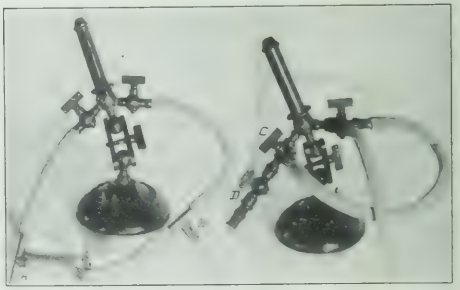



Fig. I Fig. II

in the amount of air which suffices for an equal volume of coal or water gas. Adjustment of a coal gas burner for natural gas requires cutting down of the gas-air ratio, which unfortunately is opposed by the higher pressure at which natural gas is usually supplied.

The best flame obtainable with a blast lamp in the ordinary way is not very hot and smells of escaping gas, which is not only disagreeable but also likely to

have a reducing action on platinum. Except with small flames it is impossible to mix sufficient air with the gas in the regular place at the tip of the burner without using so large an excess that the flame necks down and blows out. Mixing can be effected by placing a burner an inch or so from the lamp tip. The flame then starts mainly from the auxiliary burner, allowing the required air to be sucked into the intervening space. This serves for heating dishes, etc., but the flame is noisy and too poorly defined for glass-blowing.

Improvement was effected by admitting air to the gas current at a point back of the burner, as shown in Fig. I. Part of the air is diverted at A and mixed with gas at B. It proved essential at the pressures used, that the air follow the straight course at B with the gas entering at right angles. Fig. II shows the same arrangement incorporated in the lamp by shifting of parts and addition of a few stock fittings. Cock C replaces the pinchcock of Fig. I. D is a three-way cock made by drilling an open two-way cock from surface to center of stopper and cutting away from the stopper the partition between the new hole and half the old one. This was added to permit escape of air cut off from the lamp, thus allowing better regulation and relieving rubber connections from the high pressure of our laboratory air pipes. For small flames the cross connection can be closed; for larger it can be opened until the flame reaches the desired diameter next the burner tip. In this way, with air at 20 lbs. per sq. in. and natural gas equivalent to 20 in. of water, there can be maintained quiet flames with sharp 3 in. inner cones or good diffuse flames of larger dimensions.

Research Laboratory, National Carbon Company
Cleveland, Ohio

# ADDRESSES

## THE HARDWOOD DISTILLATION INDUSTRY IN AMERICA[1]

By Edward H. French and James R. Withrow

In view of the economic importance of the utilization of wood waste, and the increasing interest manifested in this utilization, it naturally surprises the inquirer that there is practically no literature upon this industry from the point of view of actual American practice. It may not be without value, therefore, to consider the progress made in hardwood distillation, and to trace its development from its inception in this country. We have gathered together consequently and classified much of the information which we have acquired in the plants of this industry during an experience in it totaling about 25 years.

This tracing of the development of an industry of the magnitude of this one is peculiarly interesting to the engineer, since it shows the necessarily slow evolution of the industry in the hands of the unscientific manipulator, and serves not only to emphasize the advantages possessed by the modern chemical engineer, but also to indicate how much more rapid the development might have been in the hands of experienced chemical engineers. It indicates also that in the future, under the direction of the competent engineer, important advances may be made much more rapidly than in the past. This latter statement is significant when it is remembered that progress thus far has been due either to accident or very often to workmen endeavoring to minimize the laboriousness of their work. As plants are operated in 12-hour shifts, this desire to economize energy may be readily understood.

For much of the historical information collected we desire to express our appreciation to Mr. Robert Mackay, who has been active in this industry for so many years. In fact during the past fifteen years our own continued intimate acquaintance with Mr. Mackay has been not only of unusual pleasure but of continuous instruction. A history of this industry would be incomplete without mention of the fact that, due largely to his personality and integrity, the firm with which Mr. Mackay is identified has had the unusual experience, in an extensive industry, of supplying engineering materials for every plant of this nature in the United States and Canada with perhaps two exceptions, for a period covering the past 25 years.

### EARLY HISTORY

While charcoal burning was doubtless carried on in the earliest days in this country, it was not until 1830 that James Ward[1] began the manufacture of pyroligneous acid, at North Adams, Mass. No claim is made that the pyroligneous acid was carried further though it may have been. We have, ourselves, no information on this matter other than the above citation. As far as we can ascertain, it was not until 1852 that works in the modern sense were inaugurated for the distillation of wood for the production of volatile products, and their semi-refined products. This does not appear in agreement with W. L. Rowland,[2] who is later cited by Monroe and Chatard and C. L. Campbell,[3] all of whom state that the manufacture of acetate of lime and methyl alcohol was started in the United States about 1867 by James A. Emmons and A. S. Saxon, in Crawford Co., Pa. Our information in this case comes from various manufacturers who have been in this business from the earliest times or at least whose family connections with it go back to the beginning. One of these sources is Mr. Neil Patterson, whose father was in charge of the original "Scotch Works," built in 1852.[4] In this year the Turnbull Company, of Glasgow, Scotland, who were engaged there in the copper and iron industry as well as that of wood distillation, built the first operation in this country, by way of expanding their "old country" business. The place chosen for this location was known as Millburn, New York, now Conklin's Station, on the D. L. and W. R. R., not far from Binghampton.

The Turnbull Company brought with them their apparatus as well as men experienced with their methods. On account of these Scotch workmen the works became known as the "Scotch Works," and this name has clung to it to the present time, although the original workmen gradually went with new operations which started shortly after this one. They had much to do with the subsequent expansion of the industry, all of them being later in charge of new works.

It is interesting to note in connection with this first plant, that it was a type that was copied in detail in the construction of those that followed, for many years afterward. All these plants were equipped with cast-iron cylinders 42 in. in diameter and 9 ft. long, set in pairs; thus each pair held about $1^1/_4$ cords of wood. The wood was cut 7 ft. long and the charge "run

[1] Read before the 7th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 4, 1914.

[1] Monroe and Chatard, "Chemicals and Allied Products," 12th Census, United States, *Bull.* **210**, 34.

[2] Special agent 10th U. S. Census on Chemical Products and Salt, p. 23.

[3] *Met. and Chem. Eng.*, **1910**, p. 185.

[4] Mr. J. L. Stuart of Corbett and Stuart, one of the earliest firms in this business in this country, informs us that the date 1852 given by Mr. Patterson for the building of the Turnbull plant should be 1849.

off" every 12 hours, and 6 days a week. The stills and pans were operated during these early days exclusively by direct firing. The fuel used for the retorts, stills and pans was the charcoal produced, over which was poured the residual tar to make a quick fire.

This original works was followed in 1865 by Emmons & Co., of Brookdale, N. Y. In 1868 Alonzo Smith started a plant at Sturroco, Pa. Keery Brothers, Cadosia; Mandaville, Emmons, Corbett and Mitchell, Livingston Manor, N. Y.; King and Co., Acidalia, N. Y.; Hilton & Co., Hiltonsville, N. Y.; Brand & Schlayer, Frink & Ross, Tyler & Hall, Inderlied & Co., Bayless & Berkalue, and Wright & Co. were also early in the field.

During the early part of this period of development, the chief product desired was acetate of lime, for which from 12 to 15 cents per lb. was obtained. The alcohol demand was almost negligible; that made was of very inferior quality and was kept in barrels, and most of it was lost by evaporation or through some "illegal vent." The charcoal also had but little commercial value and was largely consumed as fuel at the works, although a small local demand gradually developed, starting with the neighboring tinsmith.

The change from the old charcoal heaps or pits to the kilns probably came quite early and perhaps before any of the improvements we have mentioned. It was not until 1876, after the retort system was well established and markets for its products had been developed, however, that Dr. H. N. Pierce's inventions made it possible to utilize partially the products wasted in the smoke from the charcoal kilns in Michigan, where great quantities of charcoal were prepared for blast furnace use.

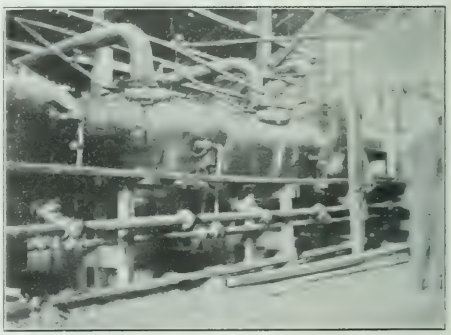
The earliest attempt at refining alcohol, so that it might be of commercial value, was made by a Mr. Pollock, a chemist, living just out of New York City. In a short time a demand began to develop for this product, which steadily increased, and up until 1880 was at all times up to the dollar mark. It was during this period that the need of better refining was felt, as it was realized that a large loss was entailed in the refining operations. This necessity accounts for the coming of the Burcey pans in the early seventies. These are copper containers placed in the vapor line above the stills, with deflectors inside to project the vapor against the upper shell of the container, upon which a stream of water runs, causing fractional separation of the water from the alcohol vapor. The increase of alcohol product resulting from this improvement, together with the increasing market demand, made a central refinery necessary, and the producers united in building a refinery at Binghampton, N. Y., known as The Burcey Refining Company. This was in the middle seventies, and the plant is still in operation. It has served a good purpose, and to it was due perhaps more than to anything else the substitution of steam for direct fire distillation.

Before leaving this early history, it should be mentioned that the Turnbull plant, and in fact several succeeding plants, had but four pairs of retorts or 5 cords capacity to the charge; thus by obtaining two charges within 24 hours their total wood consumption was about 10 cords per day. Today there are single plants operating 160 cords daily. Thus we have an illuminating comparison, at least as far as size is concerned, of the development of the industry.

### DESIGN OF APPARATUS

Even at the present time, there remain many plants using the old original retort system, with one very slight modification. Those first in service were of cast iron, while the later ones have shells of steel with riveted cast-iron necks and fronts. The purpose of this change was due to the fact that in the early operations, since the wood was then of much less value than later, and high yields were not so important, it was charred at a very high temperature, in order to increase as much as possible the capacity of the plant by shortening the time of firing. As cast iron was much more durable for these high temperatures than steel, the use of cast-iron retorts was universally practiced. When, however, with the coincident rise on the cost of wood, it was found that lower temperatures gave an increase of all products, it was seen that steel could be employed to advantage, for its lower weight permitted the turning of the retort. This turning refers to the saving in apparatus universally practiced and consists merely in the removal of the brick setting when the side in contact with the fire becomes buckled, rolling over the retort and placing the uninjured part next the fire, thus materially increasing the life of the retort. This modern retort is of uniform size and design in all plants which still use this type of apparatus. The shell, as originally, is 42 in. in diameter and 9 ft. long, supported at the ends in a cast-iron cradle and having a cast-iron front, with door and lugs, for pinning the door shut. At the rear is a neck 10 in. in diameter, to which is attached the condenser.

The evolution of the condenser is especially interesting, in view of the fact that when the original condenser was installed each succeeding plant accepted it as being of proper size, and the new installation was made the same size. Then from time to time some one would discover that an addition would yield more product and at once the arbitrary sized unit was changed.



ANCIENT TYPE OF COPPER STILL—IN A NOW DISMANTLED RETORT PLANT. FORMERLY DIRECT FIRED, THEN CONVERTED TO STEAM HEATED

Originally the worm condenser was used, but it soon became apparent that the heavy carbon bodies caused clogging, and soon the log condenser was substituted and was used until the introduction of the upright tubular one. These log condensers were made by attaching, by a copper tee, a large-sized copper pipe, called the log, to each of a pair of retorts. Near the ends of this pipe were copper connections, joining the large log to a smaller one, and this in turn was similarly connected with others progressively decreasing in size. The whole log condenser lay in a plane at an angle of 45° and the whole was surrounded by a wooden box with water inlet at bottom and outlet at the top. The joints were simply slip joints and were slipped together and "sweeled;" that is, wrapped with a cloth liberally covered with red lead, which, after becoming dry or "set," offered a suitable and effective joint. At the ends of the logs were removable slip joint caps, for cleaning purposes, so that the cleaning from the heavy tarry and carbonaceous bodies was easily accomplished.

The first really important change in the general style of operation was that of replacing the old retort by the oven, which was done in the middle nineties and is claimed to have been first tried out at Straight Creek, Pa. This change was wholly mechanical, and consisted merely of substituting for the retort

a large rectangular oven, equipped with rails on the bottom for the purpose of carrying cars. These cars were loaded with wood and could be quickly pulled in and out mechanically and the charcoal unloaded outside the oven, greatly increasing the economy in this part of the operation, over the slow hand drawing of the charcoal of the retort system.

There appear to be, however, many more advantages in this style of operation than the mechanical advantages which were

Typical Pennsylvania Wood Yard

at first anticipated, as an increased yield of products is obtained, due undoubtedly in part to more advantageous manipulation, but in our opinion also to the different chemical reactions that take place. In the old retort system complete carbonization of the wood took place in about 16 hours, and it required in the oven system 24 hours; yet the temperature of the gases at the neck are higher in the latter, running at a maximum under skilful manipulation to about 330 to 360° C., while in the former case the operation was consummated at not over 290° maximum. This maximum temperature is obtained about midway, or two-thirds, of the run, at which time a very decided exothermic reaction takes place, and care must be exercised that the liquor is not "burned;" *i. e.*, that the temperature is not permitted to rise. If this happens, undue formation of condensation products results, which is immediately indicated by an increased flow of gas and a darkening of the crude liquor. This exothermic reaction, which also takes place in coal distillation, probably accounts for the increase in temperature of the uncondensed gases in the oven system, since no greater proportionate radiation takes place in this system than in that of the retort construction. At this particular stage, on account of the nature of the source of heat (exothermic changes in the wood), a much more uniform temperature throughout the oven is maintained. This gives an excellent illustration of the possibility of considerable alteration, even in the chemistry involved in a process, when we change the mechanical manipulation.

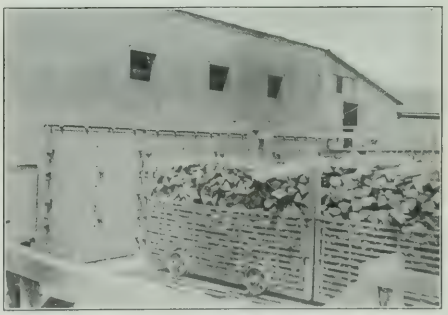
An additional advantage obtained by this oven system is that the charge of residual charcoal may be drawn while the oven is still hot, thus economizing on the fuel necessary for reheating, while a partial cooling is necessary in the hand-drawn retort system. The time lost during this cooling was saved in one design at Dahoga, Pa., where the retort at the conclusion of firing was removed by a crane from its vertical setting and replaced at once by a previously charged retort. It is stated in the meager literature on this industry that "this type is probably most used."[1] This Dahoga installation, though it operated for many years, was the only plant of this type that ever was installed in this country, as far as we are aware, and certainly there is little likelihood of any existing now, for this one was recently converted into an oven plant.

There is still a third system, which should be at least mentioned, namely the kiln system. This was really the second in date of development, but the oven system was so closely allied in design and operation to the original retort system that the two were taken up together. The fact is, we would expect the logical development to have been: charcoal heap—charcoal pit—charcoal kiln—by-product charcoal kiln—retorts—ovens; but this does not appear to have been the case, in this country at least. As in the coke industry, we do not appear to have gone from bee-hive oven to by-product bee-hive oven, directly, but through the by-product oven, an outside and distinct invention. So in this industry, the charcoal kilns were converted into the by-product kiln system only after the development of the retort system.

When charcoal was produced in kilns, from 20 to 86 cords of wood were placed in a kiln constructed of bricks, and wood was used as fuel for carbonizing. The volatile products were lost through the opening provided at the top. With the advent of markets for charcoal and acetate, some charcoal manufacturers placed a pipe connecting this opening with a suction fan and a condenser and thus collected the volatile products. The amount of product thus recovered is but a fraction of that recovered in a retort or oven system. In Pierce's system the flat-topped circular kilns usually hold 50 cords. They are heated by gas burned in a furnace under the kiln. For the sake of brevity, a description of these interesting kiln plants will be omitted since their recovery of by-products is low and they are confined almost exclusively to the blast furnace plants of Michigan, where they are steadily and rapidly being displaced by oven plants.

### YIELDS

The low yield from the kiln system, which runs about 100 lbs. acetate of lime and 4 gal. of alcohol per cord, together with the low yields obtained by *rapid or quick* firing, plainly show that there is a mean temperature which gives the maximum yield. Just what the curve of efficiency is, has never been definitely determined in a commercial plant, to our knowledge, though we have given it much experimental attention and others doubtless have worked on it also. In fact, there are so many factors to be considered in a comparison of experimental operations on a commercial scale that while the factors causing increased or lessened results are known, it is difficult to obtain



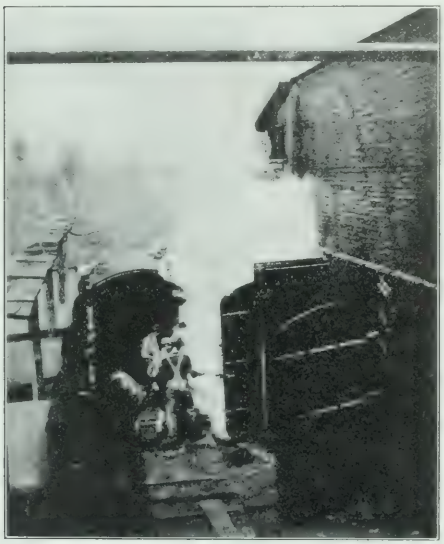
Loaded Wood Cars at Ovens

accurate definite knowledge as to just how much each factor contributes to the results. For example, we know that Michigan plants under approximately the same construction and operation obtain less product per cord than those of New York and Pennsylvania, without certain knowledge of the relative influence of the various contributing factors.

This lack of definite data on a commercial scale, so deplorable in most industries, results from the difficulty of obtaining suc-

[1] *Met. and Chem. Eng.*, **1910**, p. 155.

cessive tests with all conditions alike, for we well know that any variation, for instance of temperature, has a peculiar relation to the results obtained. In addition, it goes without saying that the variety of species of the wood enters largely into the results obtained, and even the part of the tree used may cause variation. For example, a charge made up wholly of heartwood will give better yields under the same conditions than a charge of slabs, making due allowance for the bark. Again we have found that, weight for weight, cord-wood obtained from the mature or virgin trees will yield higher than the small second growth; also we are convinced of a noticeable difference in results from wood of the same species grown on high and dry places, and that from low or marshy soil, the latter giving a slightly lower yield. Indeed it is interesting to hear the experienced operator maintain that wood cut in the winter months will give better results than that cut while the sap is running. We are, however, unable to verify this expression, and it is possible that some other factor may have been responsible for this often repeated statement. It is also held by many operators that, eliminating the consideration of extra fuel necessary for the charring of green or unseasoned wood, the results are not the same in finished product as from well seasoned wood. We can see from these statements that, with so many factors to be considered, it is extremely difficult to determine which enter most into the discrepancies between the various systems: retort, oven and kiln. However, from the purely practical standpoint we do know that there is a marked difference between yields obtained from the different systems as well as from the two general localities extensively operating.



START OF OVEN PULLING

If we compare the results obtained by the same system operated in the Allegheny Mountains with that of the Lake Superior region, we find that by taking the results on a yearly basis from a well operated plant and calculating the wood on a basis of a cord 8 × 4 by 52 in., there should be obtained conservatively 216 lbs. of 80 per cent acetate of lime, 11.3 gallons of 82 per cent crude wood alcohol, and 52 bushels of charcoal. The yield from the Lake district is slightly under this in alcohol and decidedly so in the acetate yield, which is 175 to 180 lbs. on continued operation. However, here again we have at least two factors and it is difficult to determine their relative influence. First, in the eastern field, beech predominates while in the other hard maple is in larger proportion, and also slab wood is used much more largely. In fact, we have been unable to obtain data from a continued operation in which at least a small proportion of slabs was not used.

### CONSTRUCTION

At this point it may be well to take up the question of construction, especially of the most successful and modern system, that of the oven, which is, with the exception of the mechanical manipulation, similar to the retort system.

The ovens are of uniform height and width, in most plants being 6 ft. 3 in. wide and 8 ft. 4 in. high, the length determining the capacity, running from 26 to 54 ft. and holding from five to ten cords. The steel used in the shell is usually $^3/_8$ in. while the bottom and back heads are of $^1/_2$ in. material. Ovens are built either with doors at both ends in order to withdraw the residual charcoal coincidently with refilling the oven with the wood-loaded cars, or in many cases, with a door at one end, the oven being loaded after the charcoal has been run into the coolers. In any event, the door is hung upon a cast-iron frame riveted on the oven. This frame has a groove of about 1 in. for the use of asbestos packing and the cast-iron door is hung to the frame by riveted cast-iron hinges. The oven is stiffened by means of angle irons riveted perpendicularly on the sides, and on one side near the top are riveted 30 in. cast-iron nozzles, usually two in number, to which are attached the condensers.

The first ovens installed were placed upon piers in the setting, upon which were iron plates and rollers to accommodate expansion of the oven, but in the later settings the ovens are suspended from Tee rails laid across the brick setting at the top and supporting the oven by means of U bolts riveted thereto. The bottom of the oven is equipped with clips for holding the rails which carry the wood cars. These cars vary but slightly in length in different plants, running from 10 ft. 4 in. to 12 ft. 4 in. inside length and about 78 in. high; thus each car holds from 2 to $2^1/_2$ cords of 52 in. wood. Each has four 18 in. wheels with roller bearings running on $2^7/_{16}$ in. turned steel axles.

Immediately in front of the ovens are two charcoal coolers arranged in series and approximately of the size of the ovens. In the first the hot charcoal is drawn from the retort, where it stands for 24 hours. From this cooler it is drawn into the second one for another 24 hours of additional cooling. These coolers are made of very light iron with cast door frames riveted on each end, and light sheet iron doors. No bottoms are required, as the coolers are simply placed on the ground and banked along the sides and doors with loose dirt.

To the nozzles heretofore mentioned are connected the condensers. These are upright tubular condensers, made with copper hoods having a removable head, and are bolted to gun metal heads which are bored for the copper tubes, usually $1^1/_4$ in. O. D. seamless copper, and expanded into these gun-metal heads, the whole surrounded by a steel water-jacket with water inlet at the bottom and outlet at the top. Connected to a bottom pan bolted on the lower head is a goose-neck trap for trapping off the non-condensable gases, thus separating them from the pyroligneous liquor, which is run into a wooden tank. The gas from the charge is carried into a main gas line which runs to the boilers where the gas is injected under them by a small steam jet. This jet performs the additional and very important function of serving to reduce any back pressure on the ovens, thereby preventing leaks. In order to prevent this suction from becoming too pronounced and drawing over the lighter volatile products through the condenser into the gas line, a butterfly or clapper valve is arranged on the line and regulated

by a spring so set that any undue suction opens the valve, thus relieving the line.

PRIMARY DISTILLATION OPERATION

After this general outline of the first stage of the construction let us follow the operation to this point. After the loaded cars are run into the ovens the doors are pinned shut with taper pins driven into lugs which are parts of the castings of the door frames. The fires are started under the ovens and in about an

CHARCOAL COOLERS IN A NEW YORK PLANT

hour the water distillation and first dissociation begins, the distillate being of a very light yellow color and having a tannin-like odor, and running about $2^1/_2$ per cent of acid during the first hour when well seasoned wood is used. Gradually this acid content rises until about the fifteenth hour, when the content should be running from 12 to 14 per cent. After a few hours running, a small percentage of light tar begins to appear and steadily increases until at the latter end of the run tar is by far the larger constituent of the distillate. The acid content of the watery constituent gradually diminishes until it is almost negligible.

The product obtained under the usual practice, with average wood of at least a year's seasoning, is from 215 to 220 gallons of crude pyroligneous product giving an acid titration of 8 to $8^1/_2$ per cent and an alcohol content of 4 to $4^1/_2$ per cent. The tar yield is from 22 to 25 gallons to the cord, with a residual charcoal in the cars of about 52 bushels of 20 lbs. each. With

DUMPING CHARCOAL

green or unseasoned wood the total distillate is diluted and will run from 275 to 325 gallons of liquid

In the early stages of the run the non-condensable gases are largely air and carbon dioxide. Therefore for the first few hours, and even after much of the hydrocarbons and carbon monoxide are accumulating in the gases, they have no fuel value. However, the percentage of carbon dioxide diminishes rapidly, and from the middle to the end of the run the oven gas has an important fuel value. The total amount of gas will run from 11,000 to 12,000 cu. ft. per cord.

As we have already intimated, the influence of the temperature of dissociation is extremely important, and the yields are very dependent upon its regulation, *e. g.*, if, during the height of the run, the temperature at the neck of the oven materially exceeds 750° F. much greater volumes of non-condensable gases are being formed, together with an excessive amount of tar, and it is quite possible to lose from 5 to even 10 per cent of charcoal, together with a serious loss both of alcohol and acid content. Rapid firing, however, without reaching excessive limits, will materially increase the acid content at the expense of the alcohol, while slow even firing, operating the oven at a period in excess of the usual 24 hours, will increase the alcohol production somewhat and lessen that of the acid.

The interesting results obtained from excessive firing arise, as we hope to show later, both from a difference in the chemical dissociation and also from the subsequent formation of condensation products.

In drawing the hot charcoal from the ovens, quantities of combustible gas remaining in the ovens would cause explosion on the opening of the doors. This is obviated by the introduction of live steam into the front of the oven for a short time before the drawing is made.

HANDLING THE CRUDE DISTILLATE

The crude distillate or pyroligneous acid, called in the works "raw liquor," is first pumped into a series of wooden settling tubs, connected by brass piping. The first tub, where the greatest amount of tar settles, is connected near its top with an overflow pipe to the second tub. The second tub is connected with the third by a pipe somewhat lower, and this series of drops is continued so that the last tub is drawn from within about 18 in. from the bottom. The raw liquor thus settled free from tar is as a rule continuously run into the copper stills. These copper stills are for the purpose of distilling off the lighter volatile products away from the tars and oils which remained in solution in the settled liquor. They are from 7 to 10 feet in diameter with proportionate height, made of 12 to 14 gauge cold-rolled copper, and equipped with a steam coil, usually of 3 or 4 in. seamless drawn copper tubing starting from about 18 in. from the top and running helically around the walls and on the bottom to midway between the center and periphery. For a 2,000 gallon still, from 300 to 400 sq. ft. of heating surface should be used. In addition each still should be supplied with a live steam jet applied at the bottom and preferably through a copper ring having small steam openings.

After a copper still has run continuously for some time it gradually becomes filled with deposited tar and its flow of distillate diminishes. When this has reached a stage of very slow production, as it does every four days, the feed valve is closed and the live steam jet is opened, distilling the tar with live steam, thus obtaining considerable quantities of acid and light oils. This latter distillate is run into separate tubs, where the light oil on the top is withdrawn before the acid liquor is pumped into the original copper still distillate, which has been run into a wooden "mixing tub." The tar from the settling tubs is usually distilled in a separate tar still, sometimes made of wood, and distilled as has been that just described. This practice is followed as it permits the separation of the oils independently and without allowing them to come in contact with the original distillate, in which a portion would dissolve; thus the bulk of the distillate contains less impurities by this practice.

The mixing tub is usually from 12 to 14 ft. in diameter and 4 ft. high, having a very heavy wooden stirring arm fastened to the end of a heavy shaft, operated by a slow moving gear at the top. Slaked lime is slowly added to the liquor in the tub,

which contains its own indicator, the liquid changing at the neutral point to a pronounced wine color. For maximum yields, however, probably owing to the acetic esters present, the addition of lime should be continued until this color has been followed by a yellowish one and until a bead appears or bubbles form on the surface and disappear slowly. A very small further addition of lime at this point causes the acetate to stick to the pans when evaporated and prevents satisfactory crystallization. Under-neutralization also causes inferior quality in crystallization, and before final drying the acetate has a decided black color instead of a rich yellow-brown; also there is an accompanying loss in product owing to the esters lost.

From the mixing tub the neutralized liquor is jetted or run into an iron still known in practice as the "lime lee" still. In a few plants this is equipped with either Burcey pans, or in some more modern works with a fractionating column, although most plants do not fractionate at this point. The customary practice is simply ordinary distillation. The crude alcohol starts over at about 20 per cent on a Tralle scale but quickly rises to 35 and at times 40 per cent, gradually dropping in percentage to from 15 to 20, at which strength it continues for some time and then drops rapidly to 5 or 6 per cent, at which point it seems to hold stationary again for a long period. After all of the alcohol has been distilled over, a valve in the vapor neck is closed and the residual acetate solution is blown, by means of

SODA STILLS—WOOD ALCOHOL REFINERY

live steam pressure applied in the still, to an iron settling pan above the top of the ovens, where the excess lime and insoluble impurities settle out in a few hours. The acetate liquor is then drawn into flat steam pans having a jacketed bottom for steam supply, the pans usually being about 16 ft. long by 8 ft. wide and 18 in. deep. Here the acetate liquor is boiled rapidly until crystals appear on the surface near the edges, when the steam is reduced so that the crystalline film which forms at once on the top does not break, which would cause it to fall to the bottom and form a hard crust. Care must be exercised in this "seeding" process as it is called, or a great quantity of this exceedingly hard crust or scale will be produced, which is unfit for the market. After this "seeding down" has continued until the whole mass in the pan has reached a very thick mushy consistency, it is shoveled out on the acetate or "kiln floor," which is a smooth brick or tile covered floor over the top of the ovens. Here the acetate is continually turned until dried and ready for sacking and shipment.

The "weak alcohol" from the "lime lee" still, containing from 9 to 12 per cent of acetone and alcohol, is accumulated and distilled in an iron still having either 5 or 6 Burcey pans or a column. This distillate is the final crude product produced by the works, and is usually shipped to a central refinery, although a few plants refine their own product. In this distillation all the product coming over above 60 per cent is run into the storage tank, and the lower fraction is put back with the lime lee distillate for further distillation. The finished crude is sold on a basis of 82 per cent and contains about 16 per cent acetone.

Returning to the copper still residue, the tar from these stills, as well as that from the tar still, is run into a sump and from there jetted under the boilers for fuel. The two fuel products, gas and tar, furnish approximately 35 or 40 per cent of the necessary fuel for all operations.

Before leaving this subject of operation it might be said that many of the earlier plants omitted this copper still distillation, neutralizing the raw liquor directly after settling and thereby obtaining the "brown acetate" of commerce, which is today practically without market. This brown acetate runs from 60 to 65 per cent acetate.

### PRODUCTION COSTS

The costs of producing the products above mentioned have been on a constantly increasing scale, owing in a large measure to the increasing cost of cord-wood and stumpage. During the past fifteen years, in the eastern district, stumpage in suitable location has been sold for as low as 15 cents per cord, while today 75 cents to $1.00 is the approximate average. The cost of cutting varies from $1.15 to $1.35 per cord in fair timber and in scattered timber $1.50 is sometimes paid. Today, including transportation, piling, etc., this will make the cost on board oven cars $4.00 to $5.00 per cord, though wood is being put in for as low as $3.50 by users of mill-waste or by those having long standing holdings.

This gradual rise in the cost of wood is due to natural causes, among which are the increase in stumpage cost due to the ever-decreasing supply, and the natural rise in labor, together with increased length and cost of transportation. With the exception of one possibility, there appears to be no hope of any future lowering of costs. This one exception, a new cord-wood splitting machine, appears from our examination to have merit, and presents an entirely new system of cord-wood production. It is generally conceded that cutting and hauling the large log is less expensive than cutting and handling the cord-wood at the stump. The tree is therefore cut in logs and large limbs and transported to the machine, where a slide carries it first to a cross-cut saw, which cuts it into the proper lengths. The sawed pieces continue to a platform where they are either split in halves or quartered by one blow. The split wood automatically moves by a slide to the railroad car or wagon. It is claimed that under suitable conditions 50 cents per cord, or in some instances even more, may be thus saved. We have been unable to see continued operations of this machine as yet, and consequently can not verify this saving cost, but are inclined to believe that at least some reduction in wood cost is possible by this means.

The cost of fuel for a crude works, in addition to the tar and gas used, of course varies with the available supply. In the New York and Pennsylvania districts, when coal is used, this cost will amount on an average to $1.15 per cord, and when natural gas at 15 cents per 1000 cu. ft. is used the cost is but slightly more. The labor at the plant is usually counted at $1.25 per cord.

The following summation of production costs will be generally accepted as a fair basis in considering investment in new installations.

PRODUCTION COSTS PER CORD OF WOOD

| | |
|---|---|
| Wood (maximum) per cord | $5.00 |
| Fuel | 1.15 |
| Labor | 1.25 |
| Lime, 0.96 bu. at 19 cents | 0.18 |
| Bags (acetate) | 0.14 |
| Freight (acetate) 16 cents per 100 | 0.35 |
| Freight (alcohol) | 0.10 |
| Selling commission acetate | 0.11 |
| Insurance 0.068 per cord<br>Taxes 0.112 per cord<br>General expense | 0.57 |
| Total | $8.85 |

### PRODUCTION VALUES

With the present slump in markets the values herein set down are low, especially that for acetate of lime. The past 10-year average would be about $2.00 per hundred, while at present the market is slow at $1.75 per hundred.

| | |
|---|---|
| Alcohol (82°), 11 gal. at 25 cents | $2.75 |
| Acetate of lime, 216 lbs. at 1.75 | 3.78 |
| Charcoal, 52 bu. net at 6¼ cents | 3.38 |
| Total crude value | $9.91 |

This gives a production cost of $8.85 and a sales value of $9.91 per cord. It will be noted that no selling costs except in the case of acetate of lime have been included, because, in the works not refining or making the finished products, which are in number far in excess of those who do refine, the alcohol is sold under contract to the refiner, and the charcoal is either, as in the case of those plants in the Lake district, consumed at iron furnaces in connection with the plants, or as in the eastern field handled by a general sales agency controlled by the manufacturers, proportionately to their daily production capacity, yielding to the producer about the above-mentioned figure at present.

These production costs are based on the yields in the eastern field, which as pointed out were higher than those of the Lake region. This discrepancy is compensated, however, by the fuel and wood costs being lower in the Lake region, owing to the fact that in most instances mill-waste is used. The general relation between the two fields of operation, in this production cost and product value, is therefore approximately the same. It is undoubtedly true that many manufacturers can show much greater net profit than the above figures indicate, because of cheaper wood and fuel and in some instances because of plant design.

### COSTS OF INSTALLATION

Eliminating the cost of wood supply, $2000 per cord per day production is counted as a reasonable installation cost for a plant as described, for producing crude products. For instance, the cost of boilers, ovens, cars, coolers, pumps, etc., is substantially $650. Copper work, including stills, condensers, piping, etc., approximates $450. Brickwork for ovens and boiler settings, etc., will come to about $190. These three general items are more or less about a fixed estimate, varying of course somewhat upon the price of materials at the time. The location, buildings and general costs vary with the design and the desire of the builder. However, the above stated general figure of $2000 is a fairly accurate estimate, unless elaborate construction is undertaken.

### LARGE SCALE EXPERIMENTATION

Realizing the possibilities and necessity of counterbalancing the increasing cost of production, several large operators have made extensive large scale experiments with a view to increasing yields and lowering production costs. Unfortunately the results obtained thus far have not justified the expenditures made, in spite of many optimistic claims,[1] owing in a measure to the many unlooked-for complications which arise between the laboratory and the works scale. Of the great amount of work which has been done along this line with which we happen to be familiar, space permits the citation of but a few illustrative instances.

In the fall of 1908 certain men largely interested in the business went to Germany to investigate developments there and returned with a process for eliminating the copper stills and making gray acetate of lime directly from raw liquor, a proposal which had already been made and studied in this country. This process had been reputed to be in successful operation in Germany. It was in fact merely the application of the cup column to the neck of the ovens. The cups and openings were of course of larger size than in the customary column, but in effect this really was all that could be claimed for the new appliance. It was held that the pyroligneous vapors, passing through the condensed tarry liquor, were freed from their impurities by this means and that gray acetate could be produced from the resulting raw liquor by direct neutralization. Educated or impressed by the then incomplete American investigations mentioned, these men permitted themselves to be carried away by the assurances of the German engineers and, as has happened several times in our industrial chemical development in more or less identical circumstances, without any experimental investigation they equipped a large plant with this apparatus at an enormous expense, the copper work for which alone exceeded $80,000. The plant did not prove satisfactory.

It will be at once seen from foregoing statements in this article, that there were two fundamental reasons which explain, in our opinion, the failure to obtain the desired results. *First*, as pointed out, mechanical clogging of the apparatus would occur, as was the case in the original worm condenser; and *second*, as we believe, the valuable products readily form condensation products with the unsaturated hydrocarbons and aldehydes present in the distillate. Certainly the passing of these vapors through the hot tarry liquid would tend to increase this chemical reaction. Moreover, the apparatus caused back pressure on the ovens and required a suction to overcome this objection. This increase of suction would tend to bring the vapors through the cups and the condensers at a more rapid rate, which of course would lessen their efficiency.

Later another process, also brought from Germany, was tried, which was in effect the same as the one above described, except that the vapors were forced through a body of hot tar for the purpose of washing them, but this also was not successful. In our opinion this failure was for the same fundamental chemical reason as mentioned above.

A process for accomplishing this result, but not as yet entirely developed, from which some very satisfactory results have been obtained, is based upon a totally different theory from those mentioned. This method places a fractional condenser on the neck of the oven, which is maintained at a temperature sufficient to liquefy the high boiling tars and oils. These, however, are largely mechanically carried along by the uncondensed and non-condensable gases, while a part of the tar is run off through a gooseneck on the bottom of the fractional condenser; the uncondensed vapors and the non-condensable gases with their suspended tar and oil liquids are carried into the bottom of a centrifugal basket or drum, installed in a copper container and having small perforations inside of the drum, which is supplied with wings to give a rapid motion to the gases. This centrifugal action throws the liquid particles or mist against the side of the container, on which are deflectors set at an angle opposite to the direction of the moving drum. Thus the condensed bodies are forced to the bottom of the container and out of the zone of circulation, through a gooseneck into the tar receiver, while the vapors continue to a second condenser where they are condensed, the wood gas being trapped off in the usual manner.

This process has given uniformly increased yields of product but exact data as to saving, yields and cost of operation have not been determined as yet. A little over 1 H. P. is necessary for the operation of a 7-cord machine until speed is attained; then ¾ H. P. is necessary.

The increase in product yield with this method is probably due to the fact that the vapor contact with the condensed and unsaturated bodies present is reduced to a minimum.

Another attempt at fuel conservation, which it seems should be possible of accomplishment, relates to the evaporation of the acetate liquor. As has been seen, much heat is necessary for this evaporation, and this method attempts to utilize the high

[1] *Met. and Chem. Eng.*, **1910**, p. 434.

temperatures of the gases at the oven's neck before they enter the condensers. We are not aware of any installation of this nature although patents have been issued for accomplishing this end. Nevertheless, as it involves what appears to be a wholly mechanical manipulation there should be no great difficulty in saving at least a portion of this waste heat. Here again it can be seen that experimentation to accomplish this end is costly, since all experimental changes necessitate considerable financial outlay if tried on a large oven, and also involve interruption of regular operation which must from time to time inevitably occur.

Under this head of experimentation may properly come an elaborate attempt to utilize hardwood sawdust for alcohol manufacture. This was undertaken in 1903 by a well known lumber company in Cincinnati, who endeavored to destructively distil sawdust continuously by means of an endless belt which carried the sawdust through an oven for the purpose of carbonizing, tapping off the pyroligneous vapors and obtaining an uninterrupted production of charcoal, which was briquetted. The distillate was handled in the usual manner.

It can be readily seen that sawdust can not be destructively distilled in bulk, as is cordwood, for the insulating space between the particles prevents the heat from going through the mass. This explains the reason for the endless belt.

No expense was spared either in buildings or equipment, the buildings being of stone and the equipment of the best, the whole costing probably $200,000. Notwithstanding this outlay, the operation was a complete failure, the plant being dismantled within a year and the buildings used for other manufacture. The high fuel cost in attempting to overcome the resistance to radiation in such a mass was an important item in the high production cost which resulted in the failure. In addition, sawdust charcoal is a more dangerous fire-risk than common charcoal, in the handling of which in the ordinary plant, special arrangements are necessary.

Within the past five years some plants have installed double and triple effect evaporators with a view to fuel economy, and reports as to the results are very contradictory, but the continued use indicates at least partial success. One Michigan plant is successfully drying its acetate with a drum and belt drier. Vacuum drying for acetate has been tried, but we are unaware of any success as the resultant product is a powder, while the market demands the crystal.

### REFINING

From the time of the formation of the already mentioned Burcey Refining Company, the usual plan of manufacture contemplated only the production of the crude product as described, selling the products, those of the Eastern field, largely to a Buffalo refinery and the Michigan manufacturers to Detroit. Up until the passage of the Denatured Alcohol Bill by Congress they received a price usually ranging from 40 to 75 cents a gallon for the crude alcohol. After the passage of this act, and with the purchase of the Detroit plant by the one at Buffalo, the price of crude was at times as low as 15 cents per gallon, and during this period of adjustment intense depression prevailed among the crude producers, as it was feared that ethyl alcohol would largely supplant methyl. It was found, however, that the trade, particularly the paint trade, preferred wood alcohol even at a slightly higher price, and this fact virtually saved the industry. With the formation of a refining company among eastern crude operators representing somewhat over 1,000 cords daily production, and the erection of a refinery at Olean, N. Y., the monopolistic control of refining was immediately reduced. A very acceptable dead rental was paid to the crude producers for their uncompleted refinery, as well as a substantial increase for their crude product, which eventually reached and is maintained at about 25 cents per gallon of 82 per cent product.

The method first employed by refiners was merely that of fractional distillation, and we all perhaps remember the yellow, ill-smelling wood alcohol of commerce. Later, and for a long time, bleaching powder and sulfuric acid were used before the final distillation. This materially improved the product, but with the improvement of the columns used, treatment with sodium hydroxide and distillation is all that is necessary. The NaOH serves the purpose of polymerizing the aldehyde impurities and saponifying the tarry matter. The esters present are also affected. The formerly objectionable acetone present, which distilled with the heads, now has its own market value under the name of acetone-alcohol and is used in varnish removers, as a solvent in the rubber and other industries and also as a carrier for acetylene gas in lighting systems. Thus this 16 to 18 per cent of impurity is now in fact an added value to the refiner.

### MARKETS

Prior to the present unfortunate European situation, the average production of acetate of lime from the manufacturers in this country amounted to approximately 7,000 tons monthly, and we are informed that the total European and Canadian production is almost equal to this, of which tonnage Austria-Hungary furnished about two-thirds. The plants in Europe, however, are usually on a very small scale in comparison with those in this country. Sweden alone has plants of a size in any way comparable with the larger ones here. Of the production of acetate in this country, from 50 to 60 per cent is exported, a considerable percentage to or through Belgium. Of course, it will be understood that these statements refer to the market situation before it became demoralized by the European war, although for a year prior to the declaration of war there had been a pronounced stagnation of the markets both at home and abroad.

Of the acetate of lime consumed in this country, by far the largest percentage goes into acetic acid production. The hardwood industry is therefore vitally connected with this acetic acid industry, and one of the most important developments in the last decade is the successful beginning made in combining the crude manufacture and this refined product manufacture in the same plant. Such combination plants have shown crude acetic acid yields in continuous operations running 92 to 96 per cent of theory using 5 per cent sulfuric acid in excess of that theoretically required, and giving on a continued daily production of 4,000 lbs., with a yield of 91 per cent of the possible theoretical yield, refined acetic acid of the finest double distilled quality.

The chief individual acetic acid market demands in this country are from the manufacture of white lead, paint colors, and the textile and leather industries, although in the aggregate the small consumers, such as the laundries, ink and drug trades, use great quantities. This country prohibits the manufacture of acetic acid vinegar but its production is permitted abroad.

The consumption of export acetone produced in this country is chiefly by England, and Italy is just now a large consumer. The industry is in a particularly thriving condition at the present time, owing to the use of acetone in production of explosives for the European war. There should be obtained 20 to 22 lbs. of acetone per 100 lbs. of acetate used, and in connection with the crude works acetone production is very profitable, as the general operating expenses are low. Of course its use in this country was very large for explosive manufacture and for the production of chloroform under the well-known Rump patents, regarding which there was so much patent litigation some years ago and which as you know were upheld. In comparatively late years, however, a large Michigan concern has produced chloroform commercially from carbon tetrachloride, which has probably influenced somewhat the acetate

consumption for this manufacture. There are 4 plants in the United States producing acetone for the market and within the past week ground has been broken in Pennsylvania for a 5th plant. There is but one plant operating in Canada to our knowledge.

Ten years ago the steel industry consumed by far the major percentage of charcoal produced. This percentage, however, has decreased considerably, owing to the improved methods for steel production. Many industries such as cutlery and car wheel manufacture demanded charcoal iron, but in these and many other instances coke iron has been substituted. This falling off in the proportionate use of charcoal in iron production has been made up in an increased domestic demand. Charcoal is now sold in small paper sacks in many cities for use both in hotels and private families.

The production of crude wood alcohol amounts to between 10,000,000 and 11,000,000 gallons per year, and of course it has innumerable uses, including those of the paint industry which is the largest single user.

Space will not permit, in a general article such as this, of going into details regarding production and markets of the other products such as formaldehyde, creosote, etc., which are directly or indirectly derived from hardwood distillation.

### DISTRIBUTION OF PLANTS

Although not in agreement with any published figures, we place the distribution of distillation plants as follows:

| Location | No. of Plants Oven | Kiln | Retort | Cords Daily Oven | Kiln | Retort | Total No. Cords Daily Plants | Cords Daily |
|---|---|---|---|---|---|---|---|---|
| Michigan | 8 | .. | .. | 1032 | .. | .. | .. | .. |
| | .. | 5 | .. | .. | 1050 | .. | 13 | 2082 |
| Pennsylvania | 33 | .. | .. | 1424 | .. | .. | .. | .. |
| | .. | .. | 13 | .. | .. | 215 | 46 | 1639 |
| New York | 7 | .. | .. | 256 | .. | .. | .. | .. |
| | .. | .. | 17 | .. | .. | 362 | 24 | 618 |
| Wisconsin | 2 | .. | .. | 96 | .. | .. | .. | .. |
| | .. | 1 | (oven-kiln) | | 250 | .. | 3 | 346 |
| Kentucky | 1 | .. | .. | 20 | .. | .. | 1 | 20 |
| West Virginia | 1 | .. | .. | 49 | .. | .. | 1 | 49 |
| Tennessee | 1(a) | .. | .. | 32 | .. | .. | 1 | 32 |
| Vermont | .. | .. | 1 | .. | .. | 16 | 1 | 16 |
| Total in U. S. | 53 | 6 | 31 | 2909 | 1300 | 593 | 90 | 4802 |
| Canada | 9 | .. | .. | 424 | .. | .. | .. | .. |
| | .. | .. | 1 | .. | .. | 48 | 10 | 472 |
| Total in America | 62 | 6 | 32 | 3333 | 1300 | 641 | 100 | 5274 |

(a) A recently constructed 16-cord retort plant now being converted into an oven plant.

These figures will mean more if we remember that 5,000 cords of wood represent a pile 4 ft. high 52 in. wide and 7.5 miles long weighing when seasoned approximately 10,000 tons, thus showing the importance and size of the industry in this country.

### CONCLUSION

It will be evident that the chief economic drawback in the present manufacture is the fact that most of the plants do not manufacture the finished products; thus in general it may be inferred that two sets of freight charges, commissions and handling expenses are required before the products reach the consumer. For instance, with acetate of lime at $2.00 the net return to the producer is about $1.75 per hundred. A large part of this difference could easily be saved by manufacturing the finished product at the crude plants.

Hitherto such combinations of crude and finished product manufacture have been thwarted in the majority of cases by an almost complete monopoly of the finished products by certain groups of chemical manufacturers, who by various manipulations maintained control of markets, or who were able to dominate the situation, as in the case of acetic acid, by their regional control of sulfuric acid manufacture, or even attempted control of pyrites importation. The violent market fights which have developed because of these facts have been carried through successfully in more than one instance by the crude manufacturer, because of his advantageous situation, and it is certain that these attempts, therefore, to thwart the natural economic development of this industry will sooner or later collapse to a great extent, or the refiner will be compelled to either go into the crude business himself or combine with the crude manufacturer.

We have attempted to show the difficulties met and the expensive experimentation that has been undertaken in the past for the improvement of this industry, and have pointed out some of the results thus obtained. When it is remembered that German statistics claim that but one of 15 serious trials of new chemical processes are successful and that this percentage amply pays for the losses entailed in the 14 unsuccessful ones, it can be seen that while these expenditures are individually unfortunate, in the aggregate this law of averages will probably hold good in the development of this industry, for its economic position demands the solution of the problems indicated.

COLUMBUS, OHIO

## DISCUSSION

By H. O. CHUTE

I am sure the thanks of the Institute are due Messrs. French and Withrow for this contribution to the history and present status in the U. S. of wood distillation and the presentation of the large number of illustrations showing actual present working plants.

While much has been previously published on this subject it has in most cases been by those familiar only with the European situation or who had been consulting European works of the subject.

It is a singular fact that most of the places named as sites of the first works still have working plants and the people and firms then engaged are still in the business. This indicates that the location of a wood distillating plant is not a temporary affair but that the wood supply usually lasts for a generation.

While the statement is true that the carbonization is an exothermic reaction yet the phenomenon is not observed unless the wood is fairly dry, *i. e.*, with from 15 to 20 per cent water. With excess of water the heat disengaged is not sufficient to evaporate the water so there is no progressive action toward the center of the retort except as produced by the fire, and the transmission of heat to the center of the retort from the walls is difficult. This shows the necessity of having dry wood for successful work. Owing to this exothermic reaction the control of the temperature inside the retort by any method of heat insulation or surrounding thermal baths is foredoomed to failure.

While the first operators brought over the Scotch methods yet later arrivals including Burcey, brought over the French methods as then and now practiced. The Burcey pans are merely the French Pistorius pans used in the rectification of grain alcohol and the Otto plant of vertical retorts located at Sargeant near Dahoga, Pa., which has been described, was built by Burcey on the French system. These worked successfully for many years though they were never duplicated in this country.

It must be remembered that wood distillation in the U. S. has developed along two different lines. The charcoal iron industry was introduced at a very early period, in fact shortly after the settlement of the first colonists and this necessitated a supply of charcoal. No attempts to save any of the by-products were tried or accomplished till Dr. Pierce introduced his system of sucking off the smoke or vapors from the kilns with a fan and recovering the alcohol and acetate from them by condensation. With the large amount of charcoal necessary to supply the furnaces and with wood plentiful and labor scarce it became advisable to use kilns; these can use green wood and wood in the form of logs and quite rough, while the retorts required the wood to be carefully cut and split to a six-inch face and dried for about a year.

It is erroneous to state that a portion of the wood is burned in the kilns to support combustion as it is the gas which is evolved that is burned. This may be observed in an ordinary grate fire as the flame comes from the gas while the wood is not consumed till charcoal is formed which gives a flameless combustion. The Pierce system originally contemplated the forcing of the gas back into the kilns after condensation but it was soon found that the gas could not be circulated indefinitely, so that now the kiln is heated entirely by starting a fire inside it and admitting a regulated amount of air to burn a part of the evolved gases so as to generate the balance. For this reason the by-products are partially burned.

It may be said for the kiln process that while it produces only about one-half the amount of by-products it produces an equal quantity of charcoal and it produces more dollars in profits per dollar of investment than the retort process. It has been said that the western works do not produce a corresponding amount of acetate compared with the alcohol, but they do not distil the tar nor the acid as thoroughly as do the eastern works.

The original installation for sawdust carbonization at Cincinnati consisted of tall vertical narrow retorts much like those used for bone char work and with revolving cones inside attached to a central pipe perforated to allow the escape of the gases evolved. These were led out at the bottom but the outlet was soon closed with tar and charcoal dust. The idea of taking the gases out at the top never seemed to occur to the operators.

If any system of conveyors for carbonizing the sawdust was used it must have been well toward the end of the work. This installation was made at a cost of about $125,000 by one who had worked on the problem in Canada for a number of years and spent much money there. Every condition was favorable as the sawdust was from kiln-dried lumber, but the project was an absolute failure and should serve as a warning.

Shortly after 1900 the retort process was established in the west in connection with the sawmills. These sawmills working on hardwood will furnish about a cord of wood from the slabs and rough logs for every 1000 ft. of lumber sawed and the sawdust and offal will furnish enough fuel for the retorts and chemical works. When wood distillation is thus carried on as a by-product of lumbering operations it is evident that the cord wood will not cost $5.00 per cord nor the fuel $1.15 per cord, and these combination plants will therefore probably survive in the struggle for existence. The extreme conservatism of those connected with this industry is shown by the fact that nearly all the plants now use practically the same apparatus and methods that were introduced by the foreigners who first came over. The small round retort has, however, been superseded by the oven, those holding about ten cords each being most popular at present. These ovens are so built that the wood is handled in two-cord cars and the cars are usually handled by a locomotive in large works. The charcoal is also handled and cooled on the same cars and there is little breakage. Some improvement has been made in the west in the method of treating the liquors for alcohol and acetate. In 1905 a process was introduced for making alcohol by distilling the crude liquor in a continuous column still producing alcohol of 25 per cent strength from acid containing 2 per cent. On standing, the oils separated from this weak alcohol and an excess of alkali was then added which polymerized aldehydes and ketones. With another distillation through a similar continuous still it was possible to produce 85 per cent alcohol perfectly miscible with water. In 1906 a multiple effect evaporator was installed which was operated with exhaust steam from the blowing engine of the blast furnace and the acid was distilled in one vessel to purify it, then neutralized and run into the other for concentration; the heat of the condensing acid vapors furnished heat to evaporate the acetate solution.

These installations were made at Ashland, Wis., and the processes were covered by patents Nos. 824,906 and 835,501; shortly thereafter nearly all the kiln plants adopted the above method for producing alcohol and a number of them have also adopted the multiple effect process for handling the acetate. Of late years several modifications of these processes have been introduced but they have not yet operated a sufficient length of time to prove their worth.

It is a singular fact that although wood alcohol is always distilled over alkali, yet the ethyl acetate is only slightly decomposed as the so-called "acetone alcohol" or "methyl acetone" from the heads of the runnings will contain about 40 per cent acetone, 40 per cent methyl acetate and 20 per cent alcohol with specific gravity corresponding to 82 per cent alcohol and a boiling point of 55.5° C. The presence of alcohol acts as a protective solvent.

In conclusion, it may be remarked that the American industry has reached a high state of perfection in the mechanical handling of materials and economical machinery. The production of wood alcohol and acetate has reached a state where more cannot be economically produced from a cord of wood. The quality of refined alcohol on the market is satisfactory and the highly refined grades are nearly C.P. The manufacture of such secondary products as acetone, formaldehyde and acetic acid is carried on successfully at some wood distillation plants.

The manufacture of formaldehyde has proved successful at some places. The manufacture of acetone should logically be at the works, thus saving freight as 5 lbs. of acetate are required for making a pound of acetone. Chemical engineering sometimes consists largely in the study of freight rates. The manufacture of acetic acid has been attempted at a number of works and abandoned though at least one plant still makes large quantities.

Acetate of lime is perhaps the most convenient method of shipping acetic acid and the manufacture nearer the market seems more logical.

The only product which is wasted is the tar. About 30,000,000 gallons of wood tar are burned under boilers every year to get rid of it. Its utilization holds out as much promise as the utilization of coal tar, but with the exception of some light oils which are used in dissolving nitrocellulose there are no valuable products made. Yet we import nearly two-thirds of the creosoting oils we use for timber preservation and as it is probable that the wood creosotes are as valuable as the coal tar creosotes for this purpose, we may hope that this industry will soon develop.

197 Pearl Street, New York City

## INDUSTRIAL USES OF HYDROFLUORIC ACID[1]

By K. F. Stahl

The larger works on Chemical Technology[2] give the following uses for hydrofluoric acid:[3]

1—Liquid or gaseous hydrogen fluoride is used for etching glass. The liquid acid leaves a smooth transparent surface, while the gas leaves a rough opaque surface.

2—Hydrofluoric acid in connection with fluorides of the alkalies and some other additions, such as acetic acid or sulfuric acid and others, are used for frosting glass. For this purpose there is in general use a solution of acid ammonium fluoride in hydrofluoric acid. This has the trade name of "White Acid" and contains about 32 per cent $NH_4FHF$ and 20 per cent HF. It works very quickly, *e. g.*, the frosting of electric bulbs requires only about a minute.

[1] Presented before the Pittsburgh Section of the American Chemical Society, October 15, 1914.

[2] Dammer, Molinari, Ed. Thorpe and Henri Moissan

[3] It is generally known that hydrofluoric acid produces very painful inflammation if allowed to come in contact with the skin. The remedy usually recommended is washing with water and then with dilute ammonia water. This is effective only with weak acids; with stronger acids, particularly the 60 per cent, washing alone, even if done immediately, does not prevent inflammation, but if the washing is continued for about half an hour by holding the affected part under flowing water the bad effects will be prevented or at least materially reduced. Washing must, of course, begin at once after the acid has come in contact with the skin. Very dilute acid, *i. e.*, up to 5 per cent, produces no ill effect by temporary contact with the skin.

3—In the manufacture of spirits from cereals to retard the development of certain bacteria. The yeast is gradually rendered immune to the effects of the acid or its salts, so that the yeast itself is not harmed, but the bacteria which cause the formation of lactic or butyric acid are killed; thus a purer product and a larger yield are obtained. Very small amounts of hydrogen fluoride are sufficient. Effront, who worked out this process, recommends from 5 to 10 g. hydrogen fluoride per 100 liters of mash. It is not used in the manufacture of whisky, as it is feared that it may have an influence on the flavor. This seems to be well founded, as the flavor of whisky is at least partly due to ethers of the fatty acids.

Ammonium fluoride is, however, used in the fermentation industry to sterilize vessels and rubber hose. But these are always carefully washed with water before they are used again.

4—For the preparation of hydrofluosilicic acid and its salts. (Moissan.)

5—To remove alkalies from the juice of sugar beets. (Thorpe.) This is probably only a proposal and it is not likely that it has ever been carried out on a large scale.

6—To remove silica and silicates from ground anthracite to be used for the manufacture of artificial coal for electrical purposes. This process was carried out for some time on a large scale by F. v. Hardtmuth,[1] but was finally abandoned again as too expensive.

7—To purify crude graphite.

8—For treating earthenware vessels to render them more porous.

The last two uses are mentioned by Prof. Prior[2] in 1903, but I could not find any details in the literature.

9—In dyeing, the antimony acid fluoride[3] is used as a substitute for tartar emetic.

10—To remove substances which have been added to silk to make it appear heavier. (Dammer.)

This process is probably used only in the laboratory in the examination of silk fabrics.

11—In the laboratory, to dissolve and to remove either free or combined silicic acid.

12—To clean sand from cast iron and to remove obstructions from natural gas or oil wells.

I have not learned how much the last named use of hydrofluoric acid is practiced.

These last two uses are apparently not practiced in Europe. They are mentioned in some of the works on chemical technology, but these all refer to an article published by myself[4] in 1896.

To those uses which have been made known through different publications, the following four, which as far as I know have not been published but are in use in the United States, can be added:

### I—CLEANING CASTINGS AND STEEL PIPES

Besides for cleaning cast iron, the acid is also used in large quantities either alone or mixed with sulfuric acid to clean steel pipes to be used to enclose electrical conduit wires. It is also very useful for cleaning brass and similar castings.

The particular advantage over other methods for the same purpose are: 1—This acid dissolves the sand direct, while other acids only loosen it and cause it to drop off by dissolving the metal underneath. Hydrofluoric acid also dissolves the magnetic iron oxide ($Fe_3O_4$) more readily than sulfuric acid or hydrochloric acid. 2—Hydrofluoric acid leaves a cleaner surface and does not penetrate into the castings as other acids seem to do. If castings which have been cleaned with sulfuric or muriatic acid are well washed and dried and afterwards covered with metal or lacquer, it happens quite often that the latter are injured by excrescences starting from the metal.

In cleaning pipes for electrical conduits only the inner side is of importance; it must be perfectly smooth, so as not to injure the covered wires when they are pulled through. On the inside of metal pipes there are patches of melted slag. These can be removed with sulfuric or muriatic acid only by losing considerable metal. This slag, being a silicate, and the magnetic iron oxide, are dissolved directly by the hydrofluoric acid. Frequently a mixture of sulfuric and hydrofluoric acids is used for cleaning such pipe.

Cast steel can rarely be cleaned to advantage with hydrofluoric acid, because the loom used for moulds is baked very hard and dissolves very slowly in hydrofluoric acid.

Castings and pipe are cleaned in the following manner: The acid is used in varying strengths, according to the condition of the material to be cleaned and the available time. One part 30 per cent hydrofluoric acid is mixed with 4 to 40 parts of water, which gives a solution containing 6.0 to 0.7 per cent hydrofluoric acid. The weaker acid is preferable if enough vessels are on hand to leave the castings in the acid pickle sufficiently long. It requires about 12 hrs. to clean castings with 1 per cent acid. Comparatively more acid is required if stronger acid is used, but the time of cleaning is reduced.

Round or square wooden tanks without any protective covering are generally used. For economy in handling small castings they should be placed in a second wooden vessel perforated on the sides and slightly smaller than the first one. This has the advantage that the sand which falls off remains on the floor of the inner vessel, is lifted out with it and is thus removed from further action of the acid. The inner vessel together with the castings can be dipped directly in the wash water.

Heating accelerates the action of the acid bath, which can be used repeatedly if for every fresh batch of castings about $^1/_3$ of the amount of acid originally used is added.

If the castings are to remain bright they should be washed with hot water as soon as they come out of the acid pickle, so that they dry off quickly; otherwise they can be washed with cold water. To the last wash water some milk of lime is usually added to prevent rusting.

### II—POLISHING CUT GLASS

Under the published uses of hydrofluoric acid, the one for etching glass was mentioned first; but it is very strange indeed that the use of strong hydrofluoric acid for *polishing cut glass*, which has been in practice here for a number of years, is nowhere mentioned. It started about 18 years ago and is at present probably in use in all of the cut glass factories in this country of which there are quite a number and some of them rather extensive. At first some manufacturers claimed that glass treated by the old process had a better polish. They were soon convinced, however, that cut glass polished with acid had a finer luster and sharper edges.

The last operation in manufacturing cut glass is the polishing of the surfaces which have previously been cut into the glass. This was formerly done with oxide of iron or oxide of tin. As every plane had to be polished separately by skilled labor it was slow and expensive work.

A finer polish is now obtained in the following manner: For vases and similar shapes, where the polish is required only on the outside, a wooden stopper is cemented in water-tight with paraffin or wax. Other surfaces which are not to be touched by the acid are also covered with asphaltum, wax or some similar substance. It is essential that all surfaces to be polished must be absolutely clean, and especially free of every trace of grease. To accomplish this, they are brushed with soda solution by girls who wear rubber gloves, then they are washed in clean water and after most of the water has dripped off they are dipped in the acid bath.

Generally a mixture of one part by weight of sulfuric acid, 66° Bé., with three parts 60 per cent hydrofluoric acid is employed. This mixture is in a lead vessel, large enough to sub-

[1] "Zeller die künstlichen Kohlen," Berlin, 1903.
[2] *Z. angew. Chemie*, **1903**, p. 195.
[3] Dammer, **1**, 371.
[4] *Z. angew. Chem.*, **1896**, p. 225.

merge the largest pieces to be polished. It is placed directly in front of a ventilating tube, through which a ventilator creates a strong suction. This protects the polisher from the strong vapor given off by the acid mixture and he needs only a rubber apron and long rubber gloves for his protection. The perfectly clean and partly dried off pieces of glassware are held one at a time from $^1/_2$ to 1 minute in the acid, and then immediately dipped into water.

By the action of the acid on the glass a thin crust is formed consisting of calcium fluoride, probably with some sulfate of lead and sodium or potassium fluoride. This is removed by brushing with water, after which the pieces are washed off in clean water and dipped again in the acid. The polish is usually complete after three dippings. Every piece is carefully inspected and defective spots are polished by hand; if the grinding was carefully done, this is rarely necessary.

Experiments undertaken to polish plate glass in the manner described did not produce satisfactory results. The surface obtained was glossy, but in place of being perfectly smooth, as is the case with cut glass, it was somewhat wavy. This difference may be caused by the materially different composition of the two glasses or by the different manner of production.

III CLEANING BUILDINGS IN INDUSTRIAL DISTRICTS

Buildings and monuments, particularly in industrial districts, obtain in course of time a dark color. This can be removed and the original color restored with hydrofluoric acid better and cheaper than in any other way; 15 per cent acid is generally used (30 per cent is diluted with the same volume of water). The workman wears rubber gloves and proceeds as follows: Two or three sq. ft. of the surface are first moistened with a brush or sponge, then painted with the 15 per cent acid (for large surfaces a whitewash brush can be used). After a minute or two the surface is scrubbed with a stiff brush and rinsed with water. The action on granite or sandstone is negligible; marble is acted on a little more and it is advisable to protect polished surfaces, as they are apt to get dull.

This process has been in use in the Pittsburgh district for about 15 years for monuments in cemeteries and for buildings, which can be made to look like new with very little expense.

IV—CLEANING ROOFS OF GREENHOUSES

The glass roofs of greenhouses are cleaned in a similar manner. During the summer these are usually whitewashed to moderate the rays of the sun. This protective covering, on which also accumulates some dust and soot during the summer, has to be removed in the fall, as during the winter all the sunlight obtainable is needed. This is done by painting the surface of the glass with 15 per cent hydrofluoric acid, using a 6 to 8 in. whitewash brush fastened on a long pole. After a few minutes, when about eight rows have been painted, the acid is washed off with water. In this manner the glass is made as clear and transparent as new, much better than was formerly possible with muriatic or oxalic acid.

If the houses are old and the panes of glass not absolutely tight, the glass in those houses where ferns, smilax and asparagus are raised should be cleaned before the plants are set out, because they sometimes get yellow spots from the fumes of the acid, which penetrate through the crevices even though the fumes are not perceptible to human beings. Other plants are less sensitive and show no ill effects.

None of the four processes described above has been patented, which is very remarkable, particularly in this country where an endless number of valueless processes are protected by patents.

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## THE NEED OF REVISED CHEMICAL STATISTICS[1]

By Bernhard C. Hesse

The information imparted by statistics is of two kinds. The first deals with domestic production and the second with international exchange of commodities.

[1] Presented at the 7th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 2–5, 1914.

The difficulty at the outset is the definition of what should appear in chemical statistics. The classification in Schedule A of our Tariff is one way of settling the question; the classification of our Census Reports is another method but what of those products on the Free List in our Tariff that are undoubtedly of interest to chemists and to chemical industries, and what of those other products and industries contained on our Census Reports dealing with industries other than those classed as chemical? The classification adopted by the Germans as illustrated by the reports in the *Chemiker Zeitung*, **1914**, p. 169, and that contained in the Monthly Summary of the Foreign Commerce of the United States, as published by the Department of Commerce, are still other methods of treatment.

Those who compile all our statistics are confronted with the responsibility of completing their task and they have, no doubt, done it very well and in the light of the very best information they can get. If there be any shortcomings affecting us in those statistics we can surely look to ourselves as the cause, in that we have not taken proper steps to designate the kinds of materials which we consider necessary for our commercial and industrial information. Also, in making any requests for changes in those statistics, we must be prepared to give heed to the requirements of others.

It is probably true that none of our present methods of handling our statistics comes so near to satisfying the needs of American chemists and chemical manufacturers as would that adopted by the Germans, and yet their classification would not fully meet our requirements.

Our international statistics, in order more nearly to be of substantial service to the chemical interests of this country, need revision but just what that revision should be I frankly confess I do not know. Neither do I believe that any other *one* man knows but I believe that we all agree that they do not fulfill the purpose.

That being the case, the question first to be considered is the remedy. I suggest that the American Institute of Chemical Engineers take the initiative and with the coöperation of all other chemical organizations in the United States ascertain what articles should be specifically enumerated in our import and export statistics; all organization and trade publications should be invited to participate, and care should be taken that every possible interest, both geographical and industrial, is provided for in such an attempt to get the sense of the chemical industry of this country. As a first approximation of such articles, it might be well to take up those that are specifically enumerated in the Tariff and then to take up those that are enumerated by class or sub-class therein. Care will have to be exercised that on the one hand the classification is not too minutely divided so as to make the work burdensome to the Federal Government and without real clarity to those who use the results, and on the other hand, that the classification be not so broad that the user cannot tell with reasonable accuracy what articles are really included in such classifications. No doubt, the German classification will be an excellent guide, but, in making the final list, the statistical data of other countries, such as Great Britain, France and Austria, should be consulted.

The advantage to be gained by such segregation would be to bring to the attention of domestic chemical manufacturers new domestic needs of chemicals supplied from foreign sources, long before such foreign sources have become successfully entrenched in the business in this country. Such things have happened and they may happen again; the way to prevent their recurrence is something of the kind just suggested.

While it is true that in many of our trade journals such information is published in each issue, yet it is unclassified and not arranged so as to be easy of inspection. Indeed, it would be asking altogether too much to expect our publications to do such

work; they publish the news and each individual should dig out his own information.

However, the Federal Government, with its large equipment, can more easily tabulate and classify such material, and print and distribute it better, quicker and cheaper than can any other available agency. It is not to be expected that this additional labor should be performed by the Federal Government without recompense. Probably a moderate subscription fee would be sufficient to cover this added expense and doubtless there would be enough subscribers to such a special compilation to prevent its being a source of serious loss to the Government.

The compilation of import and export statistics is a large task, and changes in it should not be undertaken without thorough consideration. Before requesting any such changes we ourselves should undergo every reasonable labor to ascertain what will better answer our requirements, carefully examine those suggestions and test and re-test them to see that we have made no error, and then submit them to those in charge of the statistical work. Suggestions made after such thorough study will no doubt receive correspondingly serious consideration; without some such serious, thoughtful and well-planned suggestion it is not to be expected that the Federal Government will change its present mode of handling the matter.

What has been said of import and export statistics is true of our production statistics, *i. e.*, our Census Reports, and any changes that we may have to suggest in them should be just as thoroughly and thoughtfully prepared, tested and examined as those in the export and import division.

The need of a change is apparent; just what that change shall be requires the most thoroughgoing coöperation of as many chemists and chemical manufacturers in this country as can possibly be induced to coöperate; the initiation of a work of such magnitude is not to be taken up lightly but should be carefully studied, and if positive action be decided upon, all who partake in it must be prepared to sacrifice much time, much thought and much labor.

90 William Street, New York City

# THE WAR AND OUR CHEMICAL INDUSTRIES[1]

The Northeastern Section of the American Chemical Society devoted its first regular meeting of the 1914–1915 season, on October 16th, at the Engineers' Club, Boston, to a symposium on "The Effect of the European War on the Chemical Industries of the United States." The speakers were as follows:

J. Russel Marble, of J. Russel Marble & Co., Worcester, *President of the Section*.

W. H. Bowker, American Agricultural Chemical Co., Boston.

W. D. Livermore, American Woolen Co., Lawrence.

C. A. West, of the Eastern Drug Company, Boston.

C. H. White, Professor of Metallurgy, Harvard University.

H. J. Wheeler, American Agricultural Chemical Co., Boston.

## THE HEAVY CHEMICALS

By J. Russel Marble

Members of the Section:

Our topic is one which is of universal interest and your Executive Committee thought it might be wise for the Section to spend an evening discussing the effect of the European war upon the chemical industry of the United States.

My knowledge of the chemical industries of the United States is confined chiefly to what is known to the trade as "Heavy Chemicals," that is, Soda Ash, Caustic Soda and Bleaching Powder. The Section knows the theory, and the process of manufacture, and the history of the success of this American enterprise much better than I do. The successful introduction into this country of the Solvay Process, some years ago, for treating salt, and the later process for the decomposition of salt by electricity, has practically driven from the American market the importations of most forms of soda and bleaching powder.

If the reports of the destruction of property abroad are anywhere near correct, it must be a fact that the enormous soda plant of the Solvay Brothers in Belgium has been destroyed. It is impossible for France or Germany to export any of these materials, and the English plants are reported to be running at only about one-half of their capacities because the employees have left for the army

Fortunately for this country, we have enormous deposits of salt, chiefly located in Northern New York State, under the city of Detroit, Michigan, and in Kansas and Louisiana, and we have immense water powers from which electricity can be generated.

The manufacture of various forms of soda has been especially successful in this country during the last twenty years, and the effect of the European war, in my judgment, will call for very large shipments of these chemicals to the Mediterranean, Australia, South Africa and South America, and should lead to the running of the plants in this country to their fullest capacity, so that the immediate effect of the war on the heavy chemical industry will undoubtedly lead to a larger output, and should lead to higher prices and a more profitable business for the American manufacturer.

J. Russel Marble and Company
Worcester

## THE AGRICULTURAL INDUSTRIES

By W. H. Bowker

The European war affects the agricultural industries of this country in various ways, some for the better and some for the worse. It has improved our market for foodstuffs, but it has injured our market for many raw products, especially our crop of cotton, of which we export about 60 per cent to Europe.

I am asked to speak more particularly on the effect of the European war on the fertilizer industry. There are 7,000,000 tons of fertilizer consumed in this country annually, of which probably 5,000,000 are what are called complete fertilizers, that is, containing the three essential elements of plant nutrition—nitrogen, phosphorus and potash. Broadly speaking, plants consume these three essential ingredients in about the following proportions: 1 Phosphorus; 2 Nitrogen; 3 Potash. Thus potash is a very important element of plant food, and, therefore, of complete fertilizers.

Germany, at the present time, controls the sole commercial source of soluble potash. Until recently there have been no similar deposits discovered in the world. Lately, however, similar deposits have been discovered in Spain. If they prove to be as rich and as soluble and as accessible, and it is believed they are, they will compete with the German deposits.

The potash industry has been one of the most profitable in the world. It is said that muriate of potash, the standard grade (50 per cent $K_2O$), can be mined and delivered at the seaboard of this country for $15 a ton and show a handsome profit. I am told that it was stated in debate in the Reichstag in 1910 that the best mines in Germany could mine the mineral and refine it for about $8 a ton. The price in cargo lots is from $33 to $34 per ton delivered at seaboard. Through the German Kali Syndicate the production of the mines is limited by allotment and the price arbitrarily fixed. It is stated that there have

[1] We are indebted to Mr. Hermann C. Lythgoe, Treasurer of the Northeastern Section of the A. C. S., for the collection and transmission of the articles included in this symposium.

been more than a hundred well equipped mines, with a capacity equal to six times the world's consumption.[1]

The Government is largely interested in the mines, as are also the nobility, and ruling families of Germany. Thus they are able to limit the output and maintain prices. If need be they can pass laws to nullify contracts, as they did in 1910 when the American buyers had made contracts six months previous in good faith, at $20 a ton. Six months later these contracts were practically nullified by the Reichstag which passed an *ex post facto* law, imposing a surtax of $20 a ton. This we did not regard as fair. I doubt if it would have stood in an international court.

Broadly speaking, American agriculture can do without potash for a time. Little if any potash is used in the great Middle West where the cereals are grown. The great bulk of complete fertilizers is used in the middle and eastern Atlantic states on staple crops such as cotton, potatoes, corn, tobacco, fruits and vegetables. Where we have used fertilizers rich in potash in the eastern states, or where we are practicing intelligent rotation, also plowing in green crops, we can get along for a time with less potash, and in some cases with no potash, depending upon the amount which is left over in the soil, and also upon that which becomes available by weathering.

Prof. Charles D. Woods, Director of the Maine Experiment Station, has recently issued a statement to the effect that the potato soils of Maine, especially in Aroostook County, contain sufficient potential potash to produce an average of 300 bushels of potatoes a year for nearly a hundred years, estimating that a bushel of potatoes requires about one-third of a pound of potash. Through natural agencies a certain small percentage of the soil potash is rendered available every year; nevertheless to produce the great crops in Aroostook County they use from 100 to 200 pounds of potash ($K_2O$) to the acre. What is not required for the current potato crop is left in the soil for crops which follow in rotation, such as oats, mixed grasses and clover.

In the cereal belt of the Middle West they are growing cereals at the expense of the soil; thus in the wheat belt they produce on the average about 14 bushels of wheat to the acre as against 40 bushels in Germany; 100 bushels of potatoes as against 300 to 500 bushels to the acre in Germany, and 300 bushels in Aroostook County, Maine.

In my opinion the Germans are the best farmers in the world. One of my oldest friends and best teachers was a German chemist, the late Dr. Charles A. Goessmann, who for many years was the Director of the Massachusetts Experiment Station at Amherst. I have the greatest admiration for the German scientists. They are masters of whatever they undertake. They are specialized in the highest degree.

Speaking of the German farmers and German agriculture, do you realize that Germany produces 88 per cent of her foodstuffs? She, no doubt, was well provisioned for this war, and since the women and children largely carry on the actual farm operations in Germany, she will no doubt be able to produce 80 to 90 per cent of her foodstuffs the coming year. Moreover, she has a great asset in her soil. She believes in making a fertile soil still more fertile. A fertile soil in Germany is not one which will produce crops without added fertility, but one to which they add more fertility and still more and by good seed and very thorough culture they are enabled to raise three and four times as much per acre as we do in the United States. The only farmers in America who follow the German system are the market gardeners around our great cities. They keep enriching their soils and thus they are able to produce large crops in normal seasons, and in abnormal seasons their crops are less injured by drouth, plant diseases and pests, for a well-fed crop like a well-fed man will better withstand abnormal conditions.

According to statistics published by the Department of the Interior, United States Geological Survey, Summary for 1913, pages 103 and 104, we imported into this country potash salts for that year as follows:

| | | Equivalent net tons $K_2O$ | Basis Per cent |
|---|---|---|---|
| Kainit | 465,336 long tons of *2240 lbs.* | 62,541 | 12 |
| Manure salts | 223,687 long tons of *2240 lbs.* | 50,106 | 20 |
| Chloride of potash | 475,261,595 lbs. | 118,815 | 50 |
| Sulfate of potash | 88,698,193 lbs. | 21,288 | 48 |
| | **Total,** | 252,750 | |

This is equivalent to 505,500 tons of muriate of potash, the standard grade imported; of this it is estimated that from 280,000 to 300,000 tons are used in fertilizers. The remainder is used in the arts, but more particularly in the manufacture of black powder.

Will Germany let out her potash in time of war? If she dared to do it she undoubtedly would, because it is a great source of income, but, as you chemists know, potash is the basis of many explosives and as it might fall into the hands of her enemies and be used against her she is likely to place an embargo on it; but as soon as the war is over it will come forward freely.[1]

Have we any sources of potash in this country that are worth considering at this time? As I have stated, our annual consumption of potash is about 500,000 tons. At Searles Lake, California, according to government estimates, there is a natural deposit equivalent to about 600,000 tons, or about one year's supply. A trial plant is about ready, having a capacity of about five tons daily or for 1915 say 1,500 tons. In Oklahoma there is a possible source of sulfate of potash; in Texas results seem to indicate the presence of potash about 2,200 feet below the surface. Alunite, yielding after treatment about 18 per cent sulfate of potash, exists in Utah, Colorado, Nevada and Arizona. The great source of potash in this part of the country is the feldspar and granite rocks of New England. Many of them, as you know, contain from eight to twelve per cent of potash, but as yet no commercial process has been perfected for rendering this potash quickly available to plants.

There is a great fortune awaiting the man who can invent a feasible and cheap process, but the potash must be rendered soluble in water, and it should be produced at a cost not exceeding $20 a ton (on the basis of muriate) laid down in the eastern markets, for if put to it the Germans could sell their potash at that price in this market, and even for less. So if any of you chemists have a process up your sleeve don't waste any time over it unless you can produce water-soluble potash to compete with the German source.

Now one word as to a substitute for potash. It has been claimed, and some experiments would seem to substantiate the claim, that certain crops, in the absence of potash, will substitute soda. These crops, however, are not the great staple crops like corn, potatoes, cotton, etc. Where this substitution has taken place, it has been with crops which belong to the root family. It is believed, however, that the use of available phosphates will help many crops to assimilate potash from the soil.

At a recent meeting at Mount Carmel Experiment Farm in Connecticut, Dr. Jenkins, Director of the Connecticut Experiment Station, spoke as follows:

"My opinion is that, in our general farm practice, it will pay

[1] Since the above statement was made there has appeared in the "Country Gentleman" of October 24, an article entitled "The Fertilizer Situation" in which Prof. H. A. Huston, who takes care of the Kali Propaganda for the eastern and southern states, is quoted as saying: "We have 190 mines, 40 of which would supply the world very nicely. We are prepared for almost any sort of emergency demand." The article also states "that the Syndicate is spending a million dollars a year in its world-wide campaign, about one-fourth of that sum in the United States, and any farmer who cares to study the statistics showing the enormously increased use of potash in American fertilizers during the past decade must be convinced that advertising pays."

[1] Since the above statement was made it is reported in the papers that Germany has raised the embargo on 1,000 tons *via* Rotterdam, in exchange for cotton.

better to use available phosphates more freely, and potash, in many cases, less freely than we are doing.

"I do not believe in the use of ground phosphates on our thin soils, deficient in humus, but let us stock up our land with available phosphates which we can get, in place of potash which we cannot get, and we may perhaps find a benefit to our farming from this 'war measure.'

"Do not understand me to argue against the need and the use of a liberal amount of potash in our fertilizers. I am merely stating my conviction that, on land where potash has been freely used in the past, a one year's lack of it will not seriously reduce the general crop production of the state, particularly if we will make increased use of available phosphate."

These, however, are technical questions which Dr. Wheeler, who is present and was formerly Director of the Rhode Island Experiment Station, is better able to discuss than I am.

In closing let me say there is no fear of American agriculture breaking down this year because we cannot get potash. There is no fear of its breaking down in the Middle West for some time, if we do not get potash; but the South and East, unless we have potash within two or three years, will be put to it to raise their staple crops. Let us hope that before that time arrives we shall have plenty of potash from other sources to compete with the great German deposits.

THE AMERICAN AGRICULTURAL CHEMICAL COMPANY
BOSTON

## THE TEXTILE INDUSTRY

By W. D. LIVERMORE

I cannot add anything to the knowledge of those present who are personally connected with the textile industry, but I shall try to speak in a general way, and in respect to the woolen or worsted industry only.

The first effect was felt in the fear of scarcity of money with resulting fear, cancellation of orders, trade failures, etc., which might even lead to shutdowns in the textile industry.

This phase, as the real situation developed quickly, passed and was followed immediately by some confidence that the business end of the textile industry in the woolen branch might not be injured at all by the war. About this time our anxieties regarding supplies that had usually been imported began to rise, and have not by any means been removed yet. This feature is, of course, the one that appeals most sharply to mill chemists, purchasing agents, etc. The chemist who had planned a nice vacation realized a chance to cancel it and an astonishing change of spirit came over us in our relations with our friends in the dyestuff business. We used to let them come to see us and were quite careful and even critical regarding just what brands of colors we could best use and what we ought to pay for them. In the twinkling of an eye we experienced an undreamed of change of heart.

The dealer whom we suspected of having a good stock of anything we thought we could use became dearer than a brother; we rushed out to see him about it, we wrote him and we called him frequently on the telephone and told him what a lot of business he had always done with us. And I may say that he treated us kindly—he didn't remind us of all the knocks we had given his colors in the past, and he had the opportunity of a lifetime to work off the second best colors he had had on hand for a nice long time. We took them gladly and besought him to find us some more.

Seriously, however, I suppose that the mills of this country are far more frightened than really hurt, but what the future holds we can hardly predict.

We hear very many stories of four and five times the normal price being paid freely for dyestuffs and chemicals and no doubt these stories have a basis of fact—nevertheless, I think they are largely comparable to the case of the wealthy party who pays $40.00 for a pair of $2.00 seats to the Yale-Harvard Football game. Undoubtedly he pays it, but he sits along with some 30,000 people who paid $2.00 each and who do not receive special mention in the newspapers.

If colors are going to come to us *via* Denmark, Holland and Italy, as we hope with considerable reason, we may be troubled with nothing worse than a moderate increase in cost and a necessity for carefully looking ahead and getting our supplies for a period further in advance than has been our custom, and for avoidance of exceptional dyestuffs which are not staple even in ordinary conditions.

The consumption of the United States is in the neighborhood of 15 per cent of the total production of dyestuffs in Germany.

If we can get from Germany 15 per cent of their normal annual production we can take care of ourselves quite comfortably. In support of a hope that we can do this it is easy to remember that Germany will not export any color or raw material for color in such a way that it can be obtained by the countries now hostile and that these countries include practically all the important textile producers outside Germany, Austria and Italy, and also that Austria and Germany are likely to be much too busy with the war to use their full normal amounts of color themselves. The normal stock of colors produced in advance of requirement will, therefore, last us quite a long time if we can get it over here.

As to present production in Germany I do not believe we have very reliable information. I have heard statements running from a present production of 40 per cent of normal in some places down to the closing of the factory and its use as a hospital in others.

It is also worth notice that those organic raw materials which can be converted into high explosives and other war material will be so used and wholly removed from consideration as far as our affairs go.

Some color will be obtainable from Switzerland. England, which usually furnishes a modest percentage of our supply, has practically dropped out of our market—they themselves need more than they have.

Should the worst happen and Germany be entirely closed to us by the course of war, some of the older wood colors like Logwood, Fustic and the Tannins will have a sustained boom. Whether these will be enough to go around will then be an interesting question, but I do not think we want to cross this bridge till we get to it.

As for the proposals for development of our own dyestuff manufactories I think something helpful will be done—but that it will in any very large way fill the gap I can see no great probability. It takes too large an investment, too much technical skill and experience, and even more important, too long a time.

As for the textile industry itself, and apart from this consideration of supplies, it is worth while to remember that no large amount of cloth is likely to be imported for some time—certainly not in the quantities which many of us feared as a result of the new tariff and in this way at least we ought to benefit.

For the first time in the experience of some of us we have heard talk of large orders of blankets and cloth, etc., from abroad. It may be talk only but at least it is very encouraging to those of us who think this means that we shall at any rate have the opportunity to supply our own people with their textiles for the present and that our severest competitors will be among our own manufacturers.

AMERICAN WOOLEN COMPANY
LAWRENCE, MASS.

## THE DRUG TRADE

By C. A. WEST

I wish to speak, not on the trade of dyestuffs or chemicals used in the textile industries, but more particularly on the chemicals used in the arts and in the manufacture of medicines, and I think the general opinion is that there never was such an op-

portunity for American chemists as presents itself at the present time. The fluctuations in the market during the last month have been greater than ever known before, and we are very much in the position described by Mr. Livermore—that of people willing to buy what medicines they can get.

You may be interested in a few items which I have jotted down. The normal price of benzoic acid is 22 cents per lb.; the price reached $1.25 and went up to $1.50. Carbolic acid which cost us 14 cents per lb., we could have replaced at 7 1/2 cents per lb. and we figured a loss of $20 a drum; we sold most of it for 40 to 50 cents per lb. Citric acid which was sold freely at 54 cents (at which we make an average profit of a cent a pound) went as high as $1.35 per lb. One of the large manufacturers came into our store and wanted five kegs of citric acid. We told him the price would be $1.25. Then he wanted to know how much we would charge him for 5 kegs more. We told him $1.30. Then he wanted to know how much we would charge him for 5 kegs more and we told him $1.35. For 5 kegs more, he inquired, and we told him $1.40. "Well," he said, "I guess we had better wait a little while and see what is doing."

Oxalic acid went from 7 1/4 to 22 cents, salicylic acid from 25 cents to $1.25, tartaric acid from 30 to 75 cents, arsenic from 2 3/4 to 6, nitrate of barium from 5 to 15, calomel from 60 to 90, camphor from 45 cents to $1.00, carbon tetrachloride from 7 to 15 cents, cream of tartar from 23 3/4 to 60, Epsom salts from 1 to 3, chlorate of potash from 7 1/2 to 25, potassium permanganate from 9 to 60, saltpeter from 4 1/2 to 12, quicksilver from $36 to $100 and back to $55, and oxide of zinc from 7 1/2 to 25 cents. So I might go on mentioning many others.

When I was in London the last of August I saw an order from the U. S. for Hydroquinone at $3.00 a pound, the price of which today is five times that. Such extreme prices, however, cannot be maintained for the simple reason that everybody in the country who had a surplus stock dumped it into Boston or New York for sale at the best price obtainable. But when you consider or stop to think of how this war is going to benefit American chemists I believe it will be a great gain if they only rise to the occasion.

EASTERN DEPT., COMPANY, BOSTON

## INFLUENCE OF THE EUROPEAN WAR ON THE METAL INDUSTRIES

By C. H. White

An inspection of the accompanying charts will show that at the outbreak of the war the prices of all the more important industrial metals rose, except pig-iron, copper, lead, and nickel.

Less than one-twentieth of our pig-iron is produced from imported ores. Of this about $4,000,000 worth comes from Cuba and half as much from Sweden. The war, therefore, can produce no shortage in ore; it creates almost no demand for iron; and, on the other hand, depresses business in general to such an extent that the demand for iron has grown less and less. The producers are unwilling to reduce the price to a figure lower than $14 per ton, the price at which it has been held for many months, and as the demand decreases, prefer to reduce the supply by blowing out their furnaces. Seven furnaces were put out of operation during September.

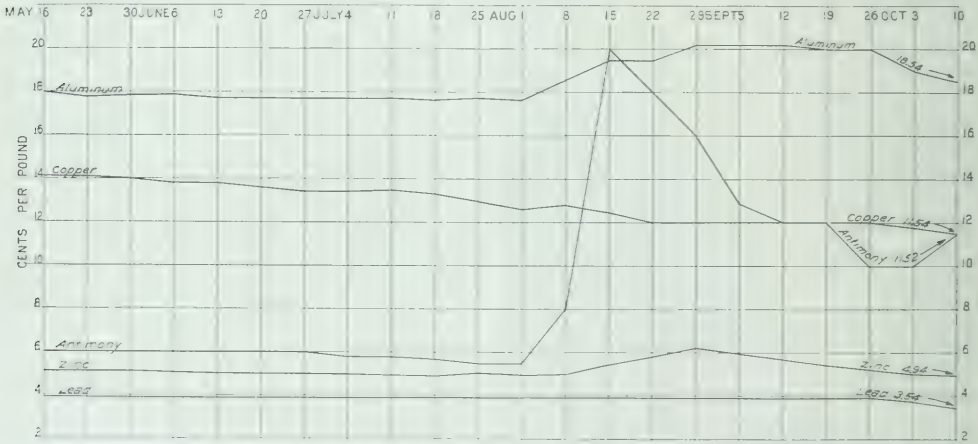
About half the copper produced in this country is exported; those countries now at war usually take most of our export The producers have been curtailing the output, but the reduction has not reached the point of holding up the price which can hardly go much lower than it is at present, 11 1/2 cents. A lower price would close many mines and this would so check production that the price would gradually go up again.

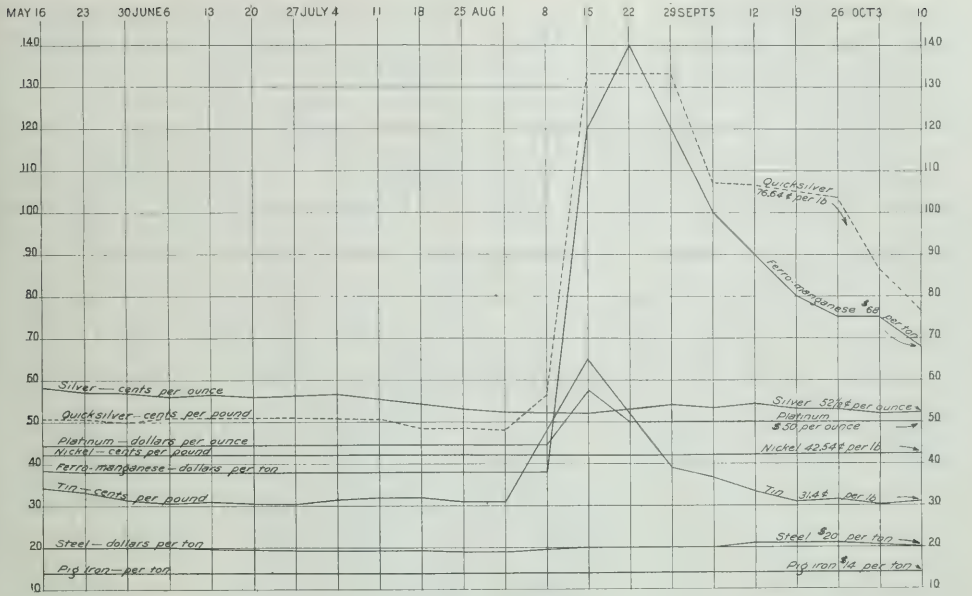
Our exports and imports of lead are about equally balanced. The imports come chiefly from Mexico, South America, and Canada. The war does not interfere with the imports and there is therefore a tendency towards the accumulation of lead, which has lowered the price from 3.9 cents, which it has maintained for many months, to 3.5 cents.

A considerable quantity of our nickel is derived from blister copper, but our chief supply comes from Canadian ores. About half the production is usually exported and the exports are no doubt seriously disturbed, but the International Nickel Company, having a monopoly, will probably maintain the price at 40 to 45 cents, which has held for a long time.

Of the metallic products which have risen in price, the most conspicuous is ferro-manganese. The price of ferro-manganese rose in two weeks after the first of August from $38 to $140 per ton. Ferro-manganese comes chiefly from England and Germany, and three-quarters of the ore from which we make ferro-manganese in this country comes from British India, Brazil, Russia, and Germany. The steel-makers were naturally afraid their supply would be cut off, and, therefore, bid up the price. This advance in the price of alloys used in steel-making, together with diminished business, increased the cost of steel. It advanced from $19 on August 1st to $21 on September 12th, but declined again to $20 on October 10th.

We are not dependent upon Germany for manganese. It was found also that certain cargoes of manganese ore from India consigned to Germany were diverted to the United States.






The price of ferro-manganese dropped in four weeks from $140 to $80, and was down last week to $68 per ton.

The war has created a demand for special forms of steel. England, I believe, has ordered 125,000 tons of sheet bars, the sheets to be used for winter barracks. The wire mills are running at 80 per cent capacity to supply barb wire for the foreign demand, and Russia, I understand, has bought all the wire cutters that could be found on the market in this country.

Our importation of tin amounts to more than $50,000,000 worth annually. The ore comes chiefly from the Malay States and Bolivia and the metal is reduced from its ores abroad. The fear of interruption of the supply put up the price from 31 cents to 65 cents per lb., but it gradually fell back to the former price of 31 cents when confidence was restored in England's supremacy at sea.

A long war should lead to the reduction of the ore in this country, especially the ores from Bolivia.

The price of zinc advanced in three weeks from 5 cents to $6^1/_4$ cents per lb., but has since declined to 4.9 cents. Because Belgium and Germany are large producers of zinc, a war involving those countries would naturally create a fear of scarcity of that metal. The United States, however, produces about as much as it consumes, and there is, therefore, no cause for alarm here. England's excess consumption over her production has been about equaled by Belgium's excess production over her consumption. It is probable that, if the war continues long, England will turn to us for zinc.

About one-third of the antimonial lead produced in this country comes in crude form from other countries. In addition to this, considerable quantities of type metal are imported. Under these conditions, war would naturally put up the price. The same is true of platinum and bismuth, which are scarcely produced in this country at all.

One-eighth of the aluminum ore treated in this country is imported, and about one-fifteenth of the metal produced is exported. We, therefore, consume a little more aluminum than our mines produce. The rise in price from about 18 cents to a little more than 20 cents per lb. indicates that there was fear of a slight shortage, but the price has recently fallen back to 18.5 cents.

We produce upwards of $1,000,000 worth of quicksilver, but to supply the demand for home consumption our imports have to exceed our exports by about $30,000 worth. The war created a demand for fulminate which put the price up from $36 to $100 per flask of 75 lbs., but, since the first scare has subsided, it has dropped again to about $60 a flask.

If the war is short, the metal industries should soon become normal again. If it is long, there will probably be still further curtailment in the production of iron and of steel, except in certain forms, and of copper and lead, but I think further declines in the prices will be small. In addition, if war continues we should expect an increase in the production of ferro-alloys and tin in this country.

Department of Metallurgy
Harvard University, Cambridge

## DISCUSSION

By H. J. Wheeler

In the course of Mr. Bowker's remarks, he mentioned the fact that "Little, if any, potash is used in the great Middle West where the cereals are grown."

In order to emphasize more fully the significance of this point I should call attention to the fact that it is but rarely that more than from 150 to 300 lbs. of fertilizer are used to the acre in the Middle West and Southwest for wheat and corn crops. The amount of potash in these goods usually ranges from 1 to 4 per cent, although 2 per cent would probably represent fully the average for those sections. This would mean that from 3 to 12 lbs. of potash is the usual amount applied to the acre, while the average application would probably be about 6 lbs.

It must be evident, therefore, that the soils of that section of the country contain enough available potash to produce quite

abundant crops, even without the aid of more. Most of that section of the United States is, however, greatly lacking in available phosphoric acid.

As is well known, gypsum is a prominent constituent of superphosphate. This is a substance which has a well-recognized liberating effect on the potash stored up naturally in the soil. On this account there is reason behind the suggestions which have occasionally appeared in the agricultural press to the effect that the use of more superphosphate would slightly lessen the need of potash. The superphosphate is also known to have a wonderfully stimulating effect on germination and the growth of young plants, and it aids greatly in hastening the maturity of the corn crop.

Mr. Bowker has mentioned the possibility of utilizing certain minerals for the manufacture of potash, and special attention has been called recently to phonolite, in particular, and to feldspar as sources of potash. In general the European experiments have not been favorable to phonolite as a direct source of potash, showing that it is greatly lacking in availability, and that it cannot compete successfully with the German potash salts.

Recently several processes have been patented for securing potash from feldspar, but it must be borne in mind that these all involve the mining and transportation of the product, grinding, fusion (generally), extraction, filtration, concentration, crystallization, and final grinding and bagging, a series of processes which, excepting under the most favorable conditions, are bound to make the potash so expensive that it can never compete with the products from the German mines at the price at which they can be sold in this country.

Experiments by Hartwell and Pember at the Rhode Island Experiment Station covering two seasons, and conducted under optimum conditions as far as the moisture content of the soil was concerned, failed to show any particular value of finely ground feldspar as a direct source of potash for plants, whereas the German potash salts gave excellent results. It should be stated that the feldspar which they used was ground so finely that all of it would pass a sieve having 200 meshes to the linear inch.

These results, therefore, utterly dissipate the faint hope of the direct economic utilization of feldspar for agricultural purposes which was held out by Cushman a few years ago.

Another point, touched upon by Mr. Bowker, was the possibility of the substitution of soda for potash in plant nutrition. In regard to this matter, it has been established beyond question by various investigators that soda cannot entirely replace the potash. Nevertheless, it is true that certain classes of plants will take up much more potash than they require, if it is present in readily available form and in excessive quantities. Under such conditions, if available soda is present, it is substituted for some of the potash with no apparent disadvantage to the plant, and at the same time the available potash of the soil is conserved.

The question of the effect of soda in connection with the growth of plants has been studied continuously at the Rhode Island Experiment Station from 1894 until the present time. Crops have been grown in the field, in pots, and also in solutions. In this last case the possibility of any indirect or liberating action of sodium salts on potassium compounds was eliminated.

The possibility of physical effects of the sodium salts which were in solution was also considered. As a result of these investigations, it was shown with cereals and other plants that whenever the supply of potash was insufficient, soda could partially take its place.

The time at disposal prevents the discussion in detail of the possible ways in which soda may act. It should, perhaps, be stated, nevertheless, that by supplying an abundance of all the essential elements but one, which is limited in amount, the minimum quantity of that one necessary to the production of a given amount of dry plant substance can be ascertained. When, however, the minimum amounts of all the necessary ingredients which are thus determined are added together, they are found to be insufficient to meet fully the needs of the plant. This extra quantity, above the sum of the minimum necessities, has been termed by the Germans as "Luxusconsum." In fact, it does not seem to matter very much whether this excess which is taken up is lime, magnesia, soda or potash. Soda, therefore, as stated before, exerts a conserving action upon the potash supply of the soil by thus aiding in satisfying this demand.

Soda also doubtless serves as a neutralizing agent to combine with the organic acids produced in the course of the synthesis of the protein compounds of plants.

It is true that sodium salts have been found to be particularly helpful to such crops as turnips, beets and radishes, although spinach and chicory do not seem to be able to make much use of it. It is probably of use in the growth of the cabbage, cauliflower and other related plants. In some instances in the Rhode Island experiments where as much as 40 lbs. of potash were applied to the acre for mangel wurzels, which is more than six times the average amount used for the cereals in the Middle West, it was found that the application of considerable quantities of either common salt or soda ash usually greatly increased or doubled the crops.

This question of the action of sodium salts has not only been studied by Hartwell, Pember, Brazeale and the speaker at the Rhode Island Agricultural Experiment Station, but it has also been studied extensively in Europe by Hellriegel, Wilfarth, Wimmer and their co-workers and successors at the Agricultural Experiment Station at Bernburg, Germany. Many of these results have been published in the "Hefts" of the "Deutsche Landwirtschafts-Gesellschaft."

Some exceedingly interesting results in the same line are reported by Wagner and Dorsch of the agricultural experiment station at Darmstadt, Germany. Smets and Schreiber in Belgium have also shown that sodium salts are of great benefit to plants under certain conditions of field culture.

In a tabulation ("Der Chillisalpeter") of the results of experiments in Europe with nitrate of soda and sulfate of ammonia, Stutzer has shown that for beets and certain root crops, nitrate of soda frequently gave better results than sulfate of ammonia, whereas the reverse was sometimes true in connection with cereals. This, therefore, coincides with the previous reference to the fact that the beet, turnip, radish, and a few related plants can make a greater use of soda than cereals, millet, and other similar plants.

THE AMERICAN AGRICULTURAL CHEMICAL COMPANY, BOSTON

# AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The Seventh Annual Meeting of the Institute was held in Philadelphia, December 2–5, 1914. The headquarters of the convention were at the Hotel Adelphia and the technical meetings were held in the large lecture hall of the Franklin Institute. The arrangements for the meeting were in charge of the local committee consisting of the members of the Institute residing in Philadelphia, with Dr. S. S. Sadtler as chairman. Great credit is due to this committee for the carefully prepared program of both papers and excursions, which insured for them the large attendance of delegates representing almost every industry and every industrial center.

The first business session convened at the Hotel Adelphia,

and the delegates were welcomed by Mr. W. C. Cattell on behalf of Mayor Blankenburg and the city administration. At the business session which followed, the results of the election of officers for the coming year were announced. Dr. George D. Rosengarten of Philadelphia was elected President. Dr. Rosengarten is a graduate of the University of Pennsylvania, class of 1890. Subsequent to graduation, he traveled extensively abroad and studied for his doctorate in Jena. In 1901 he became Vice-President of the firm of Rosengarten & Son, Inc., and took charge of the technical research and manufacture of the various products produced by that company. In 1905 he became Vice-President of the consolidated company of Powers, Weightman and Rosengarten.

Prof. John M. Stillman, of Los Angeles, was elected Vice-President; Dr. John C. Olsen, of New York City, Secretary; Dr. F. W. Frerichs, of St. Louis, Treasurer; and Prof. A. W. Smith, of Cleveland, Auditor; Thomas Griswold, George C. Adamson, J. B. F. Herreshoff and Samuel P. Sadtler were elected Directors.

After the election of officers the business session was devoted to the presentation and discussion of the reports of the officers and the various standing committees.

SOCIAL FEATURES

The Institute banquet, the principal social feature of the meeting, was held in the Green Room of the Hotel Adelphia. Dr. Chas. F. McKenna presided as toastmaster. Mr. W. C. Cattell responded to the toast of the City of Philadelphia, and gave a most charming and instructive talk on the influence of Philadelphia as an industrial center. Mr. M. C. Whitaker, Retiring President, spoke on our industrial outlook and the responsibilities of the Chemical Engineer to avail himself of the opportunities which are presented by the foreign complications. Dr. George D. Rosengarten, the President-elect of the Institute, spoke of the plans for the coming year. and referred especially to the coming semi-annual meeting, which is to be held in San Francisco in conjunction with the other chemical and engineering societies. Dr. Rosengarten was followed by Dr. Wm. H. Bower, First Vice-President of the Henry Bower Chemical Company, who spoke appreciatively of the work of Dr. Rosengarten, and the future prosperity of the Institute. Prof. A. W. Smith, Director of the Chemical Laboratory of Case School of Applied Science, Cleveland, spoke for the western delegation, and extended a cordial invitation to the Institute to hold its next annual meeting in Cleveland, and Dr. H. S. Miner, Chief Chemist of the Welsbach Company, spoke encouragingly of the activity of the American Chemical Engineers in meeting the great problems forced upon us by the European crisis.

DR. GEORGE D. ROSENGARTEN, PRESIDENT-ELECT, AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

PAPERS

**The Manufacture and Application of the Artificial Zeolites in Water Softening.** By D. D. JACKSON. The speaker discussed the scientific principles involved in the operation of the artificial zeolites in the reversible reactions utilized for the removal of insoluble-soap-forming substances from water to be used for industrial purposes. The process of manufacture of the artificial zeolites was fully explained and illustrated by experiments. Cobalt and manganese zeolites, which have been developed for certain catalytic operations such as the oxidation and removal of chlorine from certain sterilized waters, were discussed. The speaker illustrated with lantern slides the arrangement and equipment of the recently completed American plant for manufacturing artificial zeolites and showed samples of the products at the various stages of the manufacturing process. This was followed by illustrations of working installations of the filtration plants and quantitative figures were presented showing operation results, costs, etc. The paper proved to be of great interest to the members and brought out considerable discussion.

**Feldspar as a Possible Source of American Potash.** By ALLERTON S. CUSHMAN AND GEORGE W. COGGESHALL. This paper was presented by Dr. Cushman and embodied a discussion of the various problems—scientific, commercial, political and international—involved in the production of potash from the large feldspar deposits of the Atlantic states. Considerable discussion followed.

**Distribution of Industrial Opportunities.** By GEORGE OTIS SMITH, Director of the United States Geological Survey. Director Smith presented the principal address of the Philadelphia meeting. He optimistically indicated the direction for industrial development in America, and referred to many of the great problems of natural development which now await the attention of American Chemical Engineers. This address is herewith printed in full.

**The Chemical Industries of Japan.** By JOKICHI TAKAMINE. Dr. Takamine has recently returned from a trip to Japan and gave the institute a résumé of his observations of the chemical industries of that country. His lecture was amply illustrated with lantern slides and conveyed a clear and instructive impression of the industrial problems of Japan and the skill and thoroughness with which they are being developed. At the conclusion of his formal talk, Dr. Takamine was induced to show a number of colored slides illustrating the beautiful landscapes and many of the domestic and social customs and conditions of Japan.

**Hydrometallurgical Apparatus and Its Use in Chemical**

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS AT THE WELSBACH PLANT, GLOUCESTER, NEW JERSEY

**Engineering.** By JOHN V. N. DORR. Mr. Dorr discussed the possibility of applying the apparatus developed for continuous operation hydrometallurgy to the various chemical industries in which large quantities of material are handled. He illustrated the application of classifiers, thickeners and agitators to a variety of problems and elaborated particularly on the possibilities of the adoption of the principles of continuous counter-current decantation as a substitute for intermittent filtration. Mr. Dorr's lecture was illustrated by a large number of lantern slides showing the details of construction of the apparatus under discussion and also a large number of working installations. The costs of handling both the materials and products were also carefully discussed.

**Hardwood Distillation Industry.** By E. H. FRENCH AND JAMES R. WITHROW. This paper was presented by Mr. French and is published in full elsewhere in this issue. A large number of lantern slides of working installations were shown and described by Dr. Withrow.

**Need of Up-to-date Manufacturing Statistics.** By BERNHARD C. HESSE. Dr. Hesse called attention to the fact that we are in serious need of up-to-date statistics in regard to the domestic manufacture and importations. These statistics are not now forthcoming from the Government Statistical Bureaus, but we are entirely dependent upon foreign sources for such information as we are able to obtain. He urged upon the chemical engineers the desirability of dependable statistics of the right kind, and also that they formulate their needs and present them to the proper federal authorities for their consideration. As a result of Dr. Hesse's address, the Institute authorized the appointment of a committee to coöperate with the other chemical societies and report upon a specific plan for the collection, formulation and presentation of up-to-date industrial statistical matter which is so urgently needed. Dr. Hesse's address appears elsewhere in this issue.

**A Study of the Cause of Paint Failure.** By G. W. THOMPSON. Dr. Thompson presented the results of the investigations which he has conducted to establish the cause of paint failure and its possible remedy. The paper was fully illustrated by lantern slides.

**The Potash Industry.** By H. A. HUSTON. Dr. Huston discussed with considerable detail the present potash situation and its probable bearing upon the agricultural development of this country. His paper was fully illustrated by lantern slides and these were followed by a most interesting series of moving pictures, showing the operations of the various departments engaged in mining and refining potash salts.

EXCURSIONS

As is customary in the Institute, a large portion of the program was devoted to the inspection of industrial plants. The excursions were unusually well attended and the greatest interest was shown, especially in the more modern engineering developments as applied to the various industrial processes.

**Atlantic Refining Co., Point Breeze.** The members were here enabled to see the various processes developed for the refining of mid-continent crudes. The ordinary refining process is illustrated by a large number of installations. The Frasch stills were seen in operation, and the Burton process for the manufacture of motor fuel proved to be of great interest.

**United Gas Improvement Company, Point Breeze Plant.** The delegates had an opportunity to inspect the new water gas generators with the waste heat boiler installations, the physical research laboratory and the recent developments in artificial illumination and photometric apparatus.

**Welsbach Company, Gloucester.** The members spent the greater portion of one day in a detailed inspection of the various operations in this plant. The inspection was carefully organized by Mr. Miner and his staff, and the visitors had an opportunity to see the manufacture of nitro-cotton, collodion, thorium nitrate and gas mantles. The plants for the recovery of collodion solvents, camphor, and the recovery and distillation of waste ammonia liquors were also points of interest. The Welsbach Company entertained the guests at luncheon, which was served in the engine room of the metal factory.

**The New York Shipbuilding Co.** A portion of the delegates visited the plant of the New York Shipbuilding Co., in Camden, and inspected the shops and factories of this large property. A number of large merchant and war ships were seen in process of construction.

**Farr and Baily Linoleum Works.** A large delegation visited this plant and inspected the process and equipment for the manufacture of both inlaid and printed linoleums. The process was shown from the oxidation of the linseed oil to the finished product and proved to be a most interesting illustration of the modern developments obtaining in this industry.

**Commercial Museums.** One of the most interesting excursions of the convention was a visit to the Commercial Museum of Philadelphia. The inspection of this unique institution was carried out under the direction of Dr. Wm. P. Wilson, the Director of the Museum, and his corps of assistants. The plan and purpose of the museum was carefully explained to the visiting delegates and the collections proved to be most interesting and instructive.

The visit to the museum was followed by an inspection of the near-by laboratories and plant of the University of Pennsylvania.

**Barrett Manufacturing Co.** An unusually large number of visitors were the guests of the Barrett Manufacturing Co. where they were shown the working up of the light and middle oils from the various crude refineries of this company. Every operation of this process was shown, from the distillation of the oils to the refining of benzol, toluol, naphthalene, phenol and other products.

## DISTRIBUTION OF INDUSTRIAL OPPORTUNITIES

By George Otis Smith

Four constituents enter into the reaction that we term industry. Two of these, brain and brawn, are organic compounds and two are perhaps to be regarded as inorganic—money and material. None of these components is wanting here in the United States, and in fact their abundance affords the best reason for an optimistic outlook upon the present industrial situation. While in nowise overlooking the large importance of labor and engineering skill and capital as factors in the establishment of new enterprises or the expansion of old industries, I wish to address my remarks chiefly to the subject of the distribution of the raw material that is no less essential to a nation's industry.

In the highly differentiated system of production and commerce, the place factor has assumed large influence. The growth of transportation agencies makes the whole world tributary to both producer and consumer, with the result that keen competition tends to localize and specialize production. By way of contrast, think of the industrial conditions of a century ago. Our grandmothers were in a way chemical engineers. Yet to them, for instance, potash presented no international problem, but as soap-makers they utilized that home supply that gave the material its common name. In those days, as a poet has said:

> "Home was a factory, life a trade,
> And Mother a Captain of Industry."

Today facility of transportation has changed all this and industrial opportunities distribute themselves in accord with fairly definite though often complex principles. Of the four constituents of industry, labor, capital and brains are all more easily transported generally than the crude materials upon large tonnages of which the industry must depend. Thus cheap coal will attract manufacturers just as cheap land attracts farmers.

In studying the statistical record for the years since 1880, which is the period of expansion and development of the mineral industry, I have been impressed with the marvelous increase both in output and in efficiency in operation. Such facts have significance as we face the future. For this third of a century just past the growth of the mineral industry can be summed up in the statement that the value of the output has increased nearly seven-fold, while our population has less than doubled. If we compare directly the output per capita of population, the record of increase in the more important mineral products becomes really instructive or even inspiring. Thus in this period of 33 years the consumption of coal per capita has increased from less than a ton and a half to nearly 6 tons—an increase of 337 per cent. Similarly, the production of iron ore increased 357 per cent, petroleum 391 per cent, copper 1200 per cent, cement 2087 per cent; but gold and silver increased only 23 and 22 per cent respectively, while with lead the increase was 125 per cent, and zinc 638 per cent.

If statistics for the more important agricultural products are studied in a similar manner it is found that the total increases in the same period have not much more than kept pace with the growth in population. This is true of the two leading grains, corn and wheat, the one having somewhat more than doubled, the other not quite doubled, in the third of a century, so that the per capita production shows only a small percentage of increase. With cotton the gross increase has been larger, approaching 130 per cent, but wool has utterly failed to increase as rapidly as the population. It is only sugar that shows an increase, both in domestic production and in consumption, at all comparable with that of the half dozen minerals mentioned, the per capita increase being 394 per cent, or about the same as the other carbon compounds, coal and petroleum.

An even more gratifying phase of this mining development is the marked increase in man's productive capacity. Let us take the 20-year period 1889–1909 and analyze the coal-mining record. Roughly stated, the number of mine-workers a little more than doubled in that period, the output of coal more than trebled, and the capital investment more nearly quadrupled. The exact percentages are 123 per cent increase in employees, 226 per cent increase in production, and 252 per cent increase in capital. Stated in terms of efficiency, the mine-worker increased his individual output from 471 to 691 tons a year, while the average annual output per dollar of capital remained nearly the same, about two-fifths of a ton, the increase in capitalization per ton of output being less than 8 per cent. Most of this increase in capital outlay was due to equipment expenditures, the improvement in mechanical equipment appreciably adding to the mine workers' efficiency and comfort.

In iron mining the record for the same period is even more striking; the number of miners increased less than one-half, the capitalization nearly trebled, and the output nearly quadrupled. In the iron mines, then, both labor and capital became more efficient, the output per miner increasing from 385 to 995 tons and the production per dollar of capital from one-seventh to one-sixth of a ton. In the case of coal mining we know that this improvement did not halt with the census year of 1909, for since then the coal output per miner has increased another 71 tons, or more than 10 per cent in the four-year period. All this tells the story of steadily increasing efficiency of mine worker, mine equipment, and mining methods—that is, of the contributions by labor, capital, and engineering.

When I speak of the distribution of raw materials, I do not of course shut my eyes to the influence of markets upon the location of industry. The development of transportation systems makes the problem of markets a most complex one. Cheap transportation may take away a home market from an industry or it may furnish a foreign market. The industrial independence of the small community of a century ago has given way to the system under which your dinner table may represent the tribute from several continents. Even in a country so diversified as ours in its natural bounties domestic production of everything consumed is not desirable nor profitable. Exchange of commodities with foreign countries becomes necessary: for instance, just as soon as America can mine and smelt copper or produce and refine petroleum more cheaply than it can grow tea or raise sheep or cattle, then the home market for cheap meat and wool and tea necessitates a foreign market for our copper and oil.

Of course, the more we as a people are independent of goods sent from other countries the less we are dependent on a foreign market for our own products. Large imports necessitate large exports, else the balance of trade will swing too far on the wrong side. Nor can we shut our eyes to the volume of exports needed to meet the interest obligations due the foreign capital invested in our railroad and industrial securities.

So it follows that in planning industrial development independence is the goal toward which a nation should face, but not a goal which it should have either the intention or the desire to attain. As we look toward the South we find that our commerce with South America for the last four years has been one-sided to the extent of an unfavorable annual trade balance averaging more than $80,000,000. The fact that the balance of trade is against the United States in two of the three "A B C" countries should be taken only as an invitation to export more. That $80,000,000 not only measures the present opportunity for exports to South America but also suggests the chance for further development of trade relations. We need meat and hides from Argentina, tin ore from Bolivia, rubber and coffee from Brazil, nitrate from Chile, platinum from Colombia, cacao from Ecuador, wool from Peru and Uruguay, and coffee from Venezuela—what can we export in exchange?

To increase industrial prosperity this country needs to export finished rather than crude products and to import raw materials rather than manufactures. It is the product of American labor rather than the bounty of our natural resources that preferably should go into the world's markets. Betterment of industrial conditions can come best through expansion of manufacturing. The increase of the element of labor in the product exported will mean that we are not bartering away our heritage of natural resources but rather that we are using these resources as a basis simply for the expenditure of labor, which renews itself.

As the engineers of America study this matter of expansion of manufacturing, it becomes evident that the distribution of raw material and of power is the key to industrial opportunities. So narrow, however, is the usual margin between success and failure that the practical proposition can not be stated in so general terms. The chemical engineer requires not only qualitative but quantitative facts with which to start, and fortunately the geological engineer has come to realize this requirement. What are the mineral resources and where are they?—these are the two questions to be answered by the geologist. The answer to the "what" must be expressed in exact terms, and the value of this or that mineral to industry usually depends upon very specific factors. To illustrate: The knowledge, derived from a study of thousands of rock analyses, that the element potassium constitutes 2.49 per cent of the earth's crust possesses scientific interest and value; but as a starting point for practical work you chemical engineers would prefer a series of a dozen or two analyses of brines and bitterns from Western marshes and Eastern wells; yet even these analyses, however accurate, would avail little except as the geologist would furnish also a quantitative statement regarding the volume represented by such samples—that is, the extent of the deposits available for utilization. And here the scientific statement of relative abundance of potassium in the earth's crust comes in to contribute to the practical work as affording a measure of probability in extent of deposits when discovered.

A source of gratification to the Government scientist, especially in the past few months, has been the fact that under new and special demands many bits of knowledge that had before been only interesting and incidental details in the scientific study of mineral resources suddenly come to possess value recognized and appreciated by the producer and consumer. The dollar mark attached itself to these facts over night.

Already readjustment of domestic industry under present conditions has resulted in the development of American substitutes for imported material. Sales of domestic manganese ores have been made to the glass trade, and production of ferromanganese on the Pacific Coast is reported. The manufacture of zinc dust has followed the shutting off of the foreign supply, and barytes from the South has begun to replace the German imports. Medicinal oils derived from American crude have been placed upon the market by at least two refining companies and advertised as equal in every particular to the Russian article. Several firms have expressed their intention of manufacturing magnesium chloride from California magnesite, of which at least one shipment has been made to the East and others are to follow *via* the Panama Canal. In the Western States an efficient substitute has been found for the Danish flint pebbles used in the tube mills. In California, river pebbles of quartz are used, and in Idaho and Nevada pebbles are manufactured from local rock, and the reports from the mill men are to the effect that these substitutes are giving satisfaction at much lower costs.

In considering fuel and its bearing upon industrial opportunity too much emphasis can hardly be placed upon the distribution of the world's coal. Significant facts are that 98 per cent of the world's production is mined in the northern hemisphere and that of known reserves of coal of all grades the southern hemisphere possesses only $3\frac{1}{2}$ per cent. So too, not only does the United States mine and consume 40 per cent of the world's annual output of coal, but this country alone possesses five times as great a tonnage of unmined coal as does the whole of Europe and more than 1500 times as much coal as is known to exist in South America. Do not these facts contain the promise that the manufacturing industry of this country will continue to furnish manufactures for export to Europe and South America in increasing amounts?

When we consider the distribution of coal production and coal reserves, it is noteworthy that coal is mined in 30 states and that over 16 per cent of the area of the United States, not including Alaska, is underlain by coal beds. While Pennsylvania has for a century led in coal mining and thereby possessed a proud leadership in so many industries, this state does not contain the largest reserves. The center of coal production must surely continue to move westward toward the geographic center of the nation's coal reserves, which was figured several years ago as located in southeastern Nebraska—a state, by the way, of low rank both in coal output and coal reserves.

Petroleum and natural gas in their distribution in some degree supplement coal. While the states of the Appalachian and Lima-Indiana petroleum fields are mostly coal-bearing states as well, the largest oil field, both in present production and probable reserve, is in California, a state with only negligible coal resources. Taken together, these mineral fuels constitute a national asset comparable with the soil resources of this country; but the larger part of the value of the natural gas, petroleum, and coal to the nation is in their relation to manufactures.

The wide distribution of the other items in the nation's mineral treasury is no less notable than their abundance. Taking, for instance, the ores of the six important metals, the lack of localization can be seen in the record of last year's production by states. Listing the three leading producers for each of these six metals, we find no less than 13 states, including Alaska, in the competition. Missouri is the only state to rank first for two metals, lead and zinc. Montana stands second in both copper and silver, Colorado ranks second in gold and third in zinc, while Utah stands third in the production of three metals, copper, silver, and lead. These mining districts that are so productive of mineral wealth are scattered over the country from Alaska, ranking third in gold, to Alabama, third in iron ore, and from California, which leads in gold, to New Jersey, second in zinc. Such a wide distribution of ores sufficiently rich and extensive to be mined in large quantities means that the metallurgical industry is important on both the Pacific

and the Atlantic seaboards, and in most of the Rocky Mountain states as well as in several of the middle states.

Even in the two metals which at once suggest to us centralization—copper and steel, there is wide-spread production. In the mining of copper last year 23 states contributed, and the mining of iron ore is not confined to any one region, even though the ranges of Minnesota and Michigan furnished 84 per cent of the tonnage and Alabama and Tennessee $8^1/_2$ per cent. In all, no less than 28 states contribute iron ores to the furnaces of the country.

The diversity of the mineral industry is shown by the increase in number of products. Thus, while in 1880 the statistics of production covered 51 products, the table of production in current reports contains no less than 72 items. Furthermore, when the rapid growth of the industry is analyzed the more marked increase is seen in that of the nonmetallic products. The old opinion that the word "mineral" carried the idea of "metallic" is overwhelmed by the relative importance of the nonmetallic mineral products. In 1880 these constituted 47 per cent of the total output; last year more than 63 per cent. Another method of stating this relative importance is to say that the value of the nonmetals last year was greater than that of both metals and nonmetals in any year prior to 1905.

The raw-material resources of this country are so widely distributed that industry has been developing at this rapid pace at many points. I believe the tendency has been away from geographic centralization of industry rather than toward it. The State of Pennsylvania stands in a class by itself as a producer of mineral, yet its preëminence is perhaps less marked each year. Although last year its output was more than one-fourth of that of the whole country, a few years ago its share was more nearly one-third. Other factors are coming to the front each year which will create opportunities in other parts of the United States. You do not need to have these more than suggested: the South with its happy combination of coal and iron-ore in the same districts makes pig-iron production possible at minimum cost; the West with its hydro-electric possibilities available as a source of relatively cheap power for chemical and metallurgical industries; the Rocky Mountain region with its vast unutilized sources of sulfuric acid and equally great unmined stores of phosphate rock.

In these months of rapidly shifting currents of trade we may even see coals carried to Newcastle, but I will not presume to tell industrial chemists anything concerning possibilities of American manufacture of coal-tar products, so essential to other industries. However, it is not apart from the present subject to mention the amount and distribution of raw material available. Of the 115 million gallons of coal tar annually produced in by-product coke ovens, more than 22 millions are available in Alabama alone, nearly as much in Pennsylvania, 16 millions in the Indiana and Illinois region, and nearly half that in western New York. Ohio, West Virginia, Maryland, Kentucky, Wisconsin and Michigan are other important producers. Yet, so far as I am informed, few indeed are the centers where coal tar is used as a basis for chemical industry.

To return for a moment to the industrial reaction mentioned in my introductory sentence—the other ingredients necessary for producing prosperity appear at hand. A financial system already promises more mobile credits. A more sympathetic attitude of the public toward big industrial operations is indicated. The efficiency of American labor and American engineering was never questioned.

Two years ago Mr. William L. Saunders, President of the Ingersoll-Rand Company, gave his fellow mining engineers the benefit of his personal observations on manufacturing in Asia and Europe. His conclusions are of value to all engineers. He stated that manufacturing centers are not determined by abundance of cheap labor; efficient labor and the best tools are the requisites to manufacturing supremacy; *e. g.*, the cheap labor in a Japanese steel works does not yield the low labor items on the cost sheet attained by the American manufacturers with high-priced labor; and finally the real competition with American industry is that of the efficiency of German workmen, reënforced as it is by inventive engineering, rather than that of the cheapness of Asiatic labor.

In any estimate of American ability to make the most of the present opportunities for industrial expansion you can perhaps find no better measure of the inventive genius of this country than in a moment's review of what is making the European war so terrible. Strictly neutral we may be, yet from the heights above to the depths below we find American inventions "at the front"—the aeroplane, the magazine rifle and machine gun, the barbed wire, and the submarine and its torpedo. Can not our nation lead as well in the fashioning of the tools of peace as in designing the machines of war?

U. S. Geological Survey, Washington

# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

## 4TH ANNUAL REPORT OF THE DIRECTOR OF THE U. S. BUREAU OF MINES

The saving of human life in the mines, the stopping of millions of dollars of waste of mineral resources of the country, and an inventory of the wastes that are continuing are given important consideration in the recently issued fourth annual report of Dr. Joseph A. Holmes, Director of the United States Bureau of Mines.

According to Dr. Holmes, the Bureau has recorded its most notable achievement in the rescue of more than 100 entombed miners at different disasters, and the rescue of many more miners by volunteers who had been trained in life-saving work by the Bureau. Rescue and first-aid stations have been established at hundreds of mines throughout the country. The total number of miners trained by the Bureau has now reached 24,975. Yet, the loss of life is far greater than it should be with the natural hazards of the industry, and a plea is made for more extended investigations on the part of the Government. The humanitarian motives for undertaking such investigations are obvious. A sufficient economic reason is that during the past year more than 3,500 men were killed and more than 100,000 injured in the mining and metallurgical industries of the country. One-half of these fatalities and three-fourths of the injuries may be regarded as easily preventable. The money loss from the accidents may be estimated at not less than $12,000,000 a year, and this loss must be ultimately paid by the consumers of mineral products throughout the country.

The necessity for a more extensive use of safety appliances in the mines is shown by the statement that in the last five years, through lack of such appliances, more than 3,500 men have been killed in the mines and nearly 20,000 seriously injured. In Kansas, Oklahoma, Indiana and Iowa, many of the men employed in the mines to set off the explosives have lost their lives, and the recommendation is made that the shots should be fired electrically from outside the mine. In many districts the methods of shot-firing employed are still so extremely hazardous that only the most reckless men are willing to act as shot firers.

As showing the interest outside the Bureau of Mines in the life-saving campaign in the mines, many of the states are already expending in their work more than the Federal Government in all its investigations in behalf of mine safety; *e. g.*, Pennsylvania ex-

pends yearly $213,000. Also, twelve individual mining companies have rescue cars, which is four more than are operated by the Bureau of Mines.

In discussing the causes of mine disasters, Director Holmes says: "Not only have men been killed or injured from what are believed to be unnecessary electrical accidents in mining, but indirectly electrical apparatus has been responsible for mine explosions and mine fires that have extensively destroyed both life and property.

"The improper use of explosives and the use of improper explosives have directly or indirectly caused a large share of the fatal accidents and serious injuries to the men. But fully as serious as the killing or injuring of several thousand men from this cause during the past five years has been the injury to the health of the miners from poisonous gases given off by the improper explosives used.

"Each day poor ventilation and resulting bad air injure the health of thousands of miners. In most of the metal-mining states the statutory provisions are incomplete and inadequate, and there is the greatest disparity between them as to what constitutes sufficient ventilation to keep mine air pure. In fact, no adequate system of ventilation is generally in force today in the metal mines of the country."

During the year, four devices for limiting the area of mine explosions were perfected by George S. Rice, the chief mining engineer of the Bureau, and patented for the benefit of the mining industry. The director considers the development of these devices as probably the most important part of the year's work. The devices consist of barriers placed in the mines and loaded with stone dust. When an explosion strikes these barriers, the stone dust is thrown into the air and stops the further propagation of the explosion.

In the accomplishments of the year, Dr. Holmes calls attention to the statement of his engineers that with an expenditure of $15,000 they have brought about a saving of natural gas worth $15,000,000, a sum many times greater than the total cost of all the work done by the Bureau during the four years of its existence. This was done by introducing better methods in the drilling for petroleum and gas. The waste of gas stopped totaled 350,000,000 cu. ft. per day, equivalent in heating value to 17,000 tons of coal per day. In preventing the escape of this enormous quantity of gas, another saving was made, the value of which cannot be estimated—the elimination of danger to human life from the escape of this gas into the atmosphere. Dr. Holmes estimates the loss to this country each year in the development of the oil fields to be not less than $50,000,000, and that a large part of this loss is preventable. The fact that the principal oil-producing areas of the country are now believed to be well defined, and the fact that the next few years will see a constantly diminishing instead of an increasing production, unite in making imperative the need of extended inquiries.

Attention is called to the discovery of a process by the chemists of the Bureau whereby radium, which is sought much for its supposed curative qualities, can be produced at one-third of its present cost. With radium now selling at $120,000 a gram, its reduction in price to $40,000 will, it is said, result in many hospitals throughout the country being able to purchase a supply. The process devised by the Bureau's chemists has already been tested with success in the plant of the National Radium Institute, which is under the supervision of the technical staff of the Bureau of Mines.

The Bureau also claims that through its scientific method of purchasing coal according to its heat value the Federal Government has saved during the year $200,000 and that the various cities of the country that have taken up this plan of buying coal have reported a saving last year of thousands of dollars. Dr. Holmes places the present waste of mineral resources of the country at the sum of $1,000,000 per day and declares that in a large measure this waste is unnecessary. In one respect at least, the consideration of mineral waste has a basis quite different from the consideration of agricultural wastes. Our crops represent an annual production from a reasonably permanent soil; our forests may grow again, though a much longer period of time is required; and the soils themselves may be reproduced from the subsoil and the rock beneath. But of our mineral resources we have only the one supply. This supply is to a considerable extent destroyed by use, and at the present increasing rate at which we are using and wasting it, our one supply of a number of these resources will be either exhausted or largely depleted while the nation is yet in its youth.

A careful estimate indicates that in the mining of 600,000,000 tons of coal during the last calendar year there was wasted or was left underground in unminable condition 300,000,000 tons of coal. As a result of careful preliminary inquiry, it is believed that more than one-half (200,000,000 tons of coal) of this yearly waste is preventable under existing economic conditions. But the bare statement of the enormous losses does not, perhaps, express the most important part of the situation, which is that the coal we are now using and wasting represents the cream of our supplies, namely, the coal that is the best, is most easily and cheaply mined, and is nearest the great centers of industry.

The annual waste of metals in brass-furnace practice amounts to more than $4,500,000.

A preliminary inquiry as to the coking of coal in beehive ovens has shown that the total value of the by-products annually lost in this country through the use of such ovens amounts to $75,000,000. Although the desirability of developing by-product industries in this country has been recognized, such development has now become an actual need.

## BRITISH MANUFACTURE OF ANILINE DYES

Agitation in England for the establishment of a home aniline dye industry is following much the same lines as the same movement on this side of the ocean and the conclusions as to the best means of fostering the growth of such an industry bear in many cases a great similarity to the recommendations made recently by a committee of the New York Section of the American Chemical Society [THIS JOURNAL, 6 (1914), 972]. In the discussion at a meeting of the Council of the Leeds Chamber of Commerce one of the speakers stated the situation, according to the *J. Gas Lighting*, 128 (1914), 201, as follows: Some form of protection would be necessary for probably the next fifteen years. In Germany the capital sunk in this industry amounts to something like $125,000,000; and their concerns have been built-up gradually during the past 25 or 30 years. They have made a scientific study of all branches of the industry, the raw material for which has come very largely from England. By means of chemical research, they have arrived at the cheapest way of making the intermediate products as well. In Great Britain, on the other hand, the research laboratories have not devoted their attention particularly to the development of aniline dyes, or of the intermediate products which are necessary in the following up of synthetic coloring matters. Thus, the present crisis has found British manufacturers unprepared. Practically 90 per cent of the aniline colors consumed in England were imported from Germany; and the same applies more or less to the whole world. The speaker thought in the circumstances, therefore, that the Government should give some kind of protection for the working of German patents, either on a small royalty, or probably no royalty at all, while the war continued. The customs protection should be from 20 to 25 or even 30 per cent, and should continue long enough to carry the industry over its initial stages.

## NICKEL, COPPER AND MERCURY AS AFFECTED BY THE WAR

The world's production of nickel during recent years has been steadily increasing, as shown by the following figures:

| | Tons | Tons increase |
|---|---|---|
| 1910 | 20,100 | .... |
| 1911 | 24,500 | 4400 |
| 1912 | 28,500 | 4000 |
| 1913 | 30,000 | 1500 |

During the recent six or seven years there has been a remarkable expansion in the industrial uses of metallic nickel. Two-thirds of the world's supply is produced in Canada; the remaining third comes from New Caledonia and is controlled by France [*Engineering* (London), **98** (1914), 614].

A government order was issued in Canada, at the end of October, prohibiting the export of nickel to enemy countries. This contraband of war prohibition will act as an incentive to the opening out of new deposits and re-opening of old ones, several of which are situated in the United States, Greece, and other countries, all well known.

Norway possesses extensive deposits of nickel ore, much of it containing as high as 2 per cent of the metal. In former years nickel-mining was of some importance there, but competition with the richer ores of Canada and of some mines now shut down in the United States, could not be maintained, and most of the mines ceased operation. It is now stated that the mines have been reopened. The Norwegian nickel ore-mining industry was revived on a small scale some years ago, with an annual output of 70 to 100 tons, nearly all of which is used within the kingdom.

In the United States a very limited recovery of nickel is made as a by-product in the electrolytic refining of copper. The U. S. depends practically entirely on the nickel-ore mines of Sudbury, Ontario, for their supplies of the metal. The production of the Sudbury mines during 1913 reached 750,000 tons of ore, most of which was smelted to matte containing about 24,000 tons of nickel. In 1912 the production of these mines amounted to 737,320 tons of ore, while the matte produced 22,421 tons of nickel.

The recent Canadian output and the British imports from the United States are given below:

| | Canadian output | | Great Britain from U. S. (nickel oxide) | |
|---|---|---|---|---|
| | Tons | Value | Cwt. | Value |
| 1909 | ..... | ..... | 19,455 | $481,625 |
| 1910 | ..... | ..... | 17,294 | 430,675 |
| 1911 | 15,222 | $10,660,855 | 15,117 | 371,550 |
| 1912 | 20,018 | 14,013,000 | 23,679 | 584,870 |
| 1913 | 22,177 | 15,524,000 | 17,965 | 450,600 |

A portion of the matte made by the Canadian Copper Company is used for the direct production of monel metal, an alloy of nickel and copper, without the intermediate refining of either metal.

The world's production and consumption of copper have been seriously interfered with by the war, and prices are very unreliable, as no one can foresee the probable demand during the immediate future, nor the length of the war. The world's production of copper during recent years has been as follows in tons [*Engineering* (London), **98** (1914), 586]:

COPPER PRODUCTION OF THE WORLD—1910-1913

| | | | |
|---|---|---|---|
| 1910 | 891,000 | 1912 | 1,018,600 |
| 1911 | 893,800 | 1913 | 1,005,900 |

COPPER PRODUCTION OF THE WORLD IN 1913—TONS

| | | | |
|---|---|---|---|
| United States | 589,100 | Great Britain | 41,000 |
| Mexico | 90,000 | Russia | 34,300 |
| Japan | 77,200 | Spain | 23,600 |
| Australia | 41,800 | Other lands | 56,800 |
| Germany & Austria | 52,100 | Total | 1,005,900 |

The consumption of copper in several countries is given in the following table:

COPPER CONSUMPTION IN TONS

| | 1910 | 1911 | 1912 | 1913 |
|---|---|---|---|---|
| England | 148,187 | 159,736 | 148,877 | 140,300 |
| France | 92,838 | 106,408 | 106,753 | 103,600 |
| Russia | 28,237 | 31,830 | 38,818 | 40,200 |
| Germany | 208,826 | 234,985 | 253,429 | 259,300 |
| Austria | 37,150 | 41,101 | 51,374 | 37,200 |
| Italy | 32,487 | 40,949 | 34,378 | 31,200 |
| United States | 334,565 | 316,791 | 365,922 | 351,000 |

Towards the end of September, a noteworthy feature of the copper market was the action of the British Government in acquiring all the stocks of copper carried in Dutch warehouses, as this metal almost always is destined for Germany. Three cargoes of copper afloat for Holland were also taken by the British government.

The copper exported from America, practically all to Europe, during the nine months of the year and the corresponding months in the preceding four years has been as follows (in tons):

| | 1910 | 1911 | 1912 | 1913 | 1914 |
|---|---|---|---|---|---|
| January | 26,699 | 29,357 | 30,967 | 24,659 | 35,566 |
| February | 25,238 | 18,992 | 35,418 | 26,767 | 34,384 |
| March | 19,963 | 23,200 | 27,074 | 42,428 | 46,504 |
| April | 31,062 | 27,466 | 23,341 | 33,024 | 34,787 |
| May | 20,832 | 26,655 | 32,984 | 38,251 | 31,948 |
| June | 23,430 | 30,074 | 26,547 | 27,808 | 35,182 |
| July | 22,875 | 34,955 | 25,445 | 29,096 | 34,145 |
| August | 27,876 | 27,893 | 29,526 | 34,722 | 19,676 |
| September | 31,733 | 25,745 | 25,572 | 34,314 | 16,838 |

The total American exports for October have been estimated at about 16,200 tons, equal to 36,288,000 lbs.

The total value of the American copper exports may be taken at $146,000,000, of which $128,000,000 represents metal in pigs, ingots, and bars, while nearly all the remainder was exported in plates, sheets, rods, and wire. All these exports come to European countries, with the exception of about $7,098,000 worth, which were sent mainly to Canada. Trade in articles manufactured of copper and brass is comparatively small. The value of European exports of articles manufactured from copper and brass is many times that of the exports of similar goods from the United States.

British exports and imports of copper occur as ore, unwrought bars, blocks, slabs, cakes, and ingots, and copper goods manufactured; the exports and imports of copper ore during recent years have been:

| | COPPER ORE | | | | COPPER, REGULUS AND PRECIPITATE | |
|---|---|---|---|---|---|---|
| | EXPORTS | | IMPORTS | | IMPORTS | |
| | Tons | Value | Tons | Value | Tons | Value |
| 1909 | 2,333 | $220,415 | 89,153 | $4,548,600 | 65,292 | $10,960,785 |
| 1910 | 221 | 15,930 | 98,179 | 4,843,700 | 68,974 | 11,327,250 |
| 1911 | ... | .... | 86,596 | 4,278,700 | 64,873 | 10,037,160 |
| 1912 | 169 | 4,150 | 98,226 | 4,754,300 | 51,565 | 10,039,430 |
| 1913 | ... | .... | 94,265 | 5,025,300 | 39,110 | 7,247,030 |

Exports of copper ore mined in Britain are on a very limited scale and are practically ceasing as shown by the table. The imports come in small quantities from Germany, Belgium, France and Scandinavia, and in larger quantities from South America. Figures at hand show decreased imports from Chile and increased imports from the Transvaal and Australia.

The above table gives also Britain's imports of copper, regulus and precipitate. They are mainly from Belgium, Portugal, Mexico, Spain, South America, Cape of Good Hope and Australia. The exports are very limited, being last year only 1870 tons, value $19,000.

Great Britain's total copper exports and imports are shown below for the 1909–1913 period.

| | EXPORTS | | IMPORTS | |
|---|---|---|---|---|
| | Tons | Value | Tons | Value |
| 1909 | 40,440 | $13,726,500 | 288,430 | $57,846,000 |
| 1910 | 50,210 | 16,700,000 | 237,950 | 46,479,000 |
| 1911 | 50,300 | 16,870,000 | 263,740 | 46,776,500 |
| 1912 | 43,040 | 14,506,000 | 251,650 | 55,146,000 |
| 1913 | 53,200 | 20,902,000 | 257,620 | 56,560,000 |

Trading interests in quicksilver are attracting attention on account of the very extensive use of mercury in the preparation of fulminate for explosives, the present and probable future consumption of which must have an important bearing on the

market for the metal, the withdrawal of available supplies, and the future demand.

Quicksilver is put to many practical uses, such as gold-mining, but probably the most important is for percussion caps for igniting powder. The world's production is increasing; the average for the last decade has been 3728 tons. The output during recent years [*Engineering* (London), **98** (1914), 570] has been as follows, in tons:

| 1905 | 1907 | 1909 | 1911 | 1913 |
|---|---|---|---|---|
| 3336 | 3307 | 3243 | 3419 | 4171 |

The world's supply is obtained from only six countries, the main source being Spain; the Almaden mines of that country produce nearly a third of the entire quantity. Recent outputs have been as follows, in tons:

| | 1909 | 1911 | 1913 |
|---|---|---|---|
| Spain | 1000 | 1055 | 1490 |
| United States | 717 | 742 | 688 |
| Italy | 700 | 815 | 888 |
| Austria | 609 | 685 | 855 |

Ten years ago the United States' output of quicksilver was the largest in the world, exceeding 1000 tons for several successive years, but since then it has been declining; the main American supply is obtained in California, mostly from one mine. Great Britain's trade in quicksilver is peculiar, in so far as none is produced in the country; it is purchased and distributed, and, in effect, controls the world's markets in the metal. The following schedule shows the imports, exports, and British consumption, in flasks, during recent years:

| | Imports | Exports | Consumption |
|---|---|---|---|
| 1908 | 43,605 | 22,348 | 21,257 |
| 1909 | 43,163 | 22,051 | 21,112 |
| 1910 | 44,595 | 24,748 | 19,847 |
| 1911 | 46,547 | 31,438 | 15,109 |
| 1912 | 47,262 | 32,240 | 15,022 |
| 1913 | 45,348 | 26,815 | 18,533 |

The flasks contain 75 lbs. each. The consumption fluctuates within very wide limits, as shown by these figures. At the commencement of next year the effect of the war will be ascertainable on both the supply and British consumption. In Austria the quicksilver deposits occur in Idria, Western Carniola, and in Italy at Monte Amiata, Tuscany. The Mexican and Russian outputs are very limited in scale; four years ago the Russian output was only 4 tons. The price of quicksilver has risen enormously since the war commenced; the Austrian supply, controlled by the Government, is definitely cut off from the world's markets, and the Italian supply is uncertain. The Spanish supply is controlled mainly in London, and very little may be available for export. American supplies can scarcely be obtainable for export to Europe, as its consumption appears to have overtaken its production. In fact, England has been exporting quicksilver to the United States in small quantities for some years—during 1913, 154,500 lbs., to the value of $74,800.

Quicksilver imported by England was worth $36.27 per flask last year compared with $41.86 during 1911. The war has had a marked effect on English quicksilver imports, as shown by the following figures:

| Imports for: | | 1912 | 1913 | 1914 |
|---|---|---|---|---|
| August | lb. | 101,779 | 67,196 | 1792 |
| | flask | 1357 | 896 | 24 |
| September | lb. | 32,818 | 61,851 | 18,240 |
| | flask | 437 | 824 | 243 |

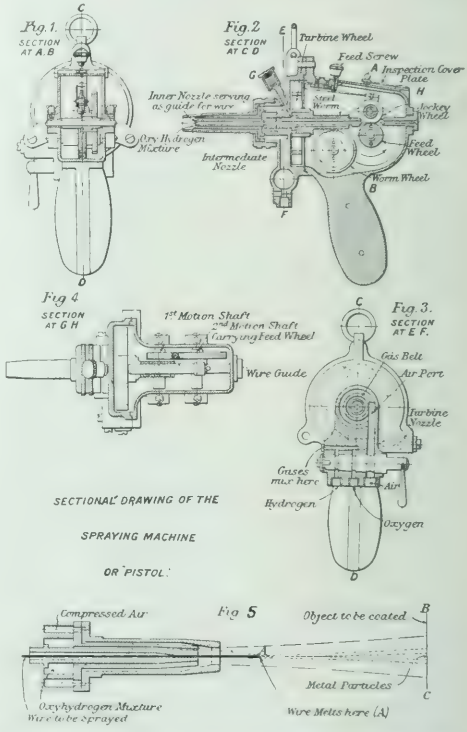
## METAL SPRAYING

An interesting device which is just emerging from the experimental stage, is one described in *Engineering* (London), **98** (1914), 382, by R. K. Morcom, for covering objects with a metallic coat by spraying them with molten metal.

The essential parts of the machine, or "pistol," as it is called, are a combined melting and spraying jet and a feed mechanism. The metal rod or wire is fed to the melting-flame formed by coal-gas, water-gas, acetylene, hydrogen, etc., burning in air or oxygen according to the metal used. The gases are supplied at such pressures as to prevent blowing out and to ensure a highly deoxidizing flame. The spraying jet can be of carbon dioxide, nitrogen, air, steam, etc., and is fed at such a pressure as to produce a sufficiently high velocity for successful coating. The various pressures must be carefully kept constant by accurate gauges and reducing-valves.

The feeding of the wire is accomplished by a small pneumatic motor, driven by the spraying medium either in series or parallel with the main jet. For small work, hand operation is sufficient, but probably, when large work is undertaken, it will prove convenient to have mechanical traverse and control.

The surface to be coated must be thoroughly clean and of an open nature to give a key for the deposit. Sand-blasting with sharp sand has been found best. Such surfaces as fabrics,




DIAGRAMMATIC REPRESENTATION OF MELTING & SPRAYING JETS IN ACTION.

wood, unglazed earthenware, and asbestos require only freedom from grease. The process in detail is the following:

The melting-jet is focused at A, Fig. 5, on the tip of the wire. The spraying-jet, cold from expansion, strongly draws forward the products of combustion in the center of its cone, and by its draught drags off minute particles of metal, either in the plastic or molten state. The central cone, therefore, consists of metal particles, some cooled to solidity, some molten, and some, perhaps, gaseous, surrounded by a protective reducing atmosphere. This cone is hurled forward with great velocity on to the object to be coated, B C, by the outer jet. There is a definite, most economical quantity of gas which should be used in the pistol, this quantity being about 1.5 cu. ft. of hydrogen per minute, and 0.5 cu. ft. of oxygen, or about 0.8 cu. ft. of coal-gas to 0.65 cu. ft. of oxygen for the present standard designs.

As at present constructed, the standard pistol uses for spray-

ing about 0.55 to 0.6 cu. ft. of air per minute for every 1 lb. per sq. in. air pressure, so that with an air supply at 80 lb. per sq. in., which is a very suitable figure for ordinary spraying, the air consumption will be from 45 to 50 cu. ft. per minute. The mass of this will be from 830 to 920 g. and the mass of metal sprayed by this air will be from about 8 g. in the case of iron to about 200 g. in the case of lead. The effectiveness of the cooling is shown by the fact that the hand can be held to receive a coating of metal without inconvenience.

## RECENT DEVELOPMENTS IN GERMAN-AMERICAN TRADE IN CHEMICALS

Of all the effects of the war, that on the trade of the various countries involved, as well as of neutral lands, is perhaps, at present, the easiest to evaluate. An attempt to study German export trade as affected by the war is made by Prof. H. Grossmann in an article in *Chem. Ztg.*, **38** (1914), 1169, in which the growth of chemical industries in Germany since the present tariff laws went into effect is studied, and their present situation is compared with that of similar industries of foreign nations. The part of the article of special interest to us is, of course, that dealing with the United States.

The year 1913 probably marks a maximum in international trade, not only for Germany, but for the whole world. In spite of the fears expressed by free traders at the time of the enactment of the German tariff of 1902, and in spite of the increase in foreign customs duties, the German export trade in chemicals has shown a remarkable growth, a fact proved not only by the export statistics and by increased earnings of exporters, but by the increase in wages and number of laborers employed.

Germany is now in the fortunate position, according to O. N. Witt [*Chem. Ztg.*, **38** (1914), 1117, 1130], of having within her own borders enormous quantities of a large number of necessary natural products such as salt, potassium chloride, coal, potatoes, sugar-beets, etc. However, many other raw products must be bought in large amounts from foreign lands, *i. e.*, now, from neutral countries; among these products are many ores and metals, oil seed, fats and oils, saltpeter, iodine, boron compounds, camphor, rubber, tanning materials, animal and vegetable fibers, raw phosphates, calcium acetate, etc. The relative scarcity of some of these has led to a rise in price since the beginning of the war. The following table is given by Grossmann to show the origin and amounts of these substances in 1913:

| Raw Product | Metric Tons | Chief Exporters |
|---|---|---|
| Ores: | | |
| Iron pyrites | 1,027,000 | Spain, Portugal, Norway |
| Chromium ores | 232,000 | France, Australia |
| Tungsten ores | 47,800 | British India, Australia |
| Bauxite | 384,500 | France |
| Raw phosphates | 926,000 | U. S. A., Algeria, Tunis |
| Saltpeter | 774,000 | Chile |
| Fats and Oils: | | |
| Oil fruits | 1,747,000 | Tropical countries |
| Vegetable oils, etc. | 579,700 | Tropical countries |
| Oil cake | 828,000 | Tropical countries |
| Mineral oil, refined | 745,000 | U. S. A., Austria-Hungary |
| Fiber Stuffs: | | |
| Cotton, raw | 478,000 | U. S. A., Egypt, British India |
| Wool, raw | 199,300 | Argentina, Austria, British South Africa |
| Flax | 71,200 | Russia, Austria-Hungary |
| Hemp | 45,700 | Russia, Italy |
| Jute | 162,100 | British India |
| Rubber | 20,500 | Brazil, Africa, S. E. Asia |
| Camphor | 8,700 | Japan |
| Calcium acetate | 20,900 | U. S. A. |
| Iodine | 258,000 | Chile |

The most important German exports in 1913 were:

| Export | Metric Tons | Chief Importers |
|---|---|---|
| Sugar, raw | 527,000 | England |
| Sugar, crystal | 490,000 | England |
| Aniline and coal tar dyes | 64,300 | U. S. A., England, China, Austria-Hungary |
| Potassium and "abraum" salts | 1,676,000 | U. S. A., Sweden, Holland |
| Potassium chloride | 393,000 | |
| Indigo | 33,300 | China, U. S. A. |

Although the chemical industries in the United States have made great progress in the last ten years, they are still dependent on Germany for many products and the same situation exists in England. It has been stated that, with the assurance of high prices and long continued protection, American industries would be able to meet demands in any line of manufacture, but Grossmann points out the difficulty of meeting the first condition, and the fact that already the American duties are not low. Glass, leather and textile manufacturers are already considering whether in case of continued exclusion of German chemical products, it would not be cheaper to close their factories altogether. Although, naturally, there is much discussion in the American press of possibilities of becoming chemically independent of Germany, little has been done practically. Other industries that suffer in this country are agriculture and the electrolytic potash industry from lack of potassium salts, while Grossmann shows among the industries favored by the war is the calcium cyanamide industry.

## BENZOL AS A FUEL

The increasing use of benzol as a fuel for motor cars abroad and its probable effect on the price of gasoline were mentioned in This Journal, 6 (1914), 259. Germany's present complete isolation from an adequate petroleum supply makes the fuel question one of anxiety and vital importance to her. *The Manchester Guardian* (England) prints statistics showing the growth of benzol production in Germany and its availability at present:

"For further supplies of motor fuel, Germany will turn to benzol. It is as good as petrol, and she makes it herself, both for various industrial purposes and for motor fuel. This has been a growing industry in Germany; and she may surprise us by a further sudden expansion of it. Benzol is obtained as a by-product from coke-ovens. In England only about one-third of such ovens are really adapted for benzol recovery; in Germany every oven is. In 1907 she produced less than 2,000,000 gals. of benzol, and bought about 1,500,000 gals. from us. By 1911 her production had risen to over 6,000,000 gals., and she took only 140,000 gals. from us. Even if the 1911 figures had not been improved upon, Germany cannot starve for motor fuel while her coke-ovens are working. To keep them working, however, entails a supply of coal, and we do not know what her stocks or present output are. It needs 17 tons of coal to produce a gallon of benzol, or 8,000,000 tons a month to maintain the normal benzol supply (on the 1911 figures). In 1912 the German Government ordered a plant capable of producing 6,000,000 gals. of benzol per annum, and three months ago they prohibited the export of benzol to France. It is unlikely that Germany neglected to stock benzol (or the coal to make it) as one of the sinews of war."

In England too, on account of the high cost of gasoline, the use of benzol as a motor fuel has been increasing steadily, but some dissatisfaction has attended its use.

Complaints are frequently received from users that, after a moderate amount of benzol has been used, a sticky deposit is noticed in the crank case, valve-stems, etc., and this eventually interferes with the satisfactory lubrication of the engine [*J. Gas Lighting*, 128 (1914), 184]. There is no doubt that benzol when properly made leaves no such deposit; but it is only too true that much of the benzol put on the market as motor spirit —supposed to be washed and refined—is really unsuitable for the purpose, and its presence is only hindering the development of this outlet for the product. Until quite recently, very little of the benzol manufactured in England was refined in the plants where it was recovered. It was generally exported in bulk in the crude state. In Germany, however, a great deal of attention has for a long time been devoted to the preparation of purified products, and a high state of efficiency has been reached in the washing and refining processes. This latter fact is undoubtedly attributable to the enormous demand for rectified products consequent on the expansion of the synthetic or coal-tar

color industry. With the increasing demand for rectified benzol for motor and other industrial purposes in England, refining plants were erected; but even now they are not always operated with the scientific exactitude characteristic of the majority of German industrial organizations. Numerous samples of so-called motor benzol when distilled at 100° to 110° C. leave a fair proportion—sometimes as much as 5 per cent—of dark colored constituents. These should have been eliminated in the washing operations, as undoubtedly their presence has a deleterious effect when the benzol is ultimately used in motor engines.

## GERMANY'S ARTIFICIAL FERTILIZERS

Under this title appears in the *Z. Ver. deut. Ing.*, **58** (1914) 1443, an article on the present importance of the fertilizer question in Germany. Three substances are considered: potash, nitrogen and phosphoric acid. As far as potash is concerned, there is no doubt of Germany's superiority over the rest of the world, but conditions are not so favorable as regards nitrogen compounds from natural sources. To overcome this deficiency has been one of the aims of German industry, and as a result the production of ammonium sulfate from the distillation of coal in gas works and coke ovens reached the total in 1912 of 492,000 tons, which far exceeds England's 379,000 or America's 151,000 tons. As a result, the nitrogen used in Germany has more and more been supplied by ammonium sulfate and correspondingly less by saltpeter; 1909 was the first year in which the consumption of the former exceeded that of the latter, and in 1912 the ratio was about 8.7 : 7.8 in favor of ammonia. This comparison shows, however, that large amounts of Chili saltpeter are still being used, and that any sudden drop in the supply of this salt, like that caused at present by the requisitioning by the government of the supplies on hand, must cause disturbance. This condition can be relieved by drawing on the surplus stored by the Ammoniaks-Verkaufsverbände. The coke ovens are still working to full capacity, so that ammonia is being produced in large amounts, but since their continued activity depends on a continued demand, while their best customers, the iron works, have greatly limited their output, other markets for coke must be found. The representatives of the fertilizer industry, therefore, in a meeting on September 18th emphasized the necessity of substituting coke for coal in every branch of industry where it could possibly be done.

To the processes of ammonia recovery from coal distillates must be added the various new processes for the fixation of atmospheric nitrogen. Those developed by Frank-Caro, Birkeland-Eyde, Schönherr and Pauling have the advantage that the production of fertilizer is their chief aim, and that their output, when the prerequisite conditions are fulfilled, can be increased according to demand without regard to other circumstances. However, their output has not yet grown to sufficient size to influence the market to any extent.

In case the war is of long duration, the Germans claim one advantage in the fact that a new process has been recently developed which will permit the nitrogen production together with the coke production to be established on a yet broader foundation. This process, that of Professor Haber is one for the synthetic production of ammonia from nitrogen and hydrogen, and is especially characterized by cheapness and practicability. Both facts have led to the fear, expressed in various circles, that the introduction of this process will bring about a serious drop in the price of ammonia, and already proposals have appeared in technical gas journals[1] looking to the working up of the gas washings for other products than ammonium sulfate. However much an injury to the coal distilling industry is to be regretted, from the point of view of the general welfare of the German Empire, it is very satisfying to know that the possibility of developing this process insures against an ammonia famine.

As for the third substance, phosphorus in the form of bone meal, calcium phosphate, etc. (guano is used in ever lessening amounts), it is well-known that the phosphorus-containing substances hitherto imported into Germany have been successfully replaced by the Thomas phosphate meal, a by-product of the Thomas steel works. The German Thomas steel industry is the greatest in the world, so that Germany should be independent of the rest of the world for her phosphorus supply as long as these works are in operation.

[1] *Jour. Gasb.-Wasserv.*, Aug. 29, 1914, p. 840.

## THE THERMAL PROPERTIES OF STEAM

Until ten or fifteen years ago steam-tables, based on Regnault's experiments, which were for the most part made before 1847, sufficed for all the needs of the practical engineer. The introduction of the throttling calorimeter for the estimation of the quality of steam had, however, led to doubts whether the accuracy of Regnault's results was as great as had been assumed, and these doubts were confirmed when the increasing use of superheated steam showed in many cases gains substantially in excess of the theoretical. Further researches, both theoretical and experimental, on the properties of steam were accordingly undertaken in many countries, and led to the publication of new steam-tables, such as those of Marks and Davis, or the new edition of Professor Peabody's tables, which fully satisfy the present requirements of engineering practice. Further experimental data have, however, been secured since the publication of these tables, and a very complete discussion of the thermal properties of steam, in which cognizance is taken of these newer results, has just been published by Professor G. A. Goodenough.[1]

In this pamphlet [*Engineering* (London), **98** (1914), 624] the whole of the available data is brought into consideration and new formulae established, which, while fitting the experimental results with great accuracy, are also consistent with each other and with thermodynamic principles, a matter of which Professor H. L. Callendar seems to have been the first to recognize the importance.

The relation found between the pressure and temperature of the steam is as follows:

$$\log p = 10.5688080 - \frac{4876.643}{T} - 0.0155 \log T$$
$$- 0.00406258\ T + 0.00000400555\ T^2$$
$$- 0.00002\left[10 - 10\left(\frac{t-370}{100}\right)^2 + \left(\frac{t-370}{100}\right)\right],$$

where $p$ is the pressure in pounds per square inch, and T the absolute temperature in Fahrenheit units, while $t$ is the temperature in Fahrenheit degrees. The absolute zero is taken as — 459.6° F. For the specific volume of the steam Professor Goodenough gives the expression:

$$v - 0.017 = 0.59465\,\frac{T}{p} - (1 + 0.05129\sqrt{p})\,\frac{C_1}{T^4}$$

where $v$ denotes the volume in cu. ft. per lb., and $\log C_1 = 10.82500$. The "heat content" of steam at different temperatures and pressures is:

$$i = 0.320\ T + 0.000063\ T^2 - \frac{23583}{T}$$
$$- \frac{C_2\, p\,(1 + 0.342\sqrt{p})}{T^4} + 0.00333\ p + 948.7$$

where

$$\log C_2 = 10.79155.$$

The entropy of superheated steam is given by the relation:

[1] "Thermal Properties of Steam," by G. A. Goodenough. *University of Illinois Bulletin*. London: Chapman and Hall, Limited. (Price, 35 cents.)

$$s = 0.73683 \log T + 0.000126\, T - \frac{11791.5}{T^2}$$

$$-0.25355 \log p - \frac{C_4 p\,(1 + 0.0342\, p)}{T^6} - 0.08085,$$

where

$$\log C_4 = 10.69464.$$

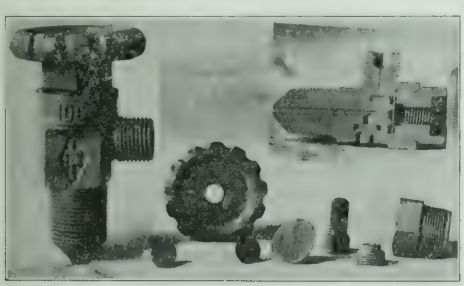
The thermal properties of steam at very high pressures and temperatures are stated to be as follows:

| Temperature °F. | Pressure Lbs. per sq. in. | Volume of 1 lb. Cu. ft. | Weight of 1 cu. ft. Lbs. | Heat content of Liquid B. T. U. | Heat content of Vapor B. T. U. | Latent heat B. T. U. |
|---|---|---|---|---|---|---|
| 600.0 | 1540.4 | 0.272 | 3.68 | 604.5 | 1164 | 560 |
| 620.0 | 1658.7 | 0.241 | 4.15 | 633.0 | 1151 | 518 |
| 640.0 | 2056.6 | 0.187 | 5.35 | 663.0 | 1136 | 473 |
| 660.0 | 2360.8 | 0.151 | 6.63 | 700.0 | 1112 | 412 |
| 680.0 | 2699.1 | 0.118 | 9.86 | 745.0 | 1080 | 335 |
| 700.0 | 3074.5 | 0.080 | 12.46 | 823.0 | 1016 | 193 |
| 706.3 | 3200.0 | 0.048 | 20.92 | 921.0 | 921 | 0 |

## A HIGH PRESSURE VALVE

The International Oxygen Company laboratory has developed a new valve for pressures up to 2,500 lbs. It is specially recommended for oxygen, hydrogen, nitrogen and similar gases. It is made of metal throughout, no packing being used in any part. The body is forged Tobin bronze, while the other parts are made of suitable metals which are non-corrosive to gases or to any weather conditions. The cross section shows the simple construction of the valve. Every part is accessible and, if worn out, can be easily replaced at little expense.

The diaphragm is made of very tough and springy material that will withstand perfectly all the strain put upon it, without any possibility of its cracking or breaking even after many years of service. The diaphragm takes the place of packing material, and in this way the usual stuffing box is entirely



eliminated. In the case of high pressure oxygen gas, the stuffing box is extremely objectionable, as one must resort to the use of rubber, leather or similar inflammable materials.

The diaphragm is slightly concave, and is normally set away from the seat of the valve a sufficient distance to permit a ful opening of the valve. It is not necessary, therefore, for the gas to raise the diaphragm; in this way all the gas from the cylinder can be used, down to atmospheric pressure.

An essential part of any high pressure valve is its safety plug. In this valve is a very ingenious device which has received the approval of the Bureau of Explosives of the Interstate Commerce Commission. The plug is filled with fusible metal melting at, or below, the boiling point of water. It is provided with three passages, each in a straight line with the direct action of the gas in the cylinder to permit the outflow of the metal; and is further provided with a hemispherical seat and a phosphor bronze disc. This safety plug is screwed into the body of the valve and forms a tight seat by compressing the phosphor bronze disc. No part of this plug projects beyond the body of the valve, thus protecting it against breakage. The safety will not blow when submitted to the direct rays of the sun or any other atmospheric condition, but will blow when placed in a fire, before the expansion of the gas can do any damage to the cylinder.

## OFFICIAL FIRE-TEST WITH TREATED WOOD

The British Fire-Prevention Committee have just issued their report No. 193, regarding a test carried out on July 1 with a match-boarded pine partition, in which the pine was impregnated by a proprietary process, with the object of making it fire-resistant. The partition comprised studs with $^5/_8$ in. grooved, tongued and beaded match-boarding on both sides, and it measured 10 ft. wide by 9 ft. high. The test was conducted under the committee's usual conditions, and was a forty-five minutes' test at temperatures that rose to 1630° F., whereupon water was applied from a stream fire engine. The main features in the official "Summary" of the test are that smoke appeared freely through several joints after thirty-eight minutes, and that after forty minutes, scorching appeared at several joints; further, that after forty-four minutes a glow was seen at four points. Upon the application of water, water came through several of the vertical joints. The fire-resistance was thus considerable for wood-work, although the minimum classification as to such a partition affording "Temporary Protection" under the British Fire-Prevention Committee's Standards—necessitating resistance for forty-five minutes—was not obtained by a few minutes. It would have been interesting if the partition had been tested side by side with a match-boarded pine partition which had not been impregnated.

## COAL IN ICELAND

The fear of a coal famine in Denmark on account of the war has caused the coal deposits at Dufansdale, in the Arnar firth, to be examined, according to *Engineering* (London) **98** (1914), 604, and the results of the investigation are understood to be encouraging. The deposits are likely to prove very extensive, and the quality is satisfactory and improves the deeper one gets. They are right upon a firth with excellent anchorage for vessels.

# NOTES AND CORRESPONDENCE

## ARGON ON A COMMERCIAL SCALE

*Editor of the Journal of Industrial and Engineering Chemistry:*

We thought it might be of interest to the American chemists to know that during the past week the American Cyanamid Company have been shipping several flasks of one hundred (100) cubic feet capacity, of ARGON, probably the first made on a commercial scale in this country. The manufacture of Argon by this company has been placed upon an industrial basis so that these shipments are being made regularly every day, and in no sense is it an experimental undertaking.

The credit for the development of this industry belongs to Mr. G. A. Hendrie of our company, and we believe it worthy of record that this fact be coupled with his name in the history of American Industrial Chemistry.

AMERICAN CYANAMID COMPANY
*Per* W. S. LANDIS

NIAGARA FALLS, ONTARIO
December 10, 1914

## THE BARBER ASPHALT PAVING COMPANY PRIZES

*Editor of the Journal of Industrial and Engineering Chemistry:*

The Barber Asphalt Paving Company has decided to offer students in Engineering Schools an opportunity to compete for $1,000 in prizes for essays on highway construction. This offer

has been made to twenty engineering schools, including all those of first importance in the country.

Prizes of $50 will be awarded to members of the 1915 classes of each of the leading educational institutions maintaining engineering courses. All papers must be in our hands by June 1, 1915, and no paper can be considered that exceeds 3,000 words in length. If as many as five papers should not be received from the students of any one school the right is reserved not to award a prize to the student of such school. The amount of original thought and investigation shown will be given especial consideration in arriving at conclusions as to the relative merit of papers.

Other subjects than the following or variations of these subjects will be freely permitted, provided that such variations do not go outside of the general subject of Asphaltic Highway Construction.

1—Comparative values of various approved forms of street pavements and roads as regards first cost, cost per year of life, ease of traction, ease of cleaning, noiselessness, dustlessness, etc., etc.

2—A general plan for street and road improvement for a city of 25,000 population, considering traffic in different sections of the city, first cost, cost of maintenance, attractiveness, availability and other factors bearing upon the proper selection of type of construction and materials.

3—Should specifications be drawn so as to admit under the same classification materials of different character, as, for instance, natural asphalts and those made from petroleums?

4—Which is preferable from the viewpoint of the public interest, separate specifications for different classes of material under which the municipality will know exactly what it is getting and pay accordingly; or a single general specification which attempts to cover all grades of materials, and results in making it possible for the contractor who gets the work at the lowest price to use the cheapest materials?

5—Relative value, advantages and disadvantages of laboratory and service tests as applied to the selection of asphaltic materials for highway construction.

6—Field study of an asphalt construction and repair plant, giving organization, output, and cost.

Several of these topics lend themselves especially well to original investigation. A study may be made, for example, of the detailed first cost and cost of maintenance of an actual group of pavements, or the actual paving or highway experience of some community may be studied.

BARBER ASPHALT PAVING COMPANY
LAND TITLE BUILDING, PHILADELPHIA *Per* D. G. PIERCE
December 3, 1914

## THE PRESENT POTASH SITUATION

*Editor of the Journal of Industrial and Engineering Chemistry:*

Judging by the numerous inquiries received, we believe that a statement of the potash situation may be of interest to your readers.

At the outbreak of the war the shipping season for potash from Germany was at its height, but since then the shipments have been made only in limited quantities. The prospect, however, is that they will increase as time goes on. Potash is not contraband of war and none of the nations at war objects to its movement in neutral ships. There is, however, great difficulty in securing railway and river facilities to move it from the mines and storehouses to the coast.

The mines are in good condition and enough workmen not subject to military service are available to keep them in operation.

Most of the leading fertilizer manufacturers have agreed to utilize their present supplies of potash in the effort to produce fertilizers with at least 2 or 3 per cent of potash next spring and the supplies on hand at the outbreak of the war were said to be sufficient for this purpose. There is therefore no reason why farmers should not secure some potash in their goods, although the usual 5 to 10 per cent may not be obtained.

42 BROADWAY, NEW YORK CITY H. A. HUSTON
December 1, 1914

## ANOTHER PLATINUM THEFT

*Editor of the Journal of Industrial and Engineering Chemistry:*

On the night of December 15th our laboratory was entered and platinum to the value of $100 taken.

Suspicion points to a young man who had made two calls at our laboratory asking for information on water, with particular reference to condenser trouble on marine work. The young man had a good knowledge of marine as well as electrical engineering and was familiar with the work on naval training.

He was a neat appearing young man with one exception, that being the stain of tobacco at the corners of his mouth. He was about 35 years of age, stood about 5 ft. 5 in. or 5 ft. 6 in. high, had sandy hair and a reddish face, was freckled, weighed in the neighborhood of 150 lbs. and was undoubtedly of Jewish descent, although he spoke with almost an English accent. He was dressed at the time in a blue chinchilla overcoat, brown soft hat, tan shoes, and dark suit. He also wore a Masonic pin and Chapter charm.

While here he made inquiries regarding other laboratories in this vicinity and we think it possible he intends working around this part of the country.

Thinking you could reach a larger field through THIS JOURNAL than we could in any way, we are writing you that you may communicate this to the chemists at large and thus avoid further losses at the hands of this person.

BRIDGEPORT HYDRAULIC COMPANY
BRIDGEPORT, CONNECTICUT F. C. BARROWS, *Chemist*
December 18, 1914

## ANNUAL MEETING OF THE CHEMISTS' CLUB

The annual meeting of The Chemists' Club, New York, was held in Rumford Hall on December 9th. The meeting was called to order by President McKenna and the reports of the various committees for the past year were submitted for consideration and action by the membership of the club. The committee appointed to canvass the ballots for the election of officers for the coming year reported the results of the vote, which were announced by the Chair as follows: *President*, M. C. Whitaker; *Resident Vice-President*, B. C. Hesse; *Non-resident Vice-President*, E. R. Grasselli, of Cleveland; *Treasurer*, Albert Plaut; *Secretary*, Reston Stevenson; *Trustees*, T. R. Duggan and P. C. McIlhiney.

As a result of the careful analysis of the operation of the Club for the three years during which it has been in the new clubhouse, the membership unanimously authorized an increase in dues, in order to strengthen the financial position of the organization and at the same time to wipe out the deficits which have accumulated as a result of its greatly enlarged policy. The new scale of dues thus established is $50 per year for resident members, $12.50 for non-resident members, and $15 for junior members.

The balance sheet of the treasurer's report shows a most healthy financial condition of the Club; with a large asset balance. Notably substantial increases in the equipment of the Library were reported, and the close of the present fiscal year leaves the Club in a highly satisfactory condition.

# PERSONAL NOTES

A meeting of the Perkin Medal Committee was called at the Chemists' Club on December 7th by President G. W. Thompson. The proposals for candidates for the Perkin Medal for 1914 were carefully discussed. Edward Weston was the unanimous choice of the committee for the medal to be conferred by the New York Section of the Society of Chemical Industry at its regular January meeting.

Arthur D. Little, Inc., of Boston, have established a popular journal of industrial chemistry, known as "The Little Journal." This journal will be published monthly and contain information in regard to industrial processes, products and plants, written in a popular but authoritative style. The first issue, which was put out in December, consisted of 20,000 copies and will be mailed without charge upon request.

The University of Michigan Section of the A. C. S., at its regular meeting on November 24th, elected the following officers: *Chairman*, L. H. Cone; *Councilor*, S. L. Bigelow; *Secretary-Treasurer*, H. H. Willard; *Executive Committee*—M. Gomberg, W. G. Smeaton and B. W. Peet.

Mr. F. P. Dewey, of the Bureau of the Mint, presented a paper on "The Recovery of Osmiridium in the Electrolytic Refining of Gold," before the Chemical Society of Washington, on December 10th.

Dr. C.-E. A. Winslow has resigned from the College of the City of New York to become director of education in the reorganized State Department of Health. His work at the American Museum of Natural History will continue as heretofore.

Mr. Henry A. Gardner, assistant director of the Institute of Industrial Research, Washington, D. C., spoke on the "Technology of Various Painting Materials" before the Rochester and Syracuse Sections of the A. C. S., on the 7th and 8th of December, respectively.

The 28th meeting of the Connecticut Valley Section of the A. C. S. was held at Springfield on December 12th. In the afternoon the Section toured the plant of the Hendee Manufacturing Company at Winchester Square, State Street. In the evening Mr. Carleton Ellis delivered an address on "Progress in the Hydrogenation of Oils."

Prof. L. H. Harris, formerly associate professor of the University of Pittsburgh, has been appointed consulting engineer to the Public Service Commission of Pennsylvania.

The December meeting of the Iowa Section of the A. C. S. was held December 12th, at Coe College, Cedar Rapids. Dr. Herman Schlundt, of the University of Missouri, spoke on the subject, "Radio-Activity of Waters;" Mr. L. H. Goebel, of the Cedar Rapids Water Works, presented a paper on the "Purification of Water." Afternoon excursions were made to the Starch Works, Quaker Oats Plant, and Packing House.

Mr. A. Fleck, demonstrator at the University of Glasgow, has been appointed physical chemist to the Glasgow Radium Committee, established to administer a large fund collected in the city for the purpose of acquiring and distributing radium for therapeutic purposes. Under the auspices of the committee, a radiometric laboratory has been fitted up at the university.

The 3rd regular meeting of the Maryland Section of the A. C. S. was held on December 19th. Dr. Ira Remsen read a paper on "Reminiscences of Liebig and Wohler."

Prof. H. A. Huston, of the German Kali Works, gave a lecture on "The Potash Industry," illustrated by lantern slides and motion pictures, before the Gamma Chapter of Phi Lambda Upsilon and the Institute of Arts and Sciences of Columbia University, on December 10th.

Mr. James G. Callan, of Arthur D. Little, Inc., Boston, addressed the Rhode Island Section of the A. C. S. on "Abrasives," on December 17th.

At the December meeting of the Detroit Section of the A. C. S. on the 18th, the following program was presented: "The Bleaching of Shellac," by Mr. C. T. Bragg, of Berry Bros.; "The Manufacture of Chemical Porcelain in Detroit," by Mr. Harry Spurrier, of the Jeffery-DeWitt Co.; "The Manufacture of Insulated Wire," by Mr. Jas. H. Bogart, of the Detroit Insulated Wire Co.; "Comparison of the Pharmacopoeias of Different Countries," by H. T. Graber, of the Digestive Ferments Co.; "Some Features of the Gas Industry," by Leigh E. Worthing, of the Detroit City Gas Co.

Dr. Arthur Romaine Hitch, formerly assistant instructor in chemistry at Cornell University, and research chemist of the Solvay Process Co., Syracuse, N. Y., has been appointed instructor in chemistry at the Rice Institute, Houston, Texas.

Prof. William J. Gies, of Columbia University, delivered an address on "The Chemical Investigation of the Cause and Prevention of Dental Caries," before the Philadelphia Section of the A. C. S. on December 17th.

The Pittsburgh Section of the A. C. S., at its meeting on December 17th, gave the following program: "The Freezing of Nitroglycerin and Its Detonation by Shock," Dr. Harold Hibbert, Mellon Institute, University of Pittsburgh; "Protein Charts," Prof. Alexander Silverman, University of Pittsburgh; "A New Process for the Manufacture of Steel," Isador Ladoff, Westinghouse Electric and Manufacturing Co.

Mr. Francis A. J. Fitzgerald lectured on "Thermitite" before the Western New York Section of the A. C. S. on December 17th.

Dr. M. L. Crossley, professor of organic chemistry at William Jewell College until 1913, and lecturer in Wesleyan University, 1913–1914, has been appointed associate professor and acting head of the Department of Chemistry in Wesleyan University. Dr. H. Lee Ward has been appointed associate professor in the department.

The *Chemical Abstracts* index began going into the mails on December 22nd. This number contains 7653 titles and the mailing of the entire issue involves the handling of six and one half tons of paper.

The Chicago Section of the A. C. S. held its December meeting on the 11th. The occasion was the Section's regular "Ladies' Night" and the program consisted of a series of Industrial Motion Pictures, showing the Iron and Steel Industry, Lead Mining, and Paint Manufacture from start to finish.

The following associates have been added to the editorial staff of the Anesthesia Supplement of the *American Journal of Surgery*: Prof. Charles Baskerville, head of the department of chemistry in the College of the City of New York; Prof. Dr. Guido Fisher, director of the Royal Dental Institute of the University of Marburg, Germany; and Dr. Torrance-Thompson, of Edinburgh.

The Revision Committee of the United States Pharmacopoeia announce that they have adopted the suggestions formulated by Dr. Charles Baskerville, in regard to the standards for purity of ether.

Prof. W. D. Bancroft was the guest of honor at an informal dinner given by the Pittsburgh Sections of the American Electrochemical Society and the A. C. S., previous to their joint meeting on December 10th.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### DEPARTMENT OF AGRICULTURE

**Food and Drugs Act, Etc.** The solicitor of this department has issued a compilation under the following title: Food and Drugs Act, June 30, 1906, and amendments of August 23, 1912 and March 3, 1913, with the rules and regulations for the enforcement of the act, food inspection decisions (40–155), selected court decisions, digest of decisions, opinions of the Attorney-General, and appendix. The completeness of the work makes it of value; the material although previously published is scattered through many small publications, some of which are difficult to obtain at this time. The present work, bound in half leather, is for sale by the Supt. of Documents at $1.00.

**Decomposition of Soil Carbonates.** W. H. MacIntire. Separate from Journal of Agricultural Research, **3,** 79–80. Best obtainable in this journal.

**The Microbic Content of Indoor and Outdoor Air.** C.-E. A. Winslow and W. W. Browne. Monthly Weather Review, **42,** 452–3. A report of a series of tests on 353 samples of air from various sources showing the range in bacterial content.

**A Nitrogenous Soil Constituent, Tetracarbonimid.** Edmund C. Shorey and E. H. Walters. Separate from Journal of Agricultural Research, **3,** 175–8. Contribution from the Bureau of Soils.

**The Production and Fertilizer Value of Citric-Soluble Phosphoric Acid and Potash.** William H. Waggaman. Department Bulletin 143, from the Bureau of Soils. 12 pp. Paper, 5 cents. This paper gives the results of the tests made to determine the fertilizing value of a slag made from a mixture of phosphate rock and feldspar; it is of interest to those engaged in investigations of fertilizer materials.

**The Nitrogen of Processed Fertilizers.** Elbert C. Lathrop. Department Bulletin 158, from the Bureau of Soils. 24 pp. Paper, 5 cents. This article reports on an investigation of the changes which occur during the manufacture of some of the processed fertilizers, and of the character and availability of the resulting materials when used in farm practice as a part of mixed fertilizers.

### PUBLIC HEALTH SERVICE

**The Chemical Disinfection of Water.** Earle B. Phelps. Public Health Reports, **29,** 2709–15. (Obtainable as part of No. 41, 5 cents.) This is a simple and brief review of the value and importance of this system of water treatment, including a description of simple apparatus by which some of the effective methods may be applied on short notice.

**The Source and Supply of Medicines.** Martin I. Wilbert. Public Health Reports, **29,** 2715–8. (Obtainable as part of No. 41; 5 cents.) The article has special reference to the interference of drug supplies by the European war conditions. The advantages of encouraging production of these drugs in America and of establishing an American drug distributing center, are pointed out.

### SMITHSONIAN INSTITUTION

**Smithsonian Physical Tables.** (By Thomas Gray.) Frederick E. Fowle. Publication 2269, Smithsonian Miscellaneous Collections. This is the sixth revised edition of the well known set of tables. Price will be given on application.

### BUREAU OF MINES

**United States Coals Available for Export Trade.** Van H. Manning. Bulletin 76. 15 pp. Paper, 5 cents. Data and average analyses are given for the available coals, with special attention to the questions of hardness, resistance to breakage in handling and other physical properties. In each case such data are given as would be useful in judging the suitability of the coal for special uses. This is also available in Spanish and Portuguese.

**Analyses of Mine and Car Samples of Coal Collected in the Fiscal Years 1911 to 1913.** Arno C. Fieldner, Howard I. Smith, Albert H. Fay and Samuel Sanford. Bulletin 85. 444 pp. Paper, 45 cents. This is a compilation of analyses with descriptions of the coals collected by the Bureau of Mines, the Geological Survey and in a few cases by state officials, the data being arranged by locality of the mine or prospect from which it was taken. It would be mainly useful in the study of the character of fuels available in various localities; but no generalizations or summaries are given.

### BUREAU OF STANDARDS

**Combustion Calorimetry and the Heats of Combustion of Cane Sugar, Benzoic Acid, and Naphthalene.** H. C. Dickinson. Scientific Paper No. 230. 67 pp. This article gives a general review of the methods and factors affecting accuracy of bomb calorimetry and includes a discussion of the principles of calorimetric design and calibration. The values given for the various substances are as follows: Naphthalene 9622 ± 2 (20°) calories per gram weighed in air, benzoic acid 6329 ± 2 (20°) calories per gram weighed in air, sucrose or cane sugar 3949 ± 2 (20°) calories per gram weighed in air.

**Standardization of No. 200 Cement Sieves.** Rudolph J. Wigg and J. C. Pearson. Technologic Paper No. 42. 51 pp. This paper discusses the results of a number of observations made to determine methods of standardizing the 200-mesh sieve and its manipulation, so that greater uniformity may be obtained in its use. In the course of the investigation a study has been made of the following:

(1) The accuracy of sieving tests, personal equation in sieving, variations in sieving values of standard sieves, and precautions necessary in sieving tests.

(2) The results of sieving tests made in 85 different laboratories and a comparison of these results with those obtained by the Bureau of Standards on some of the same sieves.

(3) Four proposed methods of standardizing sieves.

(4) The suitability of a number of finely ground materials, as compared with Portland cement, for use in calibrating sieves.

(5) The adoption of a standard value of fineness.

(6) The application of a "correction" to the sieving value of standard sieves.

(7) A revised specification for standard sieves.

**Copper Wire Tables.** Circular No. 31, 3rd edition. 70 pp. This is a reprint, with a few changes, of the circular of the same name issued about a year ago. It is accompanied by a card of copper wire tables giving in English and metric units a working table for standard annealed copper wire according to the American wire gage (B. & S.).

**Fees for Electric, Magnetic, and Photometric Testing.** Circular No. 6, 6th edition. 27 pp. This is a revised and extended edition of this publication which gives tabulations of the charges and the character of tests made by the Bureau of

Standards on electrical, magnetic and photometric testing instruments.

**Testing of Glass Volumetric Apparatus.** Circular No. 9, 7th edition. 31 pp. A revised and extended statement of standard specifications for glass volumetric apparatus, such as flasks cylinders, pipettes, burettes, etc., including the rules of the Bureau regarding apparatus which will be accepted for test and the character of and charges for certification of this apparatus.

### CONSULAR REPORTS—NOVEMBER, 1914

From the cashew-nut in India, there is obtained an **edible oil** (similar to almond oil), and from the shells a fluid called "cardole" used to **protect wood** from white ants. (P. 566.)

Owing to the scarcity of **dyestuffs** the prices for dyeing in England have been raised from 5 to 20 per cent above normal. (P. 567.)

The price of **"60 per cent acetic acid"** in England for use in the manufacture of vinegar, has risen from $90 to $140 per ton. (P. 569.)

The output of **sumac** from Sicily has shown a decided decrease in recent years. (P. 573.)

A company has been organized to prospect for **magnesite and manganese ore** near Pisa, Italy. (P. 608.)

A **potash** survey in Spain has shown the existence of marketable amounts near Barcelona. (P. 615.)

RECENT DEMANDS FOR AMERICAN GOODS OWING TO THE WAR (PP.)

SWITZERLAND—552
Petroleum
Gasoline
Transformer oil
Copper
Tin
Forged steel
Leather

RUSSIA—585
Medicines
Absorbent cotton
Iron

BELGIAN KONGO—586
Coal
Machine oil
Calcium carbide
Petroleum
Olive oil
Matches
Candles
Anhydrous ammonia
Lead subacetate
Alcohol
Caustic alkali
Miscellaneous drugs and chemicals

NORWAY—593
Hardware
Electrical supplies
Sugar
Oleo oil

IRELAND—600, 602 and 789
Window glass
Lamp chimneys
Nails
Barbed wire

SPAIN—673
Auto tires
Electrical supplies
Aluminum
Tool steel
Petroleum products
Pitch
Resin
Tallow

NEW BRUNSWICK—678
China
Glass
Porcelain
Celluloid

INDIA—682 and 865
Chemicals
Dyes
Glassware
Matches
Paper
Salt

ARGENTINE—689
Naphtha
Iron
Petroleum
Lubricating oils

GREECE—692
Sugar
Copper sulfate
Coal
Copper
Iron

CHINA—695
Aniline dyes
Window glass
Indigo
Iron
Paper

BRITISH HONDURAS—713
Coal

FRANCE—716
Linseed
Wood pulp
Sodium nitrate
Sulfur
Petroleum
Coal
Coal tar
Super-phosphate
Chemical
Pottery
China
Glassware
Rubber goods

ALGERIA—721
Sugar
Petroleum
Gasoline

CANARY ISLANDS—726
Sugar
Condensed milk
Lard

COSTA RICA—732
Beer
Paints
Perfumes, etc.

NORWAY—742
Cottonseed meal
Tallow
Electrical machinery
Kerosene

BRAZIL—752
Potato starch

MEXICO—761
Wood pulp
Writing paper

DENMARK—767
Paper
Paper stock
Petroleum
Gasoline
Oils
Varnishes

GUATEMALA—781
Enameled ware

HARBIN, CHINA—782
Electrical supplies
Dental supplies
Paper
Drugs
Photographic supplies
Tin
Galvanized iron

CEYLON—792
Beer
Cement
Corrugated iron
Hardware
Paper
Glass

NORWAY—812
Coals

AMOY, CHINA—814
Fertilizer
Matches
Paper

FORMOSA—871
Petroleum
Iron and steel
Condensed milk

SWATOW, CHINA—899
Dyes
Enameled ware
Candles
Matches
Condensed milk
Paper

CANTON, CHINA—914
Varnish
Paints
Oils
Perfumes
Explosives
Drugs
Condensed milk
Electrical apparatus

BRITISH COLUMBIA—919
Cream of tartar
Olive oil
Soap
Hardware
Drugs
Paints
Asbestos board
Electrical supplies
Glass

ANDALUSIA—929
Iron
Hardware
Enamel ware
Electrical supplies
China
Glass
Dyes
Drugs
Paints
Cement
Paper
Phosphate

STATISTICS, ETC., ON EXPORTS DURING 1912 AND 1913 TO THE U. S. (PP.)

CHINA—649 and 849
Albumen
Antimony
Bean (soya) cake
Bristles
Camphor
Cassia
Galls
Hides
Pig iron
Jute
Linseed
Musk
Peanuts
Bean oil
Cottonseed oil
Peanut oil
Rapeseed oil
Wood oil
Rhubarb
Soap stock
Vegetable tallow
Tin
Turmeric
Beeswax
Yellow wax

NORWAY—744
Seaweed ash
Chemicals
Fertilizer
Hides
Matches
Cod-liver oil
Paper
Wood pulp

NEW ZEALAND—774
Coals
Gold
Kauri gum
Hides
Tallow

The **nitrate** industry of Chili is almost paralyzed in spite of the efforts of the government to keep the plants in operation. (Pp. 685 and 819.)

Shortage of **chemical wood-pulp** in England is caused by the curtailment of production in Norway and Sweden, due to lack of fuel and chemicals. (P. 688.)

**Bean meal** obtained in Manchuria as a by-product in extracting soya beans with solvents, is preferable as a **fertilizer** to bean cake, obtained by expressing the oil from the beans. (P. 699.)

The Standard Oil Company has just completed a new **oil refinery** at Tampico, Mexico. (P. 777.)

Papyrus and tambookie grass are to be used in South Africa as **raw material for paper.** (P. 891.)

After extensive experiments, the Department of Agriculture of Ireland has concluded that while **sugar beets** can be successfully grown in Ireland, their culture would not be profitable. (P. 926.)

### GEOLOGICAL SURVEY

**Contributions to Economic Geology 1912. Part 2—Mineral Fuels.** M. R. CAMPBELL, Geologist in charge. Bulletin 541. 532 pp. 29 plates. Paper, 50 cents. This bulletin includes 26 brief reports on mineral occurrences of economic interest and preliminary reports on economic investigations. Most of these reports have been mentioned already in THIS JOURNAL at the times when they were issued as separates.

**Contributions to Economic Geology 1913. Parts 1 and 2.** Additional reports which will make up Bulletins 580 and 581 have been issued recently as follows:

(1) **The Phosphate Deposits of South Carolina.** G. S. ROGERS. Bulletin 580 J. 37 pp.

(2) **Ore Deposits in the Sawtooth Quadrangle, Blaine and Custer Counties, Idaho.** J. B. UMPLEBY. Bulletin 580 K. 28 pp.

(3) **Salines in the Owens, Searles, and Panamint Basins, Southeastern California.** H. S. GALE. Bulletin 580 L. 72 pp.

(4) **Rutile Deposits of Eastern United States** (with information concerning some foreign deposits of rutile). THOMAS L. WATSON. Bulletin 580 O. 27 pp.

(5) **The Moorcroft Oil Field and the Big Muddy Dome, Wyoming, Papers.** V. H. BARNETT. Bulletin 581 C. 34 pp. These papers describe geological investigations regarding the presence of oil in these districts. The work in the first district is not encouraging to further development of the field; in the second district further tests are needed.

(6) **Geologic and Oil Prospects in Waltham, Priest, Bitterwater and Peachtree Valleys, California, with Notes on Coal.** ROBERT W. PACK AND WALTER A. ENGLISH. Bulletin 581 D. 41 pp.

**Slate in the United States.** T. N. DALE AND OTHERS. Bulletin 586. 220 pp. and 26 plates. Paper, 50 cents. "This volume is not only a corrected and revised edition of Bulletin 275, Slate Deposits and Slate Industry of the United States, but also contains the results of all recent discoveries and studies of slate in this country. Its plan is (1) to set forth, in succinct

form, the present state of scientific knowledge as to the origin, structure, texture, and chemical and mineral composition of slate; (2) to describe in more or less detail the slates and quarries of each district; and (3) to consider the economic geology of slate, including scientific prospecting for it, methods of testing it, slate machinery, and the use of slate and slate waste, together with a tabular summary of all the slates described."

**The Constitution of Natural Silicates.** F. W. CLARKE. Bulletin 588. 128 pp. Paper, 15 cents. The announcement of this bulletin indicates its importance as follows: "This bulletin presents the results of a study of the chemical structure of the silicates found in the solid crust of the earth. From the geologist's point of view the silicates are of fundamental importance, for they form at least nine-tenths of the entire known mass of the earth's crust, and a study of their inner constitution may be reasonably expected to shed light upon many serious problems. Every primitive rock or eruptive mass contains an aggregation of silicates, each one capable of undergoing chemical change by which alteration products are formed, so that in time the rock may become transformed into new substances, quite unlike those which originally existed in it. A knowledge of the processes which thus occur, dependent on chemical structure, should be applicable to the study of the rocks and should ultimately render it possible, by investigating a metamorphosed mass, to clearly indicate its origin."

**Quality of the Surface Waters of Oregon.** WALTON VAN WINKLE. Water-Supply Paper 363. 137 pp. Paper, 20 cents. This bulletin which was prepared in coöperation with officials of the State of Oregon gives "a brief discussion of the constituents, uses, and purification of natural waters and a detailed consideration, by drainage basins, of the quality of the stream waters of Oregon, showing the nature and amount of the materials they hold in solution. The paper contains many analyses, which show that the river waters of Oregon are low in mineral content and are very good for general industrial use and for irrigation."

**Water Analyses from the Laboratory of the U. S. Geological Survey.** Tabulated by F. W. CLARKE. Water-Supply Paper 364. 40 pp. Paper, 5 cents. This bulletin contains 203 analyses, made in the chemical laboratory of the United States Geological Survey, of waters from rivers, lakes, wells, and springs in the United States as well as some mine waters. Most of these analyses have been published elsewhere, but many of the original documents are out of print and are therefore obtainable with difficulty.

**Mineral Resources of the United States, Calendar Year 1913.** In addition to those sections previously announced, separates of the following subjects have been issued; these will be reviewed next month in detail: Gems and Precious Stones, including a discussion of the metric carat; Clay-working Industries; Metals and Metallic Ores; Iron ores, Iron and Steel; Cobalt, Molybdenum, Nickel, Tin, etc.; Gold and Silver; Lead; Platinum Metals; Zinc and Cadmium; Antimony, Arsenic, etc.; Coke; Natural Gas; Fuel Briquetting; Asphalt, etc.; Borax; and Stone.

# BOOK REVIEWS

**Anesthesia.** By JAMES TAYLOR GWATHMEY, M.D. in collaboration with CHARLES BASKERVILLE, Ph.D., F.C.S. New York and London: D. Appleton and Company, 1914. xxxii + 945 p., 283 illus. Price, $6.00.

This comprehensive, distinctly modern treatise bears witness not only to the activity and success of the author and collaborator—the one a professional anesthetist of rare skill and resource, the other a scientist whose investigations on the chemistry of anesthetics have been noteworthy—in the improvement of anesthetic methods, but also to their industry and zeal in getting the work of others into a most convenient form. The amount of labor expended in the preparation must have been enormous; the whole field of rational and technical anesthetics is covered in a way planned to be helpful to the researcher and practitioner alike, and the value of the work is further enhanced by the systematic method of arrangement. While it is not exactly a composite book, ten specialists have contributed chapters.

This work differs from the others on anesthesia in properly devoting a large amount of space to the chemistry of both anesthesia and anesthetics; in supplying the most modern practice for the active practitioner and student; in suggesting many lines for further investigations; and in containing much matter hitherto never considered, or only very superficially considered, in similar treatises. It is indeed original in both plan and execution.

Twenty-one chapters consider in order: the history of anesthesia, general physiology of inhalation anesthesia, the use of rebreathing in the administration of anesthetics, nitrous oxid, ether, ethyl chlorid, chloroform, the selection of the anesthetic and technique for special operations, treatment before, during and after anesthesia, anesthesia by intratracheal insufflation, colonic anesthesia, sequestration method of anesthesia, local anesthesia, intravenous anesthesia, local anesthesia as applied in dentistry, spinal analgesia and spinal anesthesia, electric analgesia, sleep and resuscitation, mental influence in anesthesia, hypnosis in anesthesia, therapeutic uses of inhalation anesthetics, the medico-legal status of the anesthetist, a list of anesthetics, and statistics. There are three appendices: ethyl ether (supplementing Chapter V), chloroform (supplementing Chapter VII), and oxygen. The index, which occupies 48 pages, appears to be quite well done.

It is a meritorious work and one which, it may be predicted, will have a long and useful career, but it is not, unfortunately, free from marked errors of judgment and proof-reading; moreover, some important omissions occur.

It is not clear why, if the reputable houses are "anxious to provide drugs of the highest purity" (p. xi), "close chemical supervision does not always obtain" at the plants thereof. Certainly it is simple enough to prepare anesthetics of pharmacopoeial grade, and a reputable manufacturer would hardly tolerate carelessness in such operations.

As to the text of the book, it may first be indicated that, owing to the very large number of references to medical, chemical and legal literature, a journal list should have been included; and that, in order to complete the excellent chemical considerations, the detection of chloroform and ether and the estimation of these in the cadaver should have been discussed.

Other critical comments may be made as follows: Hickman was not the author of the paper referred to on p. 5, and the "general properties" of ethyl chloride were not discovered by Carlson in 1896 (p. 27; cf. p. 251). On pp. 32 to 56, the authors give a presentment of the theories on the mode of action of anesthetics. They appear to have been unencumbered with preconceived notions and to have been uninfluenced by the perhaps too general acceptance of the Meyer-Overton theory; and while they are disappointingly uncritical, except on p. 39, the statements of fact given in their conclusions (p. 55) are impartial and suggestive, if rather noncommittal. In this connection, the reviewer would suggest that the theories be suitably classified in the next edition; that, since "no attempt has been made to catalogue all the theories proposed," Spencer's valueless explanation be omitted; that Loewe's important theory of narcosis be considered; and that the exceptions of Vernon and Winterstein to Traube's theory (p. 42) be included. Apropos of the Meyer-Overton theory, it would be interesting to ascertain whether the

sensitivity of the nervous system toward anesthetics could be increased by withdrawal of lipoids. Mention might be made of the considerations of Garrod on p. 61. Page 85 is not correctly titled. It seems to the reviewer that the action of oil of bitter orange peel (p. 96) is to be attributed solely to its greater penetrating power and therefore to its ability to mask the odor of ether, and not to an obtunding action on the olfactory nerve; the action is analogous to that of the power of eriodictyon to disguise the taste of quinine. Certainly there is nothing "mysterious" in the utilization of a more odorous substance to disguise the scent of another. Figure 64, on p. 201, is inverted. Names of the manufacturers appear on the containers shown in Figs. 63 A, 64 and 117 (see also Figs. 52, 77–79, 82, 123 and 131), and not on those illustrated on p. 254. This, notwithstanding the fact that the authors did not consider it "desirable to indicate from whom certain instruments could be obtained" (p. x). The large footnote on p. 282 should have been worked into Chapter I. Footnote 2 on p. 288 is largely repeated in the text on p. 300; reference might have been made here to the "narcosis progression" analyzed by Graham Brown, in connection with which the recent work of van Leeuwen (*Arch. ges. Physiol.*, **159,** 291) is of interest. On p. 371, it should have been noted that 'when atropin is mentioned, reference is not had to the eclectic preparation' (the authors employ simplified chemical orthoepy). The use of phenyldihydroquinazoline tannate in vomiting following narcosis is not referred to on p. 379. The mechanism of oil-ether colonic anesthesia might have been further elucidated by regarding it as a "transgression" process (p. 462); this process is discussed by Morgenroth and Ginsberg in *Zentr. Augenheilk.*, **37,** 315. The physiology of local anesthesia is not discussed in Chapter XIII; much remains to be explained in this field; for instance, the actions of many local anesthetics on nerve endings and nerve trunks are not always parallel. It is not generally recognized that solubility in fat influences the results (on this point, see Fromherz, *Arch. exp. Path. Pharm.*, **76,** 257). The production of local anesthesia by cataphoresis should have received 400 words at least; a good discussion of this procedure is contained in *Hygiea*, **75,** 184. On p. 645, "Lister" should read "Liston" (cf. p. 20), and poor proof-reading occurs in line 9 on p. 677. Chapter XIX, on "The Medico-Legal Status of the Anesthetist," contains an excellent account of the physician's liability, which every practitioner might read with profit. The author of this chapter, Mr. J. W. H. Crin, states that "it is to that higher law, the ethics of the medical profession, that society must ultimately look for protection:" quite true, but far removed from the pettier aims of mere financial betterment, ethics points the way to a goal of illimitable loftiness; no matter what rules of conduct obtain in the medical profession, as in others having similar codes, it must be remembered that the moral conceptions of different individuals are widely variant. A physician may become a specialist upon his own determination (p. 684): it has been reasonably proposed that the peculiar skill requisite to so qualify him should be determined by the state medical boards, upon a procedure laid down by the American Medical Association.

Chapter XX, "A List of Anesthetics," which occupies 152 pp., is rich in bibliographic data and should be of great value for reference purposes; this chapter is, in fact, the most noteworthy section of the book, and it is evident that much time was spent in collecting the facts presented; it alone would repay those interested for the purchase of the book. Some of the bibliographies (as those on pp. 690, 694, 700, 724, 751, 766, 784, 790, 800, 807, 812 and 833) are arranged chronologically or approximately so, while others (as shown on pp. 740 and 820) are classified alphabetically according to authors' names; moreover, these bibliographies are not indexed. "Snape's calorific fluid" and "Nabolis," while mentioned on p. 536, are not included in this list; under "Air" (p. 692), it should have been noted that liquid air has been used in the production of local anesthesia in dental practice; on p. 703, line 33, reference is had to the preparations of Schleich (p. 810) and not to a treatise; it might have been noted on p. 713 that the lipoid-solubility of benzene plays a role in its action (see *Biochem. Z.*, **61,** 372); the alkaloid cevine, which produces local anesthesia, is not mentioned; papaverine, a 10 per cent solution of whose sulfate produces complete anesthesia of the conjunctiva, is omitted; potassium sulfate and chloride produce marked local narcosis (see, among others, Zorn, *Z. exp. Path. Ther.*, **12,** 529), but are not included; only *l*-scopolamine hydrobromide should be used in practice—a fact which is not mentioned on p. 810; thymacetol, the acetol ester of thymotinic acid, and possessing a pronounced local anesthetic action, is not included; and "Zeuner's Halspastillen" should not have appeared as a form of "Yohydrol." A question of interest arises in connection with quinine and urea hydrochloride (p. 805) local anesthesia; is this action due to the compound *per se* or to the formation of carbon dioxide by hydrochloric acid in the tissues? Filippi (*Lo Sper.*, **66,** 383) explains the result by the action towards lipoids peculiar to both urea and carbon dioxide; an explanation is then afforded by the Meyer-Overton theory. Since yohimbine hydrochloride possesses anesthetic properties, it would be interesting to determine the action of its isomer, corynanthine hydrochloride.

W. A. Hamor

**Chemical Technology and Analysis of Oils, Fats and Waxes.** By J. Lewkowitsch, edited by George H. Warburton. Fifth Edition, Vol. II. Macmillan and Company, London, and the Macmillan Co., 66 Fifth Avenue, New York, 1914. Price, $6.50.

Since the death of Dr. Lewkowitsch the revision of his well known treatise has been carried on by Mr. Warburton who for seventeen years was his associate. The plan, scope, and style of the work remain unchanged. The present volume covers the same ground as Vol. II of the fourth edition, but contains 944 pages as against 816 pages in the latter volume. A short section on denaturing oils and fats has been introduced and a number of oils and fats not previously regarded as sufficiently important to require mention are now described briefly. In the main however, the increase in size is due to new matter incorporated in the descriptions of the sources, preparation, analytical characters, and probable adulterants of the various oils, fats and waxes of commerce.

Statistical data are quoted freely and are brought rather closely down to date, the tables of figures for different years ending usually with 1911, 1912, or (in a few cases) 1913. Extended tabulations of chemical and physical characteristics continue to be a prominent feature of the descriptions of the individual oils and fats. In these descriptions there is relatively little discussion of the detailed technique of preparation and refining. The first thirty eight pages of the volume are devoted to a general chapter on commercial preparation, but the full description of manufacturing operations employed in the individual oil and fat industries is apparently reserved for the concluding volume.

The present volume gives evidence of more thorough revision than is usual in books of its size and appears to cover its allotted field more thoroughly than any other single work. It contains a detailed table of contents in which the materials of each group are arranged (as in earlier editions) in the order of their iodine numbers, and an index of botanical and zoölogical names, but no index of subjects. A general index for the entire work is promised with Vol. III which, according to the preface of the present volume, is already in press.

H. C. Sherman

# NEW PUBLICATIONS

By JOHN F. NORTON, Massachusetts Institute of Technology, Boston

**Assaying in Theory and Practice.** By E. A. WRAIGHT. 8vo. 324 pp. Price, $3.00. Longmans, Green & Co., New York.

**Chemical Engineering: Notes on Grinding, Sifting, Separating and Transporting Solids.** By J. W. HINCHLEY. 8vo. 112 pp. Price, $0.75. Churchill, London.

**Colloids: Ueber die Bedeutung des Lichtes für die Bildung und Stabilität Kolloider Lösungen.** By H. NORDENSON. 8vo. 164 pp. Price, $1.25. Upsala.

**Copper Alloys: British Standard Specification for Copper-Alloy Three Piece Unions.** By ENGINEERING STANDARDS COMMITTEE. Folio. Price, $1.25. C. Lockwood, London.

**Electrochemistry: Laboratory Course in Electrochemistry.** By OLIVER PATTERSON WATTS. 16mo. 148 pp. Price, $1.00. McGraw-Hill Book Co., New York.

**Ferments: Abwehr fermente. Das Auftreten blutfremider Substrate und Fermente im tierischen Organismus.** By E. ABDERHALDEN. 4th Ed. 8vo. 404 pp. Price, $3.00. Berlin.

**Food Products.** By H. C. SHERMAN. 8vo. 594 pp. Price, $2.25. The Macmillan Co., New York.

**Management: The Science of Works Management.** By J. BATEY. 12mo. 223 pp. Price, $1.25. D. Van Nostrand Co., New York.

**Testing: Resistance of Materials.** By STEPHEN ELMER SLOCUM. 8vo. 210 pp. Price, $2.00. Ginn & Co., Boston.

**Minerals: The Deposits of the Useful Minerals and Rocks, Their Origin, Form and Content. Vol. I.** By F. BEYSCHLAG, *et al.* 8vo. 542 pp. Price, $4.50. Macmillan, London.

**Oils: Chemical Technology and Analysis of Oils, Fats and Waxes. Vol. 2.** By JULIUS ISIDOR LEWKOWITSCH. 5th Ed. 8vo. 944 pp. Price, $6.50. The Macmillan Co., New York.

**Petroleum: History and Romance of the Petroleum Industry. Vol. I.** By J. D. HENRY. 8vo. 320 pp. Price, $2.50. Author, London.

**Poisons: Der chemische Giftnachweis.** By C. IPSEN. 8vo. 79 pp. Price, $1.00. Wiesbaden.

**Steel: Heat-treatment of Steel: a Comprehensive Treatise on Hardening, Tempering, Annealing Co.** 8vo. 278 pp. Price, $2.50. Industrial Press, New York.

**Ultraviolet Light: The Spectroscopy of the Extreme Ultraviolet.** By THEODORE LYMAN. 8vo. 135 pp. Price, $1.50. Longmans, Green & Co., New York.

**Ventilation: Heating and Ventilation Plants.** By C. LINCOLN HUBBARD. 2nd Ed. 8vo. 300 pp. Price, $2.50. McGraw-Hill Book Co., New York.

## RECENT JOURNAL ARTICLES

**Air: Die desinfizierende Wirkung der Gasbeleuchtung auf Zimmerluft.** By KNUD AHLBORN. *Archiv für Hygiene*, Vol. 83, 1914, No. 3, pp. 155–86.

**Air: Investigation of Sewer Air Following Boston Explosion.** By H. W. CLARK. *Engineering Record*, Vol. 70, 1914, No. 23, pp. 606–7.

**Analysis: Gasanalytische Pipette, die ein Bewegen der Absorptionflussigkeit innerhalb der Pipette gestattet.** By GEORG WEMPE. *Zeitschrift für angewandte Chemie*, Vol. 27, 1914, No. 86, pp. 584.

**Blast Furnace: The Heat Balance of the Blast Furnace.** By SIDNEY CORNELL. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 12, pp. 747–50.

**Blast Furnaces: Safety Regulations for Blast Furnaces.** By F. H. WILLCOX. *The Iron Age*, Vol. 94, 1914, No. 22, pp. 1226–7.

**Bleaching of Wool Fiber.** By A. F. MUSGRAVE. *Textile Colorist*, Vol. 36, 1914, No. 431, pp. 337–8.

**Butter: The Effect of Renovation of Butter upon the Reichert-Meissl Number and Saponification Value.** By F. O. TOUNEY AND F. W. STOCKTON. *American Journal of Public Health*, Vol. 4, 1914, No. 11, pp. 1083–5.

**Carbide: Note on the Preparation of Pure Calcium Carbide.** By M. DEKAY THOMPSON. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 12, pp. 779–80.

**Cement: Ueber die Verbindung $8CaO.Al_2O_3.2SiO_3$, der Hauptbestandteil (Alit) des Portlandzementklinders.** By ERNST JÄNECKE. *Zeitschrift für anorganische Chemie*, Vol. 89, 1914, No. 4, pp. 355–69.

**Cobalt: Ueber neue massanalytische Methoden zur Bestimmung von Kobalt neben Nickel.** By ALBERT METZL. *Zeitschrift für analytische Chemie*, Vol. 53, 1914, No. 9, pp. 537–41.

**Copper Sulfide: Determination of Cuprous and Cupric Sulfide in Mixtures of One Another.** By EUGEN POSNJAK. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 12, pp. 2475–9.

**Cotton: The Preparation of Absorbent Cotton.** By JULES GARCON. *Textile World Record*, Vol. 48, 1914, No. 2, pp. 76–8.

**Dyes: Notes on Color Mixing and Possible Future Innovations and Economical Applications in the Same.** By RAFFAELE SANSONE. *Textile Colorist*, Vol. 36, 1914, No. 431, pp. 349–52.

**Dyes: The Uses of Natural Dyestuffs.** By EDWARD S. CHAPIN. *Textile Colorist*, Vol. 36, 1914, No. 431, pp. 329–31.

**Electrolysis: Die Verarbeitung der bei der Elektrolyse der Kali-Endlangen Gewonnenen Stoffe.** By DIETZ. *Zeitschrift für angewandte Chemie*, Vol. 27, 1914, No. 84, pp. 569–72.

**Engineers: The Engineer as a Factor in Modern Warfare.** By JOSEPH E. KUHN. *Engineering Record*, Vol. 70, 1914, No. 20, pp. 526–8.

**Gas: An Electrical Process for Detarring Gas.** By F. W. STEERE. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 12, pp. 775–78.

**Industry: Panic Economics and Emergency Problems with Especial Reference to the Present Industrial Situation.** By F. A. WALDRON. *The Journal of the American Society of Mechanical Engineers*, Vol. 36, 1914, No. 12, pp. 413–7.

**Iron: A Cast Iron with Unusual Structure.** By K. W. ZIMMERSCHEID. *The Iron Age*, Vol. 94, 1914, No. 20, pp. 1120–3.

**Iron: Concentration by the Goltra Process.** By WILLIAM R. PHILLIPS. *The Iron Age*, Vol. 94, 1914, No. 20, pp. 1148–50.

**Iron: Ueber eine empfindliche eisenreaktion und über eine, Methode zur kolorimetrischen Eisenbestimmung.** By L. TSCHNGAEFF AND B. ORELKEIN. *Zeitschrift für anorganische Chemie*, Vol. 89, 1914, No. 4, pp. 401–4.

**Light as a Factor of Efficiency.** By W. A. D. EVANS. *Textile World Record*, Vol. 48, 1914, No. 2, pp. 71–4.

**Liquids: New Formulas for the Flow of Fluids in Pipes.** By A. H. ANDERSON. *Engineering News*, Vol. 72, 1914, No. 22, pp. 1066–7.

**Manganese: The Occurrence and Significance of Manganese in the Seed Coat of Various Seeds.** By J. S. MCHARGUE. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 12, pp. 2532–6.

**Manganese: Ueber die quantitative Bestimmung des Mangans im Boden.** By BELA VON HORVÁTH. *Zeitschrift für analytische Chemie*, Vol. 53, 1914, No. 9, pp. 581–93.

**Photography: Some Recent Advances in Photography.** By HENRY LEFFMANN. *Journal of the Franklin Institute*, Vol. 178, 1914, No. 6, pp. 743–9.

**Refrigeration: Insulating Materials Used in Refrigeration.** By R. L. SHIPMAN. *Refrigerating Work*, Vol. 48, 1914, No. 5, pp. 28–30.

**Sanitation: Rational Basis for the Sanitation of Rivers and Harbors.** By GEORGE A. SOPER. *American Journal of Public Health*, Vol. 4, 1914, No. 11, pp. 1089–92.

**Sewage: Shellfish Conservation and Sewage Disposal.** By GEORGE A. JOHNSON. *American Journal of Public Health*, Vol. 4, 1914, No. 11, pp. 965–8.

**Sewerage System for Panama-Pacific Exposition Grounds at San Francisco.** By WILLIAM C. WILLARD. *Engineering Record*, Vol. 70, 1914, No. 20, pp. 538–9.

**Steel: Ultimate Strength of Carbon and Nickel-Steel Models of Quebec Bridge Members.** ANONYMOUS. *Engineering Record*, Vol. 70, 1914, No. 20, pp. 541–3.

**Sugar: The Estimation of Cane Sugar and Lactose in Condensed Milk by Means of Acid Mercuric Nitrate.** By CECIL REVIS AND GEORGE A. PAYNE. *The Analyst*, Vol. 39, 1914, No. 464, pp. 476–9.

**Sugar: Versuche über die Loslichkeit und Kristallisationfähigkeit des Luchers in den Betriebssaften und Sirupablaufen.** By H. CLAASSEN. *Zeitschrift des Vereins der Deutschen Zucker-Industrie*, 1914, No. 705, pp. 807–841.

**Tartaric Acid: Die quantitative Bestimmung der Weinsäure in Getränken und besonders in Weinen.** By E. P. HÄUSSLER. *Zeitschrift für analytische Chemie*, Vol. 53, 1914, No. 9, pp. 542–61.

**Water: A Qualitative Test for Water by the Use of the Acetylene-Cuprous Chloride Reaction.** By E. R. WEAVER. *Journal of the American Chemical Society*, Vol. 36, 1914, No. 12, pp. 2462–8.

**Water: Bacteriological Standards for Water on Common Carriers.** ANONYMOUS. *Engineering Record*, Vol. 70, 1914, No. 23, pp. 617–8.

**Water: Beitrag zur Wasseranalyse: Schnelle Bestimmung des Magnesiums durch Titration bei Gegenwart von Calcium.** By VICTOR FROBOESE. *Zeitschrift für anorganische Chemie*, Vol. 89, 1914, No. 4, pp. 370–6.

**Water: Permutit und Polarit zur Wasserreinigung.** By JOHN DON. *Kolloid-Zeitschrift*, Vol. 15, 1914, No. 3, pp. 132–4.

**Water: The Ultraviolet Rays and Their Application for the Sterilization of Water.** By M. VON RECKLINGHAUSEN. *Journal of the Franklin Institute*, Vol. 178, 1914, No. 6, pp. 681–704.

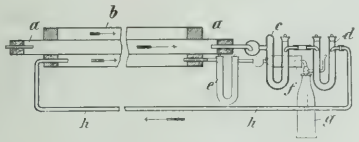
**Water Softening and Decolorization.** By W. A. SPEERY. *American Journal of Public Health*, Vol. 4, 1914, No. 11, pp. 1079–82.

**Water-Works: Municipal Ownership and Operation of Water-Works.** By M. N. BAKER. *Engineering News*, Vol. 72, 1914, No. 23, pp. 1115.

# RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Apparatus for Use in Elementary Organic Analysis. H. Brach, Oct. 6, 1914. U. S. Pat. 1,112,432.** In this apparatus a calcium chlorid tube, *c*, and a soda-lime tube, *d*, are connected in the usual manner to the combustion tube *a*. The escaping carbon monoxid and the carbonic acid which has not been absorbed, are returned through a connecting tube, *h*, to the front




portion of the outer or jacket tube *b*, in order to be completely burned while passing therethrough and to be absorbed in the soda-lime tube *e* when escaping from the tube *b*; *f* is a straight calcium chlorid tube and *g* is a wash bottle charged with a solution of palladium chlorid in order to indicate the passage of the gas and the speed of the combustion.

**Treating Mineral Oils. J. Dehnst, Oct. 6, 1914. U. S. Pat. 1,112,602.** The unpleasant odor is removed from sulfur containing mineral oils by first adding sulfur to the oil and then distilling off the portions boiling at and below 150° C. The remaining oil is then heated to a temperature above 150° C. until the evolution of hydrogen sulfide has ceased.

**Renewing Used Fullers' Earth. C. L. Parsons, Oct. 6, 1914. U. S. Pat. 1,112,650.** Fullers' earth residues resulting from oil refining processes are restored to their original condition by treatment with a solvent of the oil treated in the refining process and a solvent of the coloring matter contained in the oil. These solvents are separated from the residues.

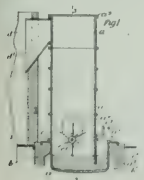
**Barium Oxid. L. E. Saunders, Oct. 6, 1914. U. S. Pat. 1,112,721.** Barium oxid is produced by decomposing barium sulfate by the heat of an electric arc maintained out of contact with the sulfate.

**Alkali Cyanogen Compounds. J. C. Clancy, Oct. 6, 1914. U. S. Pat. 1,112,893.** Calcium cyanamid and an alkali-metal sulfid are heated to a reacting temperature in the presence of carbonaceous material.

**Converting Cast-Iron into Steel or Malleable Iron. J. A. Hunter, Oct. 6, 1914. U. S. Pat. 1,112,909.** Cast-iron is heated to a high temperature but below its melting point and subjected at such temperature to the action of nitric acid.

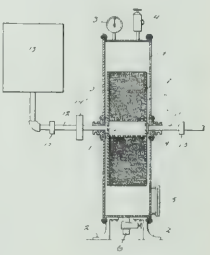
**Improvement of Inferior-Grade Rubbers. D. Spence and W. F. Russell, Oct. 6, 1914. U. S. Pat. 1,112,938.** Inferior grade rubber is subjected to the action of metallic sodium in the presence of moisture.

**Hydrogen Production. C. Bosch and W. Wild, Oct. 6, 1914. U. S. Pat. 1,113,097.** Hydrogen is produced by passing carbon monoxid and steam at a temperature between 350° C. and 650° C. over a catalytic agent in lumps containing more than 30 cobalt and a non-metallic, indifferent refractory and porous material.



**Lead Oxid. W. Innes, Oct. 6, 1914. U. S. Pat. 1,113,123.** Molten lead in the pot *a* is acted upon by the stirrer *c*, the blades of the stirrer dipping into the molten lead and throwing it upward to atomize it.

**Lard Substitute. J. C. Chisholm, Oct. 6, 1914. U. S. Pat. 1,113,151.** Oil to be hydrogenated and hydrogen are forced by centrifugal action outwardly through a porous drum formed of spirally wound wire or fine mesh wire gauze of catalytic material.



**Varying the Velocity of Detonation of Explosives. C. A. Woodbury, Oct. 13, 1914. U. S. Pat. 1,113,275.** The velocity of detonation of dynamite is controlled by utilizing large or small grains of ammonium nitrate. Where a relatively low velocity of detonation is desired, grains of ammonium nitrate of a relatively large size are employed.

**Detinning Process. W. Savage, Oct. 13, 1914. U. S. Pat. 1,113,491.** The scrap to be detinned is subjected to the action of a slime containing tin ammonium chlorid and gray tin. The slime transforms the white tin to be removed into non-adherent gray tin. The gray tin is transformed into white tin by melting.

**Electrolyte for Use in Electro-Metallurgy. N. H. M. Dekker, Oct. 13, 1914. U. S. Pat. 1,113,546.** An anode and a cathode are placed in an electrolyte consisting of a salt of the metal to be refined but no water except the water of crystallization of the salt and a current is passed through the electrolyte.

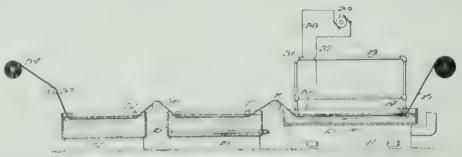
**Caoutchouc Substances. F. Hofmann & C. Coutelle, Oct. 13, 1914. U. S. Pat. 1,113,630.** The caoutchouc substance is produced by polymerizing isoprene in the presence of about 1 to 2 per cent of urea.

**Colored Caoutchouc Substances. R. Ditman, Oct. 13, 1914. U. S. Pat. 1,113,759.** The caoutchouc materials to be colored are treated with organic vat dyes and are then vulcanized by heating with sulfur at the vulcanization temperature.

**Acetic Anhydrid. W. A. Beatty, Oct. 13, 1914. U. S. Pat. 1,113,927.** Sulfuric anhydrid is mixed with carbon tetrachlorid and the products of the reaction are used to react upon sodium acetate.

**Treatment of Oils, Fats, Etc. N. Testrup, Oct. 20, 1914. U. S. Pat. 1,114,067.** Unsaturated organic bodies are hydrogenated by subjecting them in a state of minute sub-division to the action of hydrogen and a catalyzer.

**Method for Cleaning Metals. A. A. Nelson, Oct. 20, 1914. U. S. Pat. 1,114,635.** The iron or steel to be cleaned is first subjected to the action of an electric current as a cathode in a bath of a fused alkali metal salt, preferably sodium or potassium



hydroxid, whereby a thin covering or surface film of the alkali metal is deposited upon the iron or steel. The iron or steel is then passed through a bath of hot water where the alkali metal film combines with the water with such violence as to remove rust, scale, oil or other impurities upon the surface of the metal.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF DECEMBER, 1914

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid | Lb. | 31 | @ | 33 |
| Acetic Acid (28 per cent) | C. | 1 75 | @ | 2 00 |
| Acetone (drums) | Lb. | 17 | @ | 20 |
| Alcohol, denatured (180 proof) | Gal. | 33 | @ | 35 |
| Alcohol, grain (188 proof) | Gal. | 2 58 | @ | 2 60 |
| Alcohol, wood (95 per cent) | Gal. | 45 | @ | 47 |
| Amyl Acetate | Gal. | 2 75 | @ | — |
| Aniline Oil | Lb. | 30 | @ | 50 |
| Benzoic Acid | Lb. | 60 | @ | 70 |
| Benzol (90 per cent) | Gal. | 34 | @ | 35 |
| Camphor (refined in bulk) | Lb. | 44 1/2 | @ | — |
| Carbolic Acid (drums) | Lb. | 50 | @ | 52 |
| Carbon Bisulfide | Lb. | 7 | @ | 8 |
| Carbon Tetrachloride (drums) | Lb. | 12 | @ | — |
| Chloroform | Lb. | 30 | @ | 35 |
| Citric Acid (domestic), crystals | Lb. | 55 | @ | 57 |
| Dextrine (corn) | C. | 2 77 | @ | 3.02 |
| Dextrine (imported potato) | Lb | — | @ | — |
| Ether (U. S. P., 1900) | Lb. | 15 | @ | 20 |
| Formaldehyde | Lb. | 8 1/2 | @ | 9 1/2 |
| Glycerine (dynamite) | Lb. | 21 | @ | 21 1/2 |
| Oxalic Acid | Lb. | 13 | @ | 14 |
| Pyrogallic Acid (bulk) | Lb. | 1 90 | @ | 2.10 |
| Salicylic Acid | Lb. | 67 1/2 | @ | 70 |
| Starch (cassava) | Lb. | 3 1/4 | @ | 4 |
| Starch (corn) | C. | 1.99 | @ | 2 20 |
| Starch (potato) | Lb. | — | @ | — |
| Starch (rice) | Lb. | — | @ | — |
| Starch (sago) | Lb | — | @ | — |
| Starch (wheat) | Lb. | 5 | @ | 10 |
| Tannic Acid (commercial) | Lb | 60 | @ | 66 |
| Tartaric Acid, crystals | Lb | 43 | @ | 44 |

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lead (brown, broken) | Lb. | 7 1/4 | @ | 7 1/2 |
| Acetate of Lime (gray) | C. | 2.00 | @ | 2.05 |
| Alum (lump) | C. | 2.75 | @ | 3.00 |
| Aluminum Sulfate (high-grade) | C. | 1.10 | @ | 1.50 |
| Ammonium Carbonate, (domestic) | Lb. | 8 1/4 | @ | 9 |
| Ammonium Chloride, (gray) | Lb. | 6 1/4 | @ | 6 3/4 |
| Aqua Ammonia (drums) 16° | Lb. | 2 1/4 | @ | 2 1/2 |
| Arsenic (white) | Lb. | 4 1/2 | @ | 6 |
| Barium Chloride | Ton | 50.00 | @ | 60.00 |
| Barium Nitrate | Lb. | 15 | @ | 16 |
| Barytes (prime white, foreign) | Ton | 19 00 | @ | 25.00 |
| Bleaching Powder (35 per cent) | C. | 1.37 1/2 | @ | 2.00 |
| Blue Vitriol | C. | 4.35 | @ | 4.55 |
| Borax, crystals (bags) | Lb. | 3 3/4 | @ | 4 1/2 |
| Boric Acid, crystals (powd.) | Lb. | 7 | @ | 8 |
| Brimstone (crude, domestic) | Long Ton | 22.00 | @ | 22.50 |
| Bromine (bulk) | Lb. | 40 | @ | 50 |
| Calcium Chloride (lump) | Ton | 11.70 | @ | 12.00 |
| Chalk (light precipitated) | Lb | 4 1/2 | @ | 5 1/2 |
| China Clay (imported) | Ton | 14.00 | @ | 16.00 |
| Feldspar | Ton | 8.00 | @ | 14.00 |
| Fuller's Earth (powdered, foreign) | C. | 80 | @ | 90 |
| Green Vitriol (bulk) | C. | 30 | @ | 32 |
| Hydrochloric Acid (18°) | C. | 1.15 | @ | 1.65 |
| Iodine (resublimed) | Lb. | 3.75 | @ | 4.00 |
| Lead Nitrate | Lb. | 8 | @ | 8 1/8 |
| Litharge (American) | Lb. | 5 | @ | 5 1/4 |
| Lithium Carbonate | Lb. | 1.00 | @ | 1.10 |
| Magnesium Carbonate | Lb. | 4 1/4 | @ | 5 1/4 |
| Magnesite "Calcined" | Ton | 40.00 | @ | 50.00 |
| Nitric Acid (36°) | Lb. | 3 7/8 | @ | 4 1/4 |
| Phosphoric Acid (sp. gr. 1.75) | Lb. | 28 | @ | 28 1/2 |
| Phosphorus | Lb. | 35 | @ | 95 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate | Lb. | 12 | @ | 14 |
| Potassium Bromide | Lb. | 70 | @ | 80 |
| Potassium Carbonate (calcined), 80 @ 85% | C. | 5 1/2 | @ | 6 |
| Potassium Chlorate, crystals | Lb. | 15 | @ | |
| Potassium Cyanide (bulk), 98–99% | Lb | 25 | @ | 30 |
| Potassium Hydroxide | Lb. | 8 | @ | 9 |
| Potassium Iodide (bulk) | Lb. | 3 15 | @ | 3 25 |
| Potassium Nitrate (crude) | Lb. | — | @ | — |
| Potassium Permanganate (bulk) | Lb. | 15 | @ | 20 |
| Quicksilver, Flask (75 lbs.) | | 51 00 | @ | 54 00 |
| Red Lead (American) | Lb. | 5 1/2 | @ | 6 |
| Salt Cake (glass makers') | C. | 55 | @ | 65 |
| Silver Nitrate | Oz | 31 1/2 | @ | 32 3/4 |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash (48 per cent) | C. | 67 1/2 | @ | 72 1/2 |
| Sodium Acetate | Lb. | 5 | @ | 7 |
| Sodium Bicarbonate (domestic) | C. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate (English) | Lb. | 3 1/2 | @ | 4 |
| Sodium Bichromate | Lb. | 4 3/4 | @ | 5 |
| Sodium Carbonate (dry) | C. | 60 | @ | 80 |
| Sodium Chlorate | Lb. | 14 | @ | — |
| Sodium Hydroxide (60 per cent) | C. | 1.55 | @ | 1.57 1/2 |
| Sodium Hyposulfite | C. | 1.60 | @ | 1.90 |
| Sodium Nitrate (95 per cent, spot) | C. | 1.85 | @ | 1.90 |
| Sodium Silicate (liquid) | C. | 85 | @ | 1.15 |
| Strontium Nitrate | Lb. | 15 | @ | 17 |
| Sulfur, Flowers (sublimed) | C. | 2.20 | @ | 2.60 |
| Sulfur, Roll | C. | 1.85 | @ | 2.15 |
| Sulfuric Acid (60° B) | C. | 85 | @ | 1.00 |
| Talc (American) | Ton | 15.00 | @ | 20.00 |
| Terra Alba (American), No. 1 | C. | 75 | @ | 80 |
| Tin Bichloride (50°) | Lb. | 9 3/4 | @ | 10 |
| Tin Oxide | Lb. | 38 | @ | 40 |
| White Lead (American, dry) | Lb. | 5 | @ | 5 1/4 |
| Zinc Carbonate | Lb. | 8 1/4 | @ | 8 3/4 |
| Zinc Chloride (granulated) | Lb. | 4 1/2 | @ | 5 |
| Zinc Oxide (American process) | Lb. | 5 3/8 | @ | 6 3/8 |
| Zinc Sulfate | C. | 2.35 | @ | 2.70 |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax (pure white) | Lb. | 45 | @ | 57 |
| Black Mineral Oil, 29 gravity | Gal. | 12 1/2 | @ | 13 |
| Castor Oil (No. 3) | Lb. | 8 1/4 | @ | 9 |
| Ceresin (yellow) | Lb. | 10 | @ | 25 |
| Corn Oil | C. | 5.70 | @ | 5.75 |
| Cottonseed Oil (crude), f. o. b. mill | Gal. | 36 | @ | 36 1/2 |
| Cottonseed Oil (p. s. y.) | Lb. | 5 1/2 | @ | 6 |
| Cylinder Oil (light, filtered) | Gal. | 20 | @ | 25 |
| Japan Wax | Lb. | 10 | @ | 11 |
| Lard Oil (prime winter) | Gal. | 90 | @ | 92 |
| Linseed Oil (raw) | Gal. | 45 | @ | -- |
| Menhaden Oil (crude) | Gal. | 33 | @ | — |
| Naphtha, 68 @ 72° | drums | — | @ | 17 |
| Neatsfoot Oil (20°) | Gal. | 96 | @ | 98 |
| Paraffine (crude, 120 & 122 m. p.) | Lb. | 3 1/8 | @ | 3 1/4 |
| Paraffine Oil (high viscosity) | Gal. | 26 | @ | 27 |
| Rosin ("F" grade) (280 lbs.) | Bbl. | 3 80 | @ | 3.90 |
| Rosin Oil (first run) | Gal. | 25 | @ | — |
| Shellac, T. N. | Lb. | 14 | @ | 14 1/2 |
| Spermaceti (cake) | Lb. | 28 | @ | 30 |
| Sperm Oil (bleached winter), 38° | Gal | 70 | @ | 71 |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid (double-pressed) | Lb. | 9 | @ | 11 |
| Tallow (acidless) | Gal. | 62 | @ | 63 |
| Tar Oil (distilled) | Gal. | 30 | @ | 31 |
| Turpentine (spirits of) | Gal. | 46 | @ | 46 1/2 |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum (No. 1 ingots) | Lb. | 18 1/2 | @ | 19 |
| Antimony (Hallet's) | Lb. | 14 1/2 | @ | 15 1/2 |
| Bismuth (New York) | Lb. | 2.80 | @ | 2.90 |
| Bronze powder | Lb. | — | @ | — |
| Copper (electrolytic) | C. | 13 1/8 | @ | 13 1/4 |
| Copper (lake) | C. | 13 1/4 | @ | 13 3/8 |
| Lead, N. Y. | C. | | 3.80 | |
| Nickel | Lb. | — | @ | — |
| Platinum (refined) | Oz. | 50.00 | @ | 52.00 |
| Silver | Oz. | 48 1/2 | @ | 50 |
| Tin | C. | 33.75 | @ | 33.87 1/2 |
| Zinc | C. | 5.60 | @ | 5.65 |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | C. | 2.55 | @ | 2.62 1/2 |
| Blood (dried) | Unit | 2.80 | @ | 2.90 |
| Bone, 4 1/2 and 50 (ground, raw) | Ton | 30 00 | @ | — |
| Calcium Cyanamid | Unit of Ammonia | 2 30 | @ | 2.35 |
| Calcium Nitrate (Norwegian) | C. | — | @ | — |
| Castor meal | Unit | — | @ | — |
| Fish Scrap (domestic, dried) | Unit | 3.00 | & | 10 |
| Phosphate, acid (16 per cent bulk) | Ton | 7.00 | @ | — |
| Phosphate rock; f. o. b. mine | | | | |
| Florida land pebble (68 per cent) | Ton | 2.25 | @ | 2.50 |
| Tennessee (70–80 per cent) | Ton | 5 00 | @ | 5.50 |
| Potassium, "muriate," basis 80 per cent | Ton | | nominal | |
| Pyrites (furnace size, imported) | Unit | 13 | @ | — |
| Tankage (high-grade) | Unit | 2 80 | & | 10 |

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# EDITORIALS

## ANNUAL ELECTION AND REPORTS OF OUR SOCIETY

The results of the ballot for the election of officers of the American Chemical Society are recorded in the January number of the Journal of the Society. Professor Charles H. Herty was elected President of the Society for the year 1915. The new directors, elected for three years beginning January 1, 1915, are Alexander Smith and E. G. Love. The counsellors-at-large for the three-year term are E. C. Franklin, F. K. Cameron, G. B. Frankforter, and G. A. Hulett.

CHARLES HOLMES HERTY, PRESIDENT AMERICAN CHEMICAL SOCIETY

Charles Holmes Herty was born at Milledgeville, Georgia, December 4, 1867. He attended the University of Georgia for his undergraduate training, receiving the degree of Ph.B. in 1886. Entering Johns Hopkins University, he pursued graduate courses in Chemistry, Mineralogy and Geology, and received the Ph.D. degree in 1890. In 1891 he became instructor in chemistry in the University of Georgia and he served as adjunct professor there from 1894 until 1902. While on leave of absence, 1899–1900, he studied under Werner at Zürich and with Witt and von Knorre at Berlin.

In consequence of a conversation with Witt, his attention was directed to the wasteful methods practiced in the turpentine industry in America. Returning to Georgia he began investigations in the southern field, using the apparatus now known as the "Herty Cup." This pioneer work required great patience and steadfast confidence in the correctness of his views and involved much labor and tact in meeting the opposition of prejudice and ignorance. In 1902 he resigned his position in the University of Georgia to accept one with the United States Bureau of Forestry. In the Summer of 1903 he studied the turpentine industry in southwestern France and in Austria and the marketing of naval stores in London. In 1904 he resigned his position with the Bureau of Forestry and devoted his entire time to securing the manufacture of his cups on a large commercial scale and supervising their installation in a large number of districts. More than a hundred million of these cups are now in use. The saving in resinous products and in the utilization of trees as lumber has been very great.

In 1905, Dr. Herty became professor of general and industrial chemistry in the University of North Carolina and since that time he has published a number of investigations upon volatile oils, resins, etc., especially in relation to the varnish, paint, and soap industries. He has also found opportunity for some important researches in inorganic chemistry, particularly in the field of double salts and complex ammonia compounds and in connection with the hypothesis of Werner, where he has rendered valuable service. His rapid method for determining oil in cottonseed products is widely used and has proved most useful in this important southern industry.

The reports of the various officers also published in the January number of the Journal of the Society present a great deal of material which every member will find interesting and instructive. The American Chemical Society is now the largest technical society in the world, enrolling over 7,170 active members. Its local activities are divided into forty-five local sections. The society distributes 360,000 copies of its journals per year—almost 1,000 copies per day. The Board of Directors administers a budget of over $104,000 per year.

A careful study of many of the items set forth in these reports must certainly impress the reader with the substantial growth and far-reaching influence of the American Chemical Society and its valuable service to the chemical and other scientific professions.

# ORIGINAL PAPERS

## TITANIUM AND ITS EFFECTS ON STEEL[1]

By George F. Comstock

Titanium is one of the chemical elements which is widely distributed in the earth's crust in small quantities but is not especially abundant. It has a very strong affinity for oxygen, and is always found in nature as an oxide, its principal ores being rutile, the fairly pure dioxide, and ilmenite, a mixture of iron and titanium oxides. One of the element's chief peculiarities is the readiness with which it combines with nitrogen. It is one of the very few elements which will "burn" in an atmosphere of nitrogen. Its dioxide is one of the most stable compounds known, and the expenditure of great energy is required to decompose it. Thus it follows that when titanium is separated from its oxygen, it will readily re-combine with it and energy will be evolved again in the form of heat.

The value of titanium in the steel industry is due largely to the fact that its dioxide is so much more stable than iron oxide that its action in robbing melted steel of its oxygen, or "deoxidizing" it, is very powerful. In order to obtain titanium in a form useful for this purpose, it is necessary to reduce the oxides found in nature to some metallic state. There are two known ways of doing this: (1) by reduction with carbon under the intense heat of the electric arc, forming a carbide of titanium; (2) by an alumino-thermic reaction, whereby aluminum is oxidized at a high temperature at the expense of the titanium, and an alloy of titanium, aluminum and iron is produced. The carbide of titanium is the form most generally used, for reasons that will be explained below.

Before proceeding to consider the effects of titanium on steel, it may be well to explain more clearly the relation of the element to the compounds mentioned above. Arranged in the order of increasing stability we have the series:

Titanium,
Titanium carbide,
Titanium nitride,
Titanium oxide.

Each member of this series tends under favorable conditions to be converted into one of the following members. Thus metallic titanium when heated to redness in pure nitrogen forms titanium nitride, but when heated in air only, the oxide is formed. The nitride when heated to redness in air is slowly converted to the oxide, but the carbide burns vigorously in air, forming titanium dioxide. The reverse reaction, driving the oxide back to carbide, takes place only at very high temperatures and with the expenditure of great energy. Even at the temperature of the blast furnace titaniferous ores do not give more than 1 per cent of titanium in the pig iron. This is probably present partly as carbide and partly as cyanonitride, a mixture of carbide and nitride. Although in the blast furnace titanium nitride is sometimes formed, it is not present in the titanium-carbide alloy used in treating steel, for at the temperature of the electric arc furnace and with the reducing atmosphere and excess carbon used, the nitride is dissociated in favor of the carbide.

Besides titanium, there are other elements that are used more or less frequently to deoxidize steel. Among these are aluminum, manganese and silicon. The comparative efficiency of these elements as "corrective agents" for defects in steel ingots was thus tabulated by Prof. Bradley Stoughton in an article appearing in the *Railway Age Gazette*, Feb. 7, 1913, the elements being given in the order of their effectiveness:

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Prevention of blowholes | Al | Ti | Si | V | Mn |
| Removal of oxides of Fe and Mn | Ti | Si (weakly) | | | |
| *Hindering this removal* | *Al* | *Mn* | | | |
| Removal of all oxides and slag enclosures | Ti | | | | |
| *Hindering this removal* | *Al* | | | | |
| Removal of nitrogen | Ti | V(?) | | | |
| Breaking up and removal of iron sulfide | Mn | Ti(?) | | | |
| Causing a pipe | Al | Si | Ti | V | Mn |
| Hindering segregation | Al | Ti | V | | |
| *Promotion of segregation* | *Mn* | *Si* (sometimes) | | | |

A general outline of the influence of titanium on steel is given above and at the same time it is shown that for general effectiveness titanium is the best of the various deoxidizers used. For these purposes the carbide is at least as valuable as the pure metal in regard to the results obtained. As to expense there is a very great difference in favor of the carbide, as this can be obtained in carload lots for 8 cents per lb. with a titanium content of 15 to 20 per cent, while the cost of metallic titanium would be prohibitive. The material sold at this price is known as "Ferro Carbon-Titanium," and is made at Niagara Falls, N. Y. It consists of microscopic particles of titanium carbide held in a matrix similar to gray cast iron. When added to melted steel the matrix dissolves quickly, and the particles of titanium carbide are rapidly diffused throughout the bath, where they react with great vigor on the oxygen present.

The aluminothermic alloy, which contains very little carbon, is of course an alloy of both aluminum and titanium in iron, and hence its use produces the above-mentioned effects of both these elements. The chief objection to the use of aluminum is its harmful effect in hindering the removal of oxide and slag enclosures. Aluminum oxide, which is formed when steel is deoxidized by this element, is exceedingly infusible, and its tendency toward making all metallurgical slags infusible and viscous is notorious. Hence these particles of alumina (more or less pure) solidify in steel as soon as they are formed, and have no tendency to rise into the slag at the top of the ladle or mold. Moreover, by mixing with other small slag inclusions in the steel, the alumina makes them more viscous, and helps to keep them back in the metal. In the same way when silicon alone is used to deoxidize steel, the metal is filled with small inclusions of iron and manganese silicates, which do not remove themselves before solidification.

[1] Presented before the New York Section of the Society of Chemical Industry, Chemists' Club, November 20, 1914.

Titanium oxide, however, acts as a flux for silicates and other slags that may be in the steel, making them fluid enough to rise to the top of the metal and pass into the slag under conditions that might otherwise have held them back in the metal. Various researches have demonstrated this action of titanic oxide in rendering slags more fluid, when added in not too large amounts. Thus it is seen that the best cleansing action is obtained when the titanium is added without aluminum, *i. e.*, in the form of the carbide. The aluminothermic alloy should be used only in the few rare cases where the carbon of the ferro carbon-titanium alloy could not be tolerated in the steel. In soft steels the increase in carbon content from this addition as usually practiced would not be more than about 0.01 per cent so that the cases where this would make any material difference are very few indeed. Practically all the titanium used in steel in

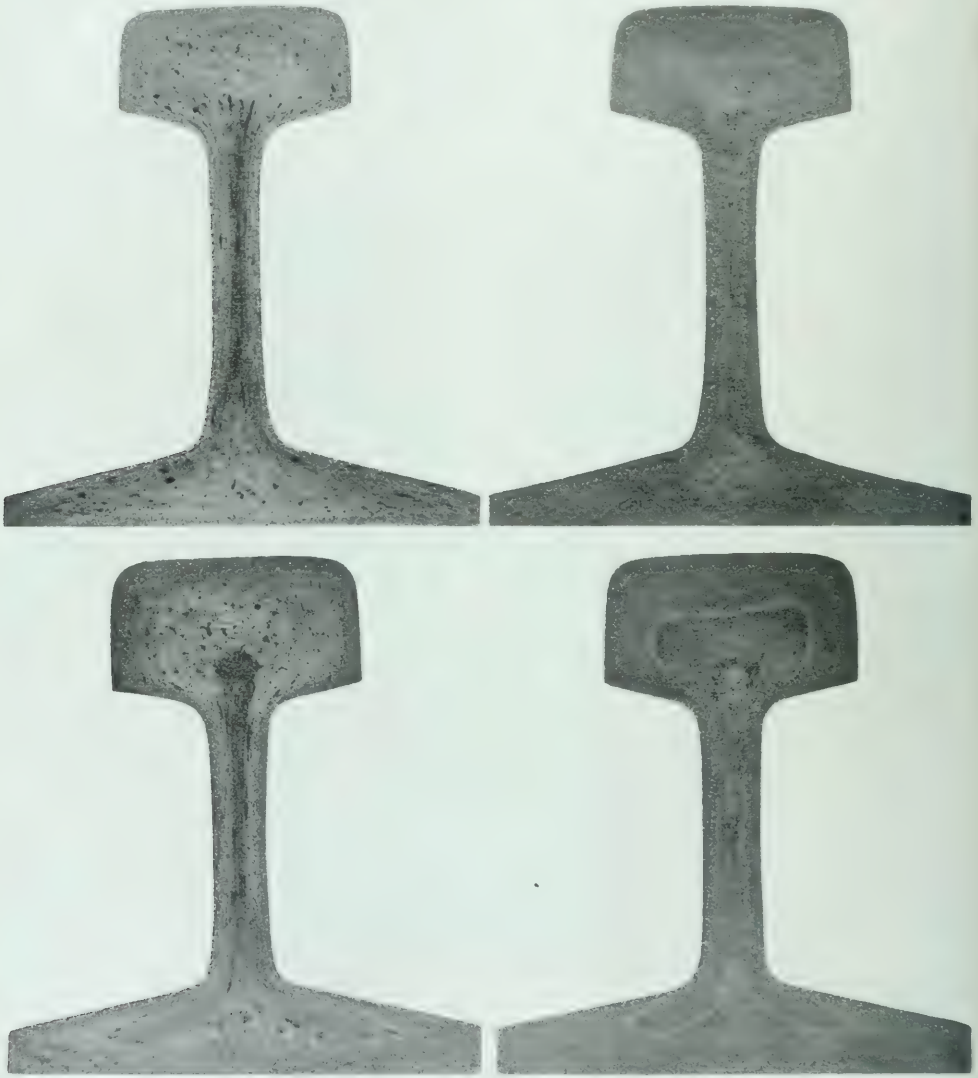


FIG. 1—SULFUR PRINTS OF UNTREATED "A" RAILS
The black spots indicate where small sulfide inclusions are thickly segregated.

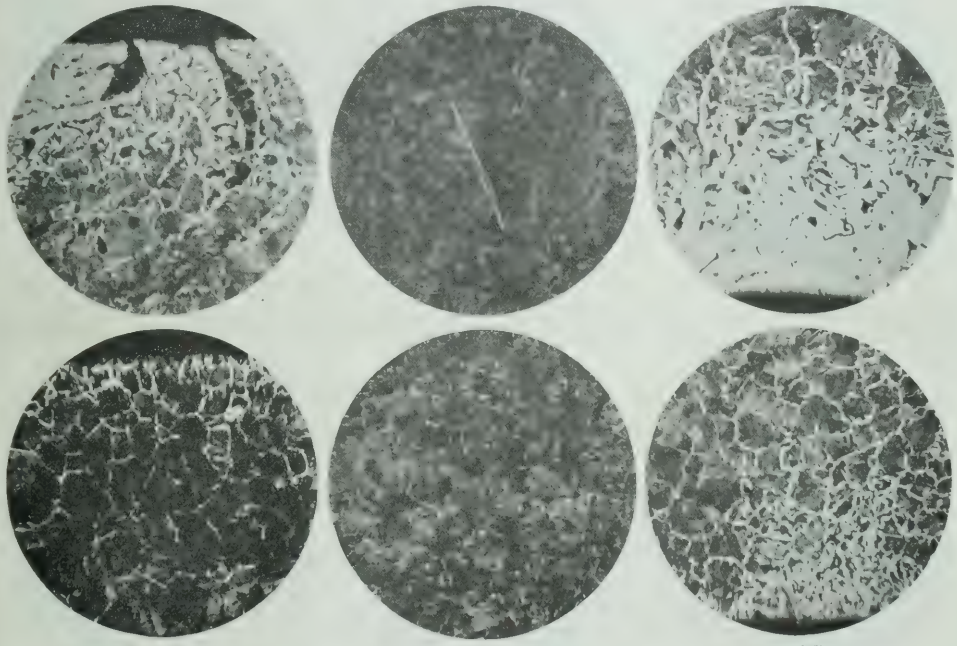
FIG. 2—SULFUR PRINTS OF TITANIUM TREATED "A" RAILS
The small size and uniform distribution of these spots are characteristic of titanium-treated rails.

this country at the present time is in the form of ferro carbon-titanium, and a large percentage of this is used for rail steel, although its use in other steels is growing steadily.

"Titanium steel," properly speaking, is not made commercially at present. Such a title naturally implies a steel whose properties are dependent to an appreciable extent on a certain content of titanium. But the advantages of the titanium-treated steels as made today are due to greater soundness, cleanness, and less segregation, and not, as far as we know at present, to the small amount of titanium left in the solid metal. In no case has over 0.025 per cent of titanium been found in any sample of titanium-treated steel analyzed at our laboratories. Of course it is possible that this very small titanium content is in some way associated with impurities so as to distribute them uniformly, thus preventing segregation, but we do not know that there is any such association and hence are not justified in considering titanium-treated steel as a true alloy steel. Under the usual conditions of manufacture it is very difficult to make steel absorb more titanium than the 0.025 per cent noted above and no use that would warrant the commercial production of a real "titanium steel" has yet been found for a product containing larger quantities.

Steels made by the Bessemer, Open-Hearth, or Crucible processes may be, and are, treated with titanium, but most of this element is used in Open-Hearth steel on account of the greater tonnage of this material manufactured. The alloy is furnished in various sizes, from lumps of about 1 inch diameter to powder, according to the quantity of steel to be treated at one time. For the best results it must be added to the melted steel as it flows from the furnace to the ladle. The addition must of course be entirely completed before the slag has begun to flow out on top of the metal. After the addition, the steel must be held in the ladle for from 3 to 10 minutes, depending on the size of alloy used and the mass of steel treated, to allow the titanium to become thoroughly diffused, the deoxidizing reactions to take place, and the titanium and other oxides to rise out of the metal into the slag. Then the steel is teemed as usual into the molds where no further additions should be made.

The amount of alloy recommended for use in rail steel is 13 lbs. per ton, which means, since the ferro carbon-titanium is guaranteed to carry over 15 per cent titanium, an addition of 0.1 per cent of metallic titanium. A higher grade alloy is not used because its rate of solution in the melted steel would be slower. The price of rails treated in this way is about 5 per cent above the price of ordinary rails. For castings and soft steels a smaller amount of alloy may be added, but in every case it is important to allow time for the reaction to take place completely in the ladle, before



Tops of Heads | Upper Central Parts of Webs | Bottoms of Flanges

FIG. 3—TYPICAL UNTREATED (UPPER) AND TITANIUM-TREATED (LOWER) "A" RAILS × 100: REDUCED BY ONE-FOURTH

The above samples (etched with picric acid) show dark crystals of pearlite with light streaks of ferrite between, except in the web of the untreated rail. This rail was badly segregated, and had a very hard and brittle spot in its web. Part of this spot is shown above, mostly pearlite with one long, light crystal of cementite or iron carbide. Note the seams at the top of the head of the untreated rail, and the scarcity of pearlite at its upper and lower edges.

the steel gets into the molds. The heat of the reaction will usually prevent the formation of a skull in the ladle, and it is not necessary to tap the steel hotter from the furnace to allow for cooling while the ladle is being held.

Smaller amounts of titanium have been tried in rail steel, with the usual precautions of holding in the ladle, etc., but the best results have not been obtained. This indicates not only that it is not safe to skimp the amount added, but also that merely holding the steel in the ladle will not give the cleanness and homogeneity that result from the titanium treatment.

these gas bubbles are trapped in the freezing metal before they can escape, blowholes are formed, and these holes may be welded together when the steel is rolled or forged. Low-carbon steels, even if treated with titanium, always contain blowholes, but, the steel being normally cleansed by the titanic oxide, they are free from slag and are closed up when the ingots are worked. If they become oxidized, however, or contain slag, they will open up as seams or remain as slag inclusions in the metal. It is well known that if steel is completely deoxidized, and no blowholes are formed, a large shrinkage cavity, or

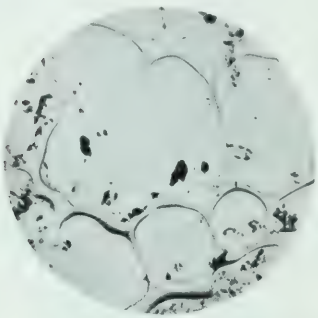


FIG. 4—TITANIUM CARBIDE × 100
Reduced by One-fourth
Made in laboratory. Large rounded grains are light violet color. Network is yellowish white, probably iron carbide. Black spots are pits caused by grinding. Not etched.

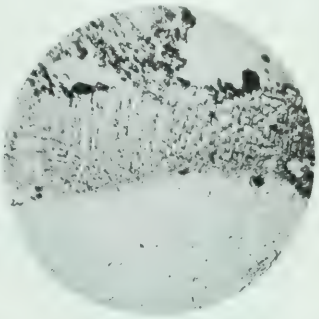


FIG. 5—TITANIUM CARBIDE × 200
Reduced by One-fourth
Near top, dissolving into steel below with particles of carbide scattered through the steel. Not etched.

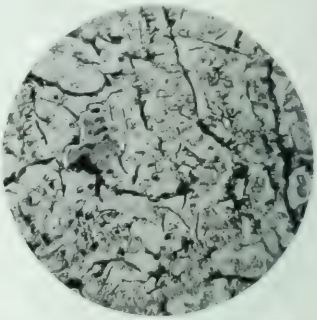


FIG. 6—FERRO CARBON-TITANIUM × 100
Reduced by One-fourth
Black streaks are graphite. Rounded grains standing out in relief are titanium carbide. Not etched.

FIG. 7—Fe-Ti-Al ALLOY × 100
Reduced by One-fourth
Titanium about 12 per cent, aluminum about 6 per cent and carbon about 0.5 per cent. Etched with $HNO_3$.

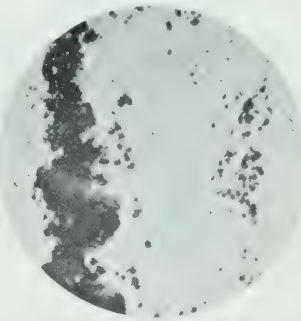


FIG. 8—Fe-Ti-Al ALLOY × 500
Reduced by One-fourth
Alloy of Swedish iron with aluminothermic ferrotitanium, showing inclusions of alumina. Not etched.

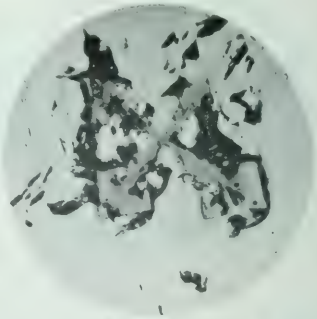


FIG. 9—Fe-Ti-Al ALLOY × 200
Reduced by One-fourth
Pink crystal of titanium nitride in aluminothermic ferrotitanium. The black spots are pits caused by grinding. Not etched.

The two great advantages of well-deoxidized steel are (1) soundness, or freedom from blowholes, and (2) absence of excessive segregation. The making of both Bessemer and Open-Hearth steel is essentially an oxidation process, the carbon being burned out of pig-iron in each case, and the steel necessarily contains a considerable quantity of oxide when first made. If this is not removed before solidification begins, the iron oxide in the steel continues reacting with the carbon, forming carbon monoxide, a gas which passes up continually in small bubbles to the surface of the metal, where it burns with a bluish flame. If some of "pipe," will form in the center of the upper part of the ingot. Titanium may cause piping, as well as other deoxidizers, but by properly designing the molds piping may be controlled so as not to give much trouble.

The dependence of segregation on deoxidation is less obvious than that of soundness. Primarily, of course, segregation is due to selective freezing. The freezing-point diagram of the iron-carbon alloys shows that with ordinary steel the first metal to freeze is of lower carbon content than the remaining liquid, and the last liquid to freeze is of higher carbon content than the already frozen solid. But with well-deoxidized steel this

selective freezing takes place in a quiet mass of pasty material, and the higher carbon liquid is so intricately entangled in the lower carbon solid that it does not have a chance to collect in the center of the ingot to any great extent, and is finally frozen together with the lower carbon material. The action is somewhat like that of a sponge holding water. But assume that this steel is not well deoxidized, but is giving off gas, produced by the reaction $FeO + C = Fe + CO$, during solidification. This gas, being of course much will be excessive segregation. Phosphorus is subject to this action in the same way as carbon; sulfur, existing in the steel as small non-metallic globules composed of a mixture of iron and manganese sulfides with a freezing point not much, if any, higher than that of the metal, is even more affected. [For this explanation of the relation between segregation and oxides in steel, the writer is indebted to Mr. N. Petinot, Metallurgist of the Titanium Alloy Manufacturing Co.]

Aluminum, and probably also vanadium and silicon,

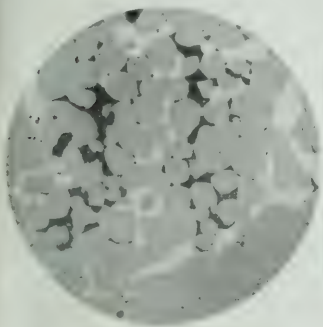


FIG. 10—TITANIUM NITRIDE × 100
Reduced by One-fourth
Made in laboratory. The rounded gray grains are bright yellow and are probably fairly pure nitride. The white substance is probably carbide, and the black, oxide. Not etched.

FIG. 11—STEEL CONTAINING TITANIUM NITRIDE × 400
Reduced by One-fourth
Pink crystal in longitudinal section from web of titanium-treated steel rail. Not etched.

FIG. 12—STEEL CONTAINING TITANIUM NITRIDE × 200
Reduced by One-fourth
The three larger spots are pink crystals in cross section of web of titanium-treated steel rail. Not etched.

FIG. 13—ALUMINA SEGREGATION IN UNTREATED RAIL × 200
Reduced by One-eighth
Inclusions in the cross section of the web of an untreated rail. These are dark bluish gray in color. By chemical analysis 0.003 per cent of alumina was found here. Not etched.

FIG. 14—SILICATE SEGREGATION IN UNTREATED RAIL × 200
Reduced by One-eighth
Silicate, or slag, inclusions in a cross section of the web. Not etched.

lighter than the metal, has a strong tendency to rise; in rising while the metal is in a pasty condition, part liquid and part solid, it opens up passages through the steel, and each bubble of gas will take with it a little of the higher carbon liquid toward the top and center of the ingot leaving the solid lower carbon material behind. This action, multiplied many times by the millions of gas bubbles given off, will result in the formation of a large body of higher carbon material in the upper part of the ingot, or in other words, there have an effect on segregation similar to that of titanium, but with vanadium the cost of this effect would be higher, and with the cheaper agents, silicon and aluminum, not only would the cleansing action of the titanium dioxide be lacking, but impurities (silicates or alumina) would be added to the steel. In this connection it should be noted that in most rail steel that has been properly treated with titanium, very small, hard, angular, pink inclusions can be found with the microscope. These are titanium nitride, possibly

contaminated with carbide, and show that the titanium has combined with some of the nitrogen dissolved in the steel, and separated it in this form. An average of many nitrogen determinations made in our laboratories by an improved method on titanium-treated rails shows a distinctly lower amount present in *solution* in the metal, than in untreated rails. No method is known for determining nitrogen that is combined with titanium in this form. Thus the difference in nitrogen content of the metal may be due merely to the locking up of some nitrogen by titanium in the pink inclusions, or also partly to the actual removal of nitrogen from the liquid steel bath. At any rate, if it is assumed that nitrogen has an injurious effect on steel, the lower amount found by analysis must be an advantage, for even if the whole amount removed from the metal itself is still present in the pink inclusions, it could have no more ill effect in this form than any other non-metallic inclusions of the same size. As the titanium nitride inclusions are never found segregated in groups or streaks, as are alumina and silicates, but are always very small, scarce, and thinly scattered, their weakening effect on the metal is practically negligible. They have been found in titanium-treated steel axles as well as rails but not in steel castings nor soft steels, where smaller amounts of titanium have been used.

FIG. 15—SULFIDE SEGREGATION IN UNTREATED RAIL × 200
Reduced by One-eighth
Inclusions in a cross section of the web. A group like this would appear as a pure black spot on a sulfur print. Not etched.

FIG. 16—SULFIDES IN TITANIUM-TREATED RAIL × 200
Reduced by One-eighth
Typical inclusions with one small dark slag inclusion (right). This shows the dirtiest spot found in the cross section of the web of a treated rail. Not etched.

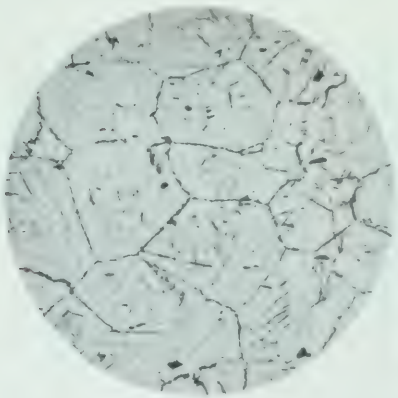


FIG. 17—BADLY SEGREGATED UNTREATED RAIL × 100
Reduced by One-twentieth
Cross section of the upper part of the web showing very brittle structure. The dark constituent is cementite or iron-carbide and the light constituent is pearlite. Etched with boiling alkaline sodium picrate.

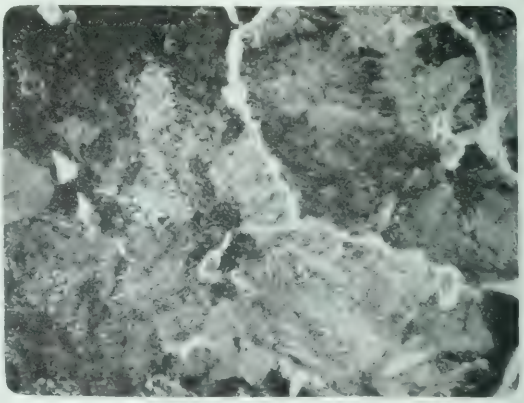


FIG. 18—TYPICAL TITANIUM-TREATED RAIL × 400
Reduced by One-twentieth
Center of head, showing normal structure: laminated pearlite, sorbite, and considerable ferrite, with a few gray sulfide globules. Etched with picric acid. (Bessemer steel.)

It is an unfortunate fact that some so-called "titanium-treated" steels have not been any better in regard to segregation than the average untreated steel. These have constituted, however, an insignificant percentage of the total number examined in our laboratories. In every case these segregated "treated" rails have not shown a titanium content of over 0.005 per cent (the average treated rails are well above this figure) and the pink nitride inclusions have also been

absent from them. These facts indicate that not enough titanium was actually added in these heats to produce the usual effects; either the heats were badly oxidized, and needed more than the usual amount of titanium, or some of the alloy was lost or wasted in the slag. It is well known that chemical reactions do not in most cases proceed rapidly to completion when only the theoretical amount of reagent is applied, but an excess of greater or less amount is usually needed. In the case of deoxidation of steel with titanium, the excess necessary is probably at least 0.005 per cent, which, it will be admitted, is a very small amount.

Having now explained the reasons for the addition of titanium to steel, and its general effects thereon, it may be of interest to give some concrete examples of the improvement, shown by testing machines and in actual service, of titanium-treated steel as compared with plain untreated steel of the same general composition. It must be emphasized again that as the amounts of titanium found in treated steels are entirely negligible, so no change in microstructure of the steel is caused by it, and the physical properties are no better than are theoretically possible with perfectly clean and sound steel of the given composition. Our most complete knowledge on this subject has been acquired with rail steel, and forty-two samples of plain and treated Open-Hearth steel rails have been exhaustively tested, physically and chemically, in our laboratories. For this purpose the samples have all been taken from the "A rails," or first rails rolled from the ingots, after the usual discards from their tops, thus representing in each case metal from the top part of an ingot, which would show the greatest amount of segregation and impurities. The "A" rails from which samples were to be taken were chosen at random from the products of various mills and at different times by the manufacturer's or the purchasing railroad's representatives, but the samples were always taken in pairs, one treated and one untreated from each rolling, so that in the final comparison the influence of the conditions of manufacture could be as far as possible eliminated. All samples submitted were tested impartially, with the same care and by the same methods, and the results have been published in our Rail Report Bulletins. The final averages of all the results are given on page 94.

Chemical analyses were made at four places on each rail: top of head, center of head, web, and flange. The lowest and highest figures for each rail were averaged, giving the average low and high results here reported.

The Landgraf-Turner endurance machine bends a thin test-bar backward and forward through a small angle by quickly alternating blows, and the results are expressed as alternations endured before fracture. The stresses applied to the test-piece are above its elastic limit.

The White-Souther endurance machine holds a test-bar in the middle, turning it very fast like an axle, while weights are suspended from its ends. The stresses applied are below the elastic limit, and the failure is thus due to fatigue. The results are expressed as revolutions endured, but many test-bars were removed unbroken after thirty or forty million revolutions.

As the above figures represent tests on twenty-one untreated rails, and twenty-one treated rails, with all other conditions kept as nearly alike as possible, it is believed that they possess real value for showing the improvement to be expected in "A" rails when properly treated with titanium. The improvement in other rails, from lower positions in the ingots, would be much less marked, but the rails that give most of the trouble in service are the segregated "A" rails; these are rendered practically as uniform and homogeneous as other rails by treatment with titanium. Titanium-treated rails are not better, probably, than the best possible untreated rail, but by this treatment the general standard of quality is unquestionably raised, uniformity is more nearly attained, and the bad heats of dangerously segregated or dirty steel are avoided.

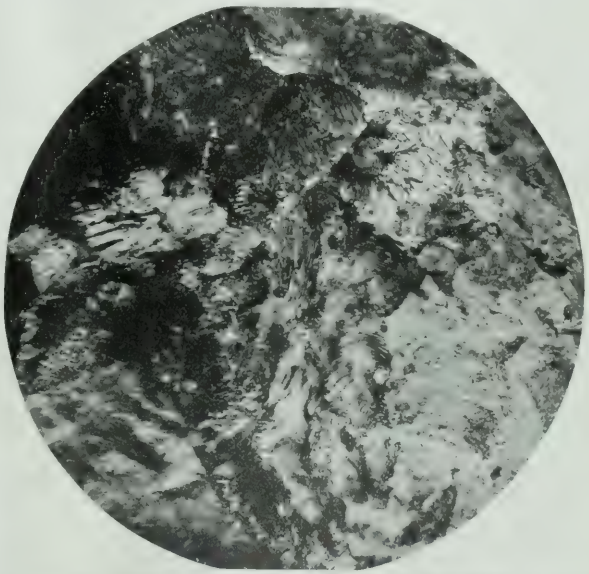


FIG. 19—TYPICAL TITANIUM-TREATED RAIL × 400 NOT REDUCED
Center of head showing normal structure, laminated pearlite, sorbite, and traces of ferrite. Etched with picric acid. (Open-Hearth steel.)

In order to acquire still more positive data on the effect of titanium on segregation in rails, seventy-nine "A" rails from different untreated heats and thirty-one similar rails from different treated heats were examined recently by means of sulfur prints and chemical analyses for carbon made on each at an upper corner

of the head and at the junction of head and web. The average difference between these two prints was 17 per cent for the untreated rails, and the worst rail showed 40 per cent, while only 29 of these 79 rails showed less than 12 per cent. For the treated rails the average difference was 3.1 per cent, and the worst one gave 11.5 per cent, none of the 31 showing over this amount.

| Chemical Analyses Percentages | Untreated Rails Low | Untreated Rails High | Treated Rails Low | Treated Rails High |
|---|---|---|---|---|
| Carbon | 0.58 | 0.82 | 0.63 | 0.76 |
| Manganese | 0.71 | 0.78 | 0.75 | 0.79 |
| Phosphorus | 0.016 | 0.026 | 0.018 | 0.023 |
| Sulfur | 0.032 | 0.058 | 0.031 | 0.040 |
| Silicon | 0.117 | 0.131 | 0.090 | 0.099 |

| Tensile Tests | Untreated Rails Head | Untreated Rails Flange | Treated Rails Head | Treated Rails Flange |
|---|---|---|---|---|
| Elastic limit | 56,071 | 55,961 | 59,738 | 60,338 |
| Ultimate strength | 118,138 | 119,385 | 124,857 | 125,690 |
| Elongation, per cent | 12.8 | 15.4 | 13.1 | 14.4 |
| Reduction of area, per cent | 14.3 | 18.5 | 15.4 | 18.2 |

| | Untreated Rails Head | Untreated Rails Web | Untreated Rails Flange | Treated Rails Head | Treated Rails Web | Treated Rails Flange |
|---|---|---|---|---|---|---|
| White-Souther | 16,550,920 | | | 23,923,628 | | |
| Brinell hardness | 220 | 248 | 216 | 226 | 235 | 227 |
| Impact resistances | 1.47 | 1.08 | 1.23 | 1.58 | 1.21 | 1.43 |
| Endurance Landgraf-Turner | 1312 | 1001 | 1324 | 1280 | 1084 | 1270 |

The impact resistances were measured with a Fremont machine, and are expressed as kilogram-meters expended in breaking a test-piece 7 by 10 mm. in cross-section.

The railroads have been acquiring data for some time in regard to the wear of titanium-treated rails in track, as compared to that of ordinary Open-Hearth rails. The results have been uniformly favorable to the treated rails, in some cases very decidedly so. For instance, on a sharp curve on the Boston Elevated Railway, titanium-treated rails laid alternately with plain rails of practically the same composition showed 41 per cent less wear after 214 days' service. In a test made by the Rock Island Railroad, titanium-treated rails in 17 months had 0.014 sq. in. abraded from their sections, on the average, while electric steel rails showed under the same conditions a loss of 0.058 sq. in., and ordinary rails 0.075 sq. in. Other instances of the same general type might also be given, but enough has surely been said to show clearly the advantages following the use of titanium in rail steel.

In axle steel it has been found similarly advantageous to use titanium for purifying the metal and preventing segregation. In steel castings the use of titanium as a deoxidizer has usually been successful and satisfactory, and in soft steel for plates and thin sheets much titanium is used. This element is preferred to any other deoxidizer because it does not leave any product of its oxidation in the steel as do aluminum and silicon, and the ingots therefore roll out smoother and the finished sheets have a better surface. Small defects on the surface of a sheet are very serious in galvanizing, so that the smoother surface of titanium-treated sheets, due to cleaner ingots, is much appreciated.

A few photomicrographs and sulfur prints are submitted to illustrate some of the points mentioned in this paper, though of course they are not intended to prove much in themselves, but merely to serve as illustrations. It is hazardous to draw conclusions from two or three trials or instances, but an average from forty or eighty tests should surely be trustworthy.

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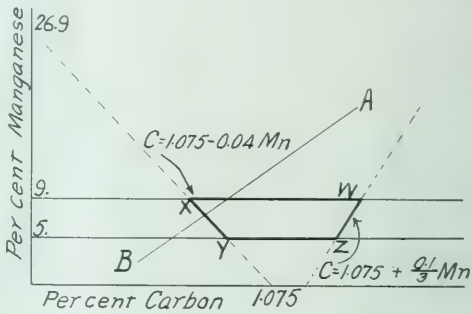
## MANGANESE STEEL[1]

By John H Hall

### COMPOSITION AND CHARACTERISTICS

Manganese steel was discovered in the early eighties, and since that time has found a place for itself wherever a steel is required that is highly resistant to wear. In the original experiments, the steel was made by mixing molten ferromanganese and carbonless Bessemer blown metal in such amounts as to give various proportions of manganese in the finished product; as a consequence the ratio of the manganese to the carbon was practically fixed, the carbon content decreasing as the manganese was diminished. With less than a certain amount of manganese, the metal proved to be extremely brittle, and in practice the manganese was seldom less than 9 per cent, the steel as generally made containing from 10 to 14 per cent manganese and from 1 to 1.5 per cent carbon. The silicon is generally from 0.2 to 0.5 per cent, the sulfur always very low (about 0.001 per cent), the phosphorus averages from 0.08 to 0.1 per cent. Small variations in the silicon and phosphorus have little effect on the properties of the steel. The sulfur is invariably low, because the manganese of the steel eliminates it by




flotation as MnS. By heating this steel to between 1000 and 1100° C., it can be made, if not of too heavy a section, to consist entirely of the metallographic constituent known as austenite.

More recent researches, in some of which the author has participated, have shown that if the carbon content of the metal is maintained at about 1 per cent, the steel will be austenitic after quenching, even if the manganese content is as low as 5 per cent or even a little less, the range of carbon content within which pure austenite can be obtained being narrow with low manganese content, and widening as the manganese content increases. This can be more readily understood by reference to the accompanying diagram showing part of the manganese steel series, in which the carbon content is plotted as abscissa and the manganese content as ordinate. Within the area WXYZ the steel consists of pure austenite when quenched. Steels immediately to the left of the line C = 1.075–0.04 Mn are more or less martensitic when quenched; steel immediately to the right of the line C = 1.075 + 0.1/3 Mn contain free cementite

[1] Presented before the New York Section of the Society of Chemical Industry, Chemists' Club, November 20, 1914.

when quenched, the amount of cementite increasing as the carbon content rises. This is also true of the prolongations of the lines for a certain distance. These lines were plotted as the result of a careful research having for its object the determination of the useful range of manganese content in these steels. The line AB represents, with no pretense at accuracy, the contents of carbon and of manganese of the steels forming the basis of the original discovery and patent. The reason why the steel was found to be martensitic and brittle when the manganese was still comparatively high, is apparent at a glance. The well-known diagram of Guillet, showing the microstructure of the steels of the iron-carbon-manganese series, is not parallel to this diagram, as Guillet's figure represents the steel in the normalized condition, whereas in this figure, the structures are those of the steel in the quenched state.

### PROPERTIES OF THE STEEL

Manganese steel has a very low conductivity for both heat and electric current, a low melting point (some 1,360° C.), a very high coefficient of expansion (making necessary a shrinkage allowance of $^5/_{16}$ inch to the foot in foundry work), and is practically non-magnetic in all ordinary conditions. In the cast state it is very brittle. The cast material after heating to 1000–1100° C. and quenching has only a moderately high tensile strength, about 60,000 to 80,000 lbs. per sq. in., a rather low elastic limit in both tension and compression, and a rather high ductility; its shearing strength is remarkably high. When rolled or forged and treated, the tensile strength is increased very greatly, sometimes reaching 150,000 lbs. per sq. in., and the ductility much improved; the other properties are not much altered. The rolled material, if untreated, is quite brittle.

The chief characteristic to which the metal owes its usefulness is its hardness. In the treated state in which the steel has to be used, this hardness is of a peculiar kind, inasmuch as hardness tests which depend upon indenting the material do not give a high figure for this steel—in fact it can be made to peen or flow in the cold under the blows of a hammer, to a considerable extent. In a way, therefore, the steel is soft; this is due to its low elastic limit. But, unless specially heat-treated, it can not be cut with tools to a sufficient extent to make machining practicable, and its resistance to most kinds of wear is extraordinary.

As the manganese content is reduced, if the carbon is kept at the proper figures, the properties change much less than was originally supposed. The strength falls off a little, the toughness diminishes progressively, and the magnetism increases a little. The resistance to wear, however, is very little altered as long as the manganese is kept above about 5 or 6 per cent, and the tendency to peen or flow decreases as the manganese content diminishes. The usefulness of these low manganese steels is, however, limited to a rather narrow field by their comparative lack of toughness; they are not extremely brittle, like the martensitic steels of the same manganese content, but they are not at all as tough as the steels containing over 10 per cent of manganese.

### USES

From this brief description of the properties of manganese steel, it will be plain that the chief use of the metal is to resist wear. Accordingly, it is very widely used for the wearing parts of stone crushers and rolls working on hard rock, for the lips and teeth of steam shovels and ladder dredges handling rock or gravel, for centrifugal pump cases and fliers, handling gritty water, for stone screens, coal cracking rolls, drive chain exposed to grit, and other service of a similar nature. For railroad and trolley frogs, switch points, crossings, etc., the cast material is very widely used, and for rails on sharp curves manganese steel is almost indispensable. These rails were formerly all of cast material, but are now very generally rolled from ingots.

It was at first thought that the steel would be very useful for car wheels, but its tendency to flow or peen under heavy cars prevented its being used for railroad work. Under light loads in mine and quarry cars, blast furnace charging barrows, etc., it is widely used. The tendency to flow or peen has also limited the usefulness of the metal for tires in such grinding mills as the Fuller and Griffin, and for the lining plates of the various forms of ball mills. In most cases this tendency has been taken care of in the design of the casting, and the steel has long been widely used for lining plates in the various types of ball mills used in the manufacture of cement. Certain of these plates, however, are in many cases made of other steels, as manganese steel has proved to peen entirely too much to make its use possible. In other cases, as for instance certain sorts of grinding mill tires, the use of a steel of lower manganese content, which peens less, has proved a successful means of overcoming the difficulty; the general application of these low manganese steels to this field is prevented by their lack of toughness, which makes it necessary to exercise very good judgment in applying them.

The mandrels used for welding iron and steel pipe have for years been made of cast iron, and have but a very short life. In the smaller sizes, a mandrel seldom makes over three lengths of pipe before it becomes so cut and scored as to be useless for further service. Ordinary manganese steel proved unsuccessful for these mandrels, as its lack of the right sort of hardness resulted in the scoring of the balls before they had made enough pipes to compensate for their high cost. Special compositions and special treatments by the score have been tried; by the use of additions of chromium, the steel can be made harder, and the treatment can be varied so that the hardness is somewhat increased without too great a sacrifice of toughness. The high coefficient of expansion of the steel, however, makes a certain amount of toughness necessary, as the balls grow hot in use and hence expand very considerably, so that if brittle they crack badly. Moreover, for reasons which will be given later, the application of heat greatly decreases the toughness of manganese steel, so that the mandrels grow brittle

with use. It must, therefore, be somewhat tough as first put in service. Hence, the successful application of manganese steel to pipe welding mandrels is still an unsolved problem.

MANUFACTURE OF THE STEEL

A simple calculation shows that the simplest and cheapest way to produce manganese steel is to mix together molten 80 per cent ferromanganese and molten soft steel containing from 0.10 to 0.25 per cent carbon. The carbon content of the ferromanganese is such that the steel resulting from this mixture is of the correct composition for the majority of uses. The steel therefore is seldom made by the crucible process, on account of the difficulty of obtaining low carbon steel by that method. This difficulty is increased by the fact that if the scrap is remelted in crucibles, the amount of carbon absorbed from a graphite pot will be excessive, because high manganese metal has a much greater tendency to absorb carbon from the graphite than metal of low manganese content. In order therefore to remelt the scrap, which for reasons of economy is essential in foundry work, it would be necessary to use clay pots, which are both troublesome and expensive. Even if the scrap were not remelted, it would be necessary to melt the low carbon steel and the ferromanganese in separate pots, as the absorption of carbon would be excessive if they were melted together in a graphite pot. Moreover, the expense of crucible melting is too great to justify the use of the process by the makers of manganese steel, except in very special cases.

The open hearth furnace can be used to produce the soft steel required, but it has its drawback. In the first place, the metal is not generally as hot as Bessemer metal, and for the majority of manganese steel foundries hot metal is essential. In the second place, most manganese steel castings are comparatively light. Hence, it is desirable that the metal be received in the foundry, not in large heats at infrequent intervals, but in small heats at short intervals. In order to make the open hearth furnace applicable under these conditions, it is necessary to use a tilting furnace and take the metal out in small lots; even then the metal generally has to be disposed of in a number of successive ladelfuls, one after the other. In most cases this is not as convenient as to have two or three heats an hour of small size for six or seven hours of the working day. Moreover, the small foundries generally find it more convenient not to pour at night, and as the open hearth furnace must be run continuously, it does not suit their purposes as well as the small Bessemer converter.

The small Bessemer plant has a number of advantages in the manufacture of manganese steel and is used in more shops than is the open hearth furnace. It makes cheap metal, though not quite as cheap as the basic open hearth furnace; it provides small lots of metal distributed over the day, it does not have to be run double turn, and it does not cost anything like as much to shut the plant down several days in the week, as it would to shut down the open hearth furnace. Even if we grant that Bessemer metal is not as good as open hearth because it is more highly oxidized, we easily see that the enormous addition of manganese will deoxidize the metal almost completely, so that this objection is not at all as valid a one as in the case of carbon steel. Moreover, the majority of manganese steel castings do not require metal any better than can be easily made in the Bessemer converter.

The steel-making problems presented in the manufacture of manganese steel are not greatly different from those encountered in any foundry, with the exception that the scrap produced, which amounts in most small foundries to some 40 or 50 per cent of the fluid metal, must for complete economy be remelted. This can be done in the open hearth furnace, although if but a single furnace is available and the chief product is manganese steel, the problem becomes a difficult one because metal containing a great deal of manganese produces a slag which cuts into the bottom of the furnace severely. In the small bottom-blown Bessemer vessel, much of the scrap produced can be used up by melting it with the pig iron in the cupola. The resulting high manganese metal can be successfully blown by taking proper precautions. In the side blown converter it has so far been practically impossible to blow high manganese mixtures, so that the users of these vessels who make a specialty of manganese steel have been quite generally forced to sell their scrap at a considerable loss. Within the last year or two, the author has conducted experiments bearing on this problem with some success.

If the scrap is remelted in the open hearth furnace, or remelted in the cupola and blown in the Bessemer converter, all the manganese contained in it is oxidized and lost in the slag. The yearly loss of money represented by this oxidized manganese amounts to a very tidy sum and many efforts have been made to remelt the scrap without loss of the manganese. This problem has been attacked in many different ways, with varying success. The most obvious solution of it is to melt the scrap in the electric furnace, which will melt it almost without loss of manganese. This is all very well from a metallurgical point of view, but when we come to figure the expense, we find that the saving, as compared for instance to remelting and blowing, is not very great. This is especially the case in shops already having a Bessemer equipment sufficient for their needs, because if they add an electric furnace to remelt their scrap, they cut down the output of the Bessemer equipment and hence raise the cost of the steel made in it. For this reason the electric furnace has not so far proved at all as useful in the manufacture of manganese steel as its inventors hoped it would. In order to make electric steel cheaply, moreover, it is necessary to use a furnace of considerable size and to keep it running continuously. This, as we have said in discussing the open hearth furnace, is a condition not well suited to the average manufacturer of manganese steel castings. The electric furnace of course produces a very high grade of metal, but as we have already said,

we do not need for manganese steel any better metal than can be easily made in the Bessemer converter.

MELTING THE FERROMANGANESE

As the total weight of ferromanganese needed for the production of manganese steel is roughly one-fifth of the weight of the blown metal, it is absolutely essential that the ferromanganese be melted. It would not be possible to add it solid to the blown metal, as the latter naturally would not be able to melt it and absorb the manganese. For many years crucibles have been used for melting the ferromanganese, in spite of the fact that crucible melting is more expensive than any other method. The expense is further increased by the fact that either hard coal or oil is commonly used for fuel, the gas burning regenerative furnaces never having been used for this purpose because of the fact that they must be run day and night. Melting in coal holes is comparatively easy, and there is no danger of the absorption of carbon from the pot, as the ferromanganese is already saturated with that metalloid. The pots are seldom covered, but this does not result in the absorption of sulfur, because it is almost impossible to make the metal absorb sulfur. The great advantage of crucible melting is that the melting losses are relatively slight, which is a most important point with so expensive a metal.

Efforts have been made from time to time to melt ferromanganese in the cupola furnace. The use of this very cheap melting method, however, has never become general because the melting losses are very high even when special precautions are taken to reduce them, and these precautions necessarily complicate the operation of the cupola. The air furnace and even the small open hearth furnace have been used to a certain extent for melting ferromanganese, but have not been generally adopted because the melting losses are quite high, and in the case of the open hearth furnace because night turn work is not commonly desirable.

The electric furnace has often been suggested as the best method of melting ferromanganese, and is being used to an increasing extent in foreign steel works making ordinary steels. It has certain disadvantages for the maker of manganese steel in large quantity. The first of these is that the total melting capacity of the furnace must be high, and this necessitates the installation of one or two large furnaces. The first cost of the furnaces is high, and to keep them idle at night results in a very considerable loss of money. The second disadvantage is that quite a large bath of metal has to be melted down and drawn off a little at a time, since the furnace will not melt the metal as fast as it is needed. Hence a considerable expense has to be incurred for the current necessary to keep the molten bath hot. In many cases, therefore, it will be found that it will not pay the maker of manganese steel to instal an electric furnace for melting his ferromanganese, unless he keeps the furnace busy at night melting manganese steel scrap. This necessitates pouring at night, which does not suit the ordinary small foundry; and in some cases the electric furnace will be found profitable in an existing shop only when the existing melting capacity must be increased, as it would not pay to run it if the output of the original equipment were correspondingly reduced.

MOULDING METHODS

The differences between manganese steel foundry practice and ordinary steel practice are due to the greater shrinkage of manganese steel and its low melting point and great fluidity. The latter properties enable the maker of manganese steel to obtain sound castings in many cases with less waste of steel in sink-heads than would be possible with ordinary steel. Chills are very extensively used to assist the action of the sink-heads, and the heads themselves are often almost completely drained, leaving a mere shell of metal. The increased shrinkage of the metal necessitates, of course, the use of a somewhat larger pattern than that used for an ordinary steel casting. This great shrinkage, and the brittleness of the steel in the cast condition, moreover, greatly increase the tendency of the castings to crack in cooling down in the moulds. The makers of manganese steel castings, therefore, are obliged to take more pains with their castings than do the ordinary steel foundrymen. The moulds and cores often have to be broken up while the casting is still hot, and the castings often have to be cooled slowly, either by burying them in sand or by placing them when hot in a hot furnace, where they are allowed to cool slowly and evenly. Many of the castings also have to be cleaned of sand and placed in the treating furnace before they have grown really cold, as they would assuredly crack were this precaution not taken. Finally this great tendency to crack necessitates the utmost care in the design of the casting, and in general the manganese steel foundryman has to avoid great variations in section between different parts of the piece to be cast. Frequently it is necessary to make very considerable alterations in the original design of the casting before undertaking to manufacture it.

HEAT TREATMENT

Manganese steel is heat-treated, as we have said, by heating it to a temperature between 1000–1100° C., and cooling it rapidly in cold water. Naturally this very drastic treatment frequently results in the cracking of the casting, so that for this reason also unevenness of section must be avoided as far as possible. The cooling in the foundry can be made slow in order to minimize the danger of cracks, but in treatment there is no way of avoiding rapid cooling. Moreover, the low heat conductivity of the metal and its high coefficient of expansion make the heating up of the castings in the treating furnace a delicate matter. If they are heated up too rapidly, the outside of the heavy portions and the whole of the lighter parts outstrip the interior of the heavy sections very greatly, much more so than in the case of ordinary steel. The great expansion of the steel gives rise under these conditions to very heavy stress, and as the steel in the cast condition is extremely brittle, these stresses are almost certain to result in the cracking of the

casting. Hence heavy and complicated castings of this steel have to be heated up extremely slowly.

### ROLLING AND FORGING

For many years the rolling and forging of manganese steel was a problem only partly solved, and many rolled shapes were made, not from an ingot, but from a cast blank which approximated the shape of the finished product. Today, however, large ingots are successfully rolled into rails and other shapes. As a general rule it is essential that the ingot be rolled or hammered at first very lightly all over and returned to the heating furnace again before much reduction of size is attempted. The ingots today are successfully brought to rolling temperatures which it was formerly thought could not be attained without risk of having the ingots crumble under the hammer or in the mill. There is not a very wide range of temperature within which the steel may be readily rolled, since if it is heated too hot it will crumble and if it is too cool it will burst the housings of the rolling mill. The heat treatment of the rolled steel is the same as that of the cast material. Frequently, however, the shape is finished slightly above the proper temperature for quenching, and is slid into the tanks of water without reheating. Very thin sections, whether cast or rolled, can be made quite tough by cooling in the air, since the toughness is roughly a function of the rate of cooling.

### METALLOGRAPHY

In the cast condition manganese steel consists of a ground-mass of austenite, containing manganiferous cementite in a network, and in many needles and small lakes within the austenite grains. These cementite lakes and networks are bounded by a zone in which the austenite is more or less transformed to troostite or sorbite. There are also places where the cementite and partly transformed austenite form a eutectic. The higher the carbon the greater the quantity of this eutectic.

On heating to the treatment temperatures, the cementite is absorbed in the austenite, and is not liberated in cooling if the cooling is sufficiently rapid. In a thin bar cooled in the air there will be but little cementite liberated. In a heavy section, there will be considerable cementite in the interior portions even after quenching, because the interior necessarily cools too slowly to restrain the separation of cementite. Hence heavy sections cannot be made as tough as light sections and there is a distinct limit to the thickness of manganese steel castings which it is practicable to manufacture.

If the steel is cooled slowly from the treatment temperature, the cementite, as we have said, is liberated in a structure more or less resembling that of the cast material. The temperature at which cementite begins to be liberated, however, is several hundred degrees lower than that at which the last traces of it are absorbed in heating. Hence the casting may be allowed to cool considerably in the furnace or in the air on its way to the tank, and yet be quite tough after quenching; but if the castings are very heavy, manifestly more cementite will be liberated in their interior portions than if they had struck the water at the maximum temperature. Hence the larger the casting the more care must be taken to prevent its cooling off before quenching.

If the quenched steel be reheated to a comparatively low temperature, its toughness is almost completely removed. This is largely due to the liberation of cementite from the austenite at a temperature of about 500° C., in a very fine network, and in countless little needles distributed broadcast through the austenite. These needles break up the continuity of the austenite, which no doubt also partially transforms, so that the steel becomes very brittle. This brittleness, in fact, is greater than that due to cooling in the air from the treatment temperature, so that if a bar of the toughened steel be reheated at one end to a white heat and cooled in the air, it will generally break when struck with a hammer at the point where it was at or slightly below red heat. The maker of manganese steel is much troubled by claims for broken castings which have been broken because the users heated the metal in order to bend or work it. Frequently, the casting breaks quite a distance from the spot where it was heated, and it is then difficult to convince the customer that it was the heating which caused the damage. But microscopic examination will prove the case beyond the shadow of a doubt.

If heated for 24 hours or more to a temperature between 500 and 600° C., the steel becomes very brittle, strongly magnetic and very much softer as tested by the drill than the steel in the cast or treated condition, although its Brinell hardness figure is raised. This treatment results in the transformation of the austenite to sorbite, and if the heating were long enough the sorbite would no doubt transform to pearlite. If the steel after this treatment is immersed in liquid air, its magnetism is increased. On reheating this magnetic material, a critical point is found at about 730° C., accompanied by loss of magnetism. If reheated to the quenching temperature and quenched the metal is austenitic and tough; if reheated to the quenching temperature and cooled slowly it will be brittle and will show the same microstructure as if it had never been made magnetic.

The controversy which is now raging as to the existence of Beta iron has involved manganese steel, and much new data have been published on the behavior of manganese steel in heat treatment. It has long been claimed by some of those who think they cannot accept the allotropic theory that there are features in the behavior of manganese steel which that theory will not explain. I personally have not yet found a feature of the metallography of manganese steel which the allotropic theory fails to explain. In fact, when I first investigated the metallography of manganese steel I was able to save myself a great deal of labor by assuming that the carbon-iron diagram and the allotropic theory would be an absolute guide in my work, and this proved to be the case.

7 RECTOR STREET, NEW YORK CITY

## THE COMPOSITION OF PAINT VAPORS

By C. A. Klein

Received January 4, 1915

In this Journal[1] a communication by H. A. Gardner, of Washington, appears under the above title. The communication purports to describe an experimental inquiry as to "The composition of paint vapors," together with a summary of results obtained, supplemented in some instances with a discussion of the data.

In the main, the results described therein can be taken as confirmatory of already well-established and accepted facts, and the present writer intends in this communication to deal with only two statements, and to offer detailed criticisms thereon:

A—Concerning the presence of carbon monoxide in paint vapors.

B—The observation as to the change in weight of linseed oil and oil-pigment paints in the process of drying.

### A PRESENCE OF CARBON MONOXIDE IN PAINT VAPORS

The conclusions arrived at by Gardner are as follows:

I—When linseed oil or similar drying oils are spread in thin layers, the absorption of oxygen which takes place is accompanied by the evolution of considerable amounts of carbon dioxide and organic substances. Carbon monoxide is also evolved in small amount.

II—Oil paints containing lead or zinc pigments do not emit volatile compounds of a metallic nature.

III—Drying paints evolve water-soluble acid substances such as formic acid, as well as acid substances which are apparently of a fatty nature. Carbon dioxide and carbon monoxide are also present in the vapors from the drying paint. The type of pigment used in the paint may directly affect the amount and character of the volatile substances produced. Basic pigments apparently stimulate the evolution of such products.

IV—Aldehydic substances are present in the vapors from drying oil paints. These substances probably have a marked bactericidal effect upon pathogenic bacteria and would thus account for the sanitary value ascribed to oil-pigment paints.

The reputed discovery of carbon monoxide in paint vapors, here stated, has become widely known, largely, through its incorporation in a later publication[2] by that author. This later publication has been reprinted in Europe,[3] and has received detailed consideration by those interested in the problem of painters' hygiene, which has been so acutely occupying the attention of government committees of inquiry in Europe.

On reading through the account of these experiments the present writer came to the conclusion that the experimental method adopted by Gardner was open to serious criticism, and that the conclusions to which he had come were not supported by any experimental evidence he had brought forward. For the detection of carbon monoxide two methods were used, *viz.*, the liberation of iodine from iodine pentoxide at 130° C. and the formation of potassium formate by the interaction of carbon monoxide with heated solid potassium hydrate with subsequent confirmation of the formate by the mercuric chloride reaction. The iodine pentoxide method was also used for the quantitative determination. In the application of both methods, however, a fundamental mistake was made in that the author ignored the fact that fuming sulfuric acid and formic acid give rise to carbon monoxide when the two are brought together. This is surprising when it is pointed out that the presence of formic acid in paint vapors is specifically stated by Gardner as a result of his own work (see conclusion III). It is, therefore, the more surprising that in view of this knowledge he should have seen fit to lead vapors known to contain formic acid through fuming sulfuric acid in an experiment designed to detect the presence of carbon monoxide. This is sufficient to render all the carbon monoxide observations of Gardner wholly invalid, even from a qualitative point of view. The figures given for carbon monoxide have, however, some interest as confirming the statement of Gardner as to the increased rate of formation of volatile products effected by basic pigments; correctly expressed, the results obtained show that linseed oil alone, or in contact with pigments, gives rise in drying to volatile products, which products, when led through fuming sulfuric acid, yield carbon monoxide, and that if it is assumed that the volatile products are of identical composition no matter what pigment is present, then the increased rate of production of carbon monoxide as described indicates an increased rate of production of volatile products by the use of basic pigments. The carbon dioxide determinations are open to serious criticism (see Section 8, p. 100), and, therefore, no deductions can be drawn therefrom.

Objection must also be made to the experiment (No. VI) made to determine the effect of turpentine, from the results of which it is inferred that turpentine increased the quantity of carbon monoxide produced. Here Gardner appears to have entirely overlooked the fact that formic acid is a product of the oxidation of turpentine,[1] so that the increased production of carbon monoxide in his apparatus necessarily follows from this cause.

The present writer has attempted to repeat the experiments of Gardner (making proper provision for the removal of formic acid vapors), and it appears that apart from the foregoing objections, certain other points of importance are brought to light, of which the following may be cited:

1—The so-called paint used by Gardner in Experiments II, III, IV and V contained 60 per cent pigment and 40 per cent linseed oil. Such a mixture has no practical importance, and, therefore, the results obtained are correspondingly denuded in value.

2—The duration of the experiments was so short that the paints were not dry at the end of the experiment and, therefore, the results can be considered to apply only to the first 5 hours' drying.

3—The statement that basic pigments apparently stimulate the evolution of such products is only in accordance with long-recognized facts, and in order

[1] This Journal, **6** (1914), 91.

[2] *Bull* **41**, published by the Scientific Sect. of Educational Bureau, Paint Mfrs. Assn. of U. S., and read before Int. Assoc. Master House Painters and Decorators of United States and Canada, Indianapolis, Ind., Feb. 2, 1914.

[3] *O. & C. Trades Journ.*, **45** (1914), 1000.

[1] Kingzett and Woodcock, *J. Soc. Chem. Ind.*, **31** (1912), 365; **29** (1910), 791.

that the information obtained from such experiments should be of practical value, it becomes necessary to realize that the function of basic pigments is to stimulate drying. In order to render comparison possible, experiments should be made in which paint is dried either to complete dryness, or that the well-known non-drying properties of certain pigments should be compensated for by the addition of driers (as is done in practice) so that paints drying at the same rate should be compared; otherwise it is impossible to draw any conclusions on experiments extending over the same length of time.

4—It is to be noted that although great care was taken that the air aspirated through the painted bottles should be free from carbon monoxide and carbon dioxide, no provisions appear to have been made that the painted bottle itself contained air of the same description. No arrangement is shown for the removal of laboratory air from these vessels prior to the addition of the paint, nor is any arrangement shown for the addition of the paint while the apparatus is in use.

5—The rate of aspiration of air through the apparatus is not stated, nor is the quantity of air passing through the apparatus recorded.

6—The coating of stoppers with paraffin is a highly dangerous proceeding unless special precaution is taken to insulate such stoppers from heat. This applies more particularly to the bottle prior to Bottle 13, from heat radiated from Burner 14. My own experience bears out that of Morgan and McWhorter[1] as to the liberation of iodine from iodine pentoxide by gases which although normally without action became active when passed through tubes jointed in this manner.

7—The amount of carbon monoxide is expressed as a percentage, but the basis on which this is expressed is not stated. The great delicacy of the iodine pentoxide method and the difficulty of exact determinations with this substance in dealing with quantities so low as those recorded in the paper, is well known to all those who have worked with the material. I wish here to place on record the fact that in my experience iodine pentoxide prepared most carefully by the method of Scott and Archbuckle[2] appears to undergo slight decomposition at a temperature of 130° C., such rate of decomposition gradually decreasing to a constant figure, which must be determined separately for each set of conditions, and allowance must be made in calculating results. My experience in this connection is wholly confirmed by that of Dr. R. W. Merriman, of Guy's Hospital, London.

I am not in agreement with Gardner in his assumption that fuming sulfuric acid is capable of destroying all organic vapors produced in the drying of paints which can liberate iodine from iodine pentoxide. The action of many organic compounds on this reagent are well known, and in these circumstances the determination of carbon monoxide is most difficult. Indeed the author himself evidently recognizes the possibility of "aldehydes" escaping absorption by the fuming sulfuric acid for in Experiment V (repeated), using KOH as detector, he specifically introduces a wash bottle of alkaline bisulfite "to collect any traces of aldehydes which, if evolved by the paints, might possibly escape absorption by the sulfuric acid." Aldehydes had previously been detected by him (see conclusion IV). No recognition of this observation appears to have been made in the iodine pentoxide determinations although the effect of aldehydes on the values obtained is too serious to be ignored. The exact method of determination is not specified though by inference it is to be concluded that the iodine released was titrated. In this connection the reference on line 28, page 94, to the determination of carbon monoxide is evidently a mistake and ought to read "carbon dioxide."

8—The figures quoted by Gardner as showing the quantity of carbon dioxide produced during the 5 hours' drying of oil or paint are open to serious objection from an analytical standpoint. In the first place, Fig. II shows a wash bottle containing distilled water (No. 9) through which the gases containing carbon dioxide were passed, prior to entering Bottles 10–13, which contained barium hydrate for the purpose of absorption. The solvent action of distilled water on carbon dioxide has surely been overlooked in this case, so that any figures obtained by titration of the barium hydrate solution in these circumstances must be of questionable value. It is noteworthy in this connection that in Experiment III, where quite similar conditions prevailed, the author recognized the possibility of solution of carbon dioxide in water through which these vapors were led; indeed he records, page 93, line 43, that "The presence of carbon dioxide in the water may partially account for the acidity" of water so treated.

Further, it appears that the use of fuming sulfuric acid (in Bottle 8), through which the volatile products are led prior to the determination of CO and $CO_2$ is a dangerous proceeding, and the effect of formic acid has already been pointed out, but it is also evident, however, that the well-known production of sulfur dioxide by the action of organic compounds on sulfuric acid has been ignored. No provision (other than a single wash bottle) was made for the removal of this gas, and no indication is given that the possible effect of this gas on the barium hydrate solution is recorded. It is the experience of the writer (working on the lines of Gardner) that further complication takes place, owing to the production of a white mist of sulfuric anhydride when gases are led through fuming sulfuric acid. This mist it is impossible to absorb completely in water, and the writer has invariably found that it traveled through many such washing bottles with only partial absorption. Washing in a single bottle of water is wholly ineffective, with the result that the precipitate obtained in the barium hydrate bottle contained barium sulfate, so that direct titration of the barium hydrate after the experiment is of no value. The production of carbon dioxide during the drying of linseed oils or paints containing this oil is not disputed, but the qualitative figures contained in the communication in question are open to serious

[illegible] 29 [illegible]
[illegible] 1901, p. [illegible]

criticism. The qualitative detection noted in Experiments I and II is not open to this foregoing objection, because in this case only 66° sulfuric acid was used, and the effects produced by fuming sulfuric acid were absent.

9—The effect of light in the drying process has evidently not been fully appreciated by the author, inasmuch as apparently in all the experiments the oils or paints were enclosed in such a manner as to partially or wholly exclude light. Such conditions have no industrial parallel, and the utility of the investigations is thereby vitiated. From a scientific standpoint the omission is important, it being a well-established fact that drying is seriously impaired by the absence of light.

In view of the foregoing criticisms, it is submitted that no single piece of evidence has been brought forward which can justify the assertion that carbon monoxide has been or can be detected in paint vapors.

In concluding the criticism of this portion of the work, the present writer desires to make it clear that his criticisms are offered in no carping spirit. It has become necessary to definitely record such criticisms in view of the publicity given to the results under discussion, and the possible influence of such statements as have been based on these results, in so far as they concern the hygiene of the painters' trade. Wide and extensive publicity has been given to the carbon monoxide theory of Gardner, not only in England, but on the Continent, and it has appeared undesirable that such conclusions should in their present state go unchallenged. It is a matter of regret that the author should have seen fit to publish the results of an obviously imperfect investigation, in view of the important issues concerned. Statements such as those contained in the publication already referred to readily gain credence in certain quarters, irrespective of scientific accuracy, and although the author explicitly stated that "tests extending over a greater period should be made to substantiate the figures presented," this reservation has not prevented the publication of his conclusions in the technical and public press of Europe, because in his later publications no such reservation appears; in point of fact the discovery of carbon monoxide in the vapors from drying oils and paints is positively asserted and it is stated that some of the symptoms of poisoning observed among painters previously ascribed to other causes can be more probably explained by the presence of this gas.

The experiments, interesting as they may be, cannot be regarded as strictly conforming to that rigid accuracy necessary for the substantiation of the evidence they purport to reveal. There is no evidence that paint vapors contain carbon monoxide.

### B—CHANGES IN WEIGHT OBSERVED DURING THE DRYING OF LINSEED OIL AND LINSEED OIL PAINTS

Gardner has investigated the change in weight observed in the drying linseed oil of paints, and in his general discussion of the results obtained from such inquiry states:

"The results obtained in Experiment II, in which the paint films showed but slight if any increase in weight at the end of the tests, are interesting. They may be partially accounted for by assuming that the amount of air passed through the tanks in 48 hours was very small. It will be well at this point to discuss the experiments on linseed and oil-pigment paints, as made by Sabin. He describes a series of tests in which various paints were applied to small glass plates, the increase in weight shown by the paints being recorded at different periods. At the end of 7 days, raw linseed oil showed a gain in weight of 18 per cent, while white lead paint showed a gain of approximately 15 per cent.

"The writer carried out a similar series of tests with a set of paints made up with 60 per cent of pigment and 40 per cent of raw linseed oil. The gain in weight of the films at the end of 7 days was as follows:

| | Per cent |
|---|---|
| Linseed oil | 14.0 |
| Corroded white lead | 6.4 |
| Sublimed white lead | 7.1 |
| Zinc oxide | 5.4 |
| Lithopone | 5.9 |

"These tests indicate that oil-pigment paints do not gain in weight to the same extent as raw linseed oil. Heretofore, however, investigators have not given consideration to the possibility that pigments may stimulate not only those processes which cause the oil to increase in weight through the absorption of oxygen, but also those processes and reactions which cause the oil to eliminate volatile substances, which might detract materially from the weight of the paint. In this connection it is of interest to cite the tests of Olsen and Rather upon the drying of linseed oil. They record a gain in weight of 18 per cent at the end of approximately 10 weeks. They also showed the elimination of approximately 5 per cent of carbon dioxide and 15 per cent of water."

Before discussing in detail the points raised by the author on this subject, it is necessary first to make some observations with reference to the film tests detailed above. The disparity between the results of Gardner and Sabin is not so great as would appear at first sight, because the figures as presented are not comparable. The results of Sabin are calculated on the oil used; indeed, this is expressly stated in the original communication of Sabin:[1] "In constructing the curves of drying, only the oil is taken into account, and the curves show the percentage gain or loss of the oil as if no pigment were present; that is, the pigment is assumed to be inactive in all cases."

In order to compare the results obtained by these two workers, it is only necessary to express their results on the same basis. The most convenient is that adopted by Sabin, *viz.*, increase of weight expressed on linseed oil content of the paint. Gardner used a paint containing 60 per cent pigment and 40 per cent linseed oil, so that, calculating the results on the same basis, the comparison is as below:

| Per cent Gain in Weight in 7 Days | Gardner | Sabin |
|---|---|---|
| Linseed oil | 14.0 | 18.0 |
| Corroded white lead | 16.0 | 15.0 |
| Sublimed white lead | 17.5 | .... |
| Zinc oxide | 13.5 | 16.0 |
| Lithopone | 14.75 | .... |

From this comparison it is evident that no serious differences exist between the results of these workers, and there is no ground for the suggestion that the later results bring to light any new feature. The observations of Sabin and Gardner as above shown are similar to those observed by many other workers, and have limited interest, because of their limited range.

[1] This Journal, 3 (1911), 7.

The observations of Sabin, as described in the original communication, are, however, much more comprehensive and consist essentially in the determination of changes in weight which take place over a lengthy period of exposure of oil and paint films (up to 8 months). As such, they have an enhanced value. In brief, they show that paint films increase in weight to a maximum value, and then slowly decrease, and that even after a period of 8 months the decrease continues. Raw linseed oil shows the same behavior but decreases in weight more rapidly than does the oil content of an oil paint. Similar observations were made by the Chemical Sub-Committee of the Netherlands White Lead Commission, appointed in 1903. These results have certain practical bearings in particular as showing that the oil portion of paints undergoes a slow but continuous decomposition on exposure to air. According to Sabin, in 24 days, films of paints containing Whiting, Terra Alba, Silica, Asbestine, Barytes, China Clay, White Lead, or White Zinc show increases in weight of between about 12 and 13 per cent, having fallen from maximum values of from 13 to 16 per cent. The following table from the report of the Netherlands Commission shows the changes in weight (decreases) in percentages expressed on the original layer of dry paint. Mica plates covered with paint were placed out of doors after having become dry.

| | Duration of Exposure in Days | | | | | | |
|---|---|---|---|---|---|---|---|
| Name of Paint | 20 | 40 | 60 | 80 | 120 | 200 | 230 |
| White lead | 2.8 | ... | ... | 4.0 | 4.1 | .... | .... |
| Zinc white | 2.9 | .. | ... | ... | 21.2 | .... | .... |
| Lithopone | ... | .. | 8.6 | ... | 35.8 | 60.8 | 83.9 |

These results show that white lead paint loses much less on exposure to the air than zinc white or lithopone, and constitute a striking refutation of the last sentence of the following statement:

"Oxide of zinc is practically without action on linseed oil; therefore, when it is ground in that medium the conditions that obtain cannot be compared with those that exist in the case of white lead. The drying of paint made from oxide of zinc is due entirely to the siccative nature of the oil itself in which the oxide of zinc may be considered as mechanically suspended. We have here a state of things more readily under control than is the case with white lead paints in which the powerful siccative action of the hydrate portion of the white lead often proceeds too far. The oil is then burnt up so to speak; the paint perishes and 'chalking' results."[1]

This and similar statements are used to decry the properties of white lead by those whose interests lie in the sale of other pigments.

It is an open question whether the behavior of paint films can be correctly studied by the use of linseed oil and pigment alone. In general, turpentine or a similar volatile thinner is present in paint when technically applied, and there is good reason to believe that such thinners may not be without effect in determining the character of the oxidation processes, more particularly in so far as the volatile products are involved.

The whole problem of the drying of linseed oil alone or when used as a paint medium is one of extreme difficulty, and at the present time such information as is available appears to be so lacking in agreement, and so contradictory, that no true explanation of the chemical changes has yet been brought forward, although many theories have been published. The formation of volatile products (other than carbon dioxide and water) during the drying of linseed oil has been known for some time, and more recently the hygienic value of these products has been appreciated. The presence of the lower fatty acids, aldehydes, etc., has been demonstrated, but as yet no detailed examination of the products has been carried out. This is a problem which few technical chemists have the facilities for attacking, and they might well engage chemists more conveniently placed who have liquid air at their disposal. By such condensation and collection of these volatile products at low temperatures and their subsequent examination it is highly probable that valuable evidence as to their chemical constitution would be obtained. The course and type of oxidation is apparently influenced by the temperature and this has important practical application.

The great disparity between the figures given for increase of weight of films by different workers indicates the difficult nature of the inquiry. The so-called "oxygen absorption values" as determined by the exposure of films to air, on open plates or the like, cannot claim to be anything more than empirical values, and have a correspondingly reduced scientific interest. In such methods there is absolute disregard of the formation of volatile products, and the values obtained in no way represent the "true oxygen absorption." The investigators who have attempted to determine the true oxygen value have realized the complicated character of the volatile products, but have in nearly every case considered that passage through calcium chloride and potash would be sufficient for their retention—a quite unjustifiable assumption in our present state of ignorance as to the true chemical character of the volatile products. These and many other problems present themselves in the detailed study of paint, and there is a wide field for the scientific investigation of the chemical changes involved in the application and use of paints.

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Enfield Highway, Middlesex, England

[1] From advertisement, page 498, "White Paints and Painting Materials," Scott, pub. by *The Modern Painter*, Chicago, 1910, and attributed to J. Cruickshank Smith in a lecture before the Institute of British Decorators.

## A STUDY OF VARIOUS TESTS UPON GLUE, PARTICULARLY THE TENSILE STRENGTH[1]

By Augustus H. Gill

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The object of this work was to compare the various tests applied to determine the properties of glue and more particularly to see if they bore any relation to its tensile strength.

### I—PRELIMINARY[2]

VISCOSITY TEST—Following the work of Fels,[3] the viscosity of 15 per cent solutions of glue at 30° C. were determined with the Engler viscosimeter; as the

[1] The experimental work of this paper was done by six students, working successively. Each worker's name is given in connection with the report of his experiments.

[2] By W. A. Marshall.

[3] *Chem. Zeit.*, **21**, 56, 70.

results obtained were unsatisfactory, the Doolittle viscosimeter was used, employing strengths of glue from 4 to 25 per cent. It was found that there was too little variation in the viscosity of solutions of glue of widely varying tensile strengths to make this method of any practical use.

JELLY TEST (LIPOWITZ)—7 g. of glue were dissolved in 96 cc. of water by allowing it to soften for 12 hrs. in the water, finally warming to complete the solution on the water bath. It was then allowed to cool, finally chilled with ice, the jelly broken in the machine and the strength reported in grams per sq. in. necessary to break the surface. Table I shows the results obtained.

DETERMINATION OF THE TENSILE STRENGTH—It was supposed to be a comparatively easy matter to glue two pieces of wood together and measure the force necessary to pull them apart. On a more careful consideration it was found that many factors entered in to complicate matters and render its execution difficult.

A cement testing machine was used in these tests, the blocks of wood being sawed out to resemble cement briquettes. These blocks were first made of maple and glued together with the grain; on subjecting these to test, the wood itself broke rather than the glued joint, at pressures varying from 180 to 370 lbs. per sq. in. All future experiments were made by gluing the maple blocks together endwise.

A 20 per cent solution of glue, made by dissolving on the water bath, was applied evenly to these end surfaces, of a sq. in. area, subjected by means of ordinary carpenter's clamps to as even a pressure as possible, allowed to dry for 24 hrs. and the joint broken. The average of three tests each is shown in Table I.

TABLE I—JELLY AND STRENGTH TESTS OF HIDE GLUES

| | JELLY TEST G. per sq. in. Average | TENSILE STRENGTH Lbs. per sq. in. Range | Average |
|---|---|---|---|
| A | 2440 | 1384–1744 | 1544 |
| B | 1969 | 1402–1685 | 1561 |
| C | 1521 | 911–1298 | 1402 |
| D | 1360 | ..... | 1282 |
| E | 1200 | 752– 944 | 1309 |

The results vary quite widely, and to try and reduce this variation, blocks the shape of briquettes were cut with a special moulding cutter across the grain of a 2-in. plank. This gave briquettes 9 or 10 in. thick instead of but 1 in., the idea being to use blocks from the same piece of wood and blocks which had been glued under identically the same conditions and then saw them apart into briquettes having the usual square inch section. The gluing was effected as before, using a 25 per cent solution of glue and the blocks were weighted with a 20 lb. weight in the center, drying them for 24 hrs. or 48. Table II shows the results of the test, the arrangement of the sections, and the length of time of drying of each piece.

TABLE II—VARYING STRENGTH IN LBS. PER SQ. IN. OF GLUE APPLIED TO A THICK BLOCK AFTERWARDS SAWN APART

| GLUE | | End | | | Center | | | End |
|---|---|---|---|---|---|---|---|---|
| E | Lbs | 820 | 1240 | 1280 | 1336 | 1424 | 1232 | 1200 | 1144 |
| | Hrs | 24 | 48 | 48 | 48 | 24 | 24 | 24 | 48 |
| B | Lbs | 1720 | 1532 | 1600 | 1344 | 1240 | 1496 | 1428 | 1520 | 1508 |
| | Hrs | 48 | 24 | 48 | 48 | 24 | 24 | 24 | 24 | 48 |

It will be noticed that with Glue E, the joints in the center of the block are the stronger, while the reverse is the case with B; this might have been because the glue was thinner at these places, due to the springing of the blocks, but it was hardly thought possible, as they were more than 2 in. deep and wide. To try and obviate this difficulty, blocks the size of a pair of briquettes were used, glued under pressure, and then sawn apart.

TABLE III—STRENGTH IN LBS. PER SQ. IN. OF GLUE APPLIED TO PAIRS OF BLOCKS

| GLUE | DRIED UNDER 2 LBS. PRESSURE A | B | C | D | E | DRIED WITHOUT PRESSURE A | B | C | D | E |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1347 | 1553 | 520 | 849 | 1108 | 1624 | 1579 | 1043 | 1385 | 1454 |
| | 1463 | 1842 | 505 | 745 | 588 | 1463 | 1543 | 1521 | 1420 | 1164 |
| Average, | 1405 | 1698 | 513 | 797 | 848 | 1544 | 1561 | 1282 | 1402 | 1309 |

## II—JOINTS AND SURFACES[1]

It was found that all of the briquettes used in Table III were more or less sprung and that, being cut against the grain, the grain of the wood was bruised and bent down. The blocks were re-surfaced by hand, using a sharp plane finely set and the tests repeated. Results were obtained varying from 262 to 1490 lbs. per sq. in. Instead of weighting the joint when drying, it was made with carpenters' clamps, obtaining less widely varying results, *i. e.*, from 524 to 1623 lbs. and from 1212 to 1695 lbs. Obviously the difficulty lay in making the joint. Among woodworkers using glue, the "rubbed joint" has a reputation for strength, and accordingly this was next tried. The glue-sized briquettes were covered with an excess of hot glue at the joint, pressed together to expel all air bubbles, and the two surfaces rubbed together until the glue became stiff and tacky, when the pieces were set aside to dry. On breaking the joints, strengths from 760 to 1960 lbs. per sq. in. were obtained. With the weaker, the joint was free from holes and flaws, but appeared glazed, whereas in the stronger the surface was uniform and presented a frost-like appearance. Probably the glazed surface represents the peeling of the glue from the wood, whereas the frosted shows the fracture of the glue.

In order to make the surfaces even more perfect, the size was removed from used briquettes by allowing them just to dip in boiling water: on drying, an even open surface was obtained, which gave the glue a chance to penetrate deeply into the wood. Rubbed joints were made, using these pieces, and results from 1248 to 1986 lbs. per sq. in. obtained. As with a cement briquette placed but $^1/_{16}$ in. off center, a difference in strength of 33 per cent may be obtained, so it is possible here that the differences may have been due to a bending moment in the test pieces which, however, would appear to be unavoidable with these briquettes so that the results just cited would seem to be the best obtainable by this method.

## III—BRIQUETTES OF MATERIALS OTHER THAN WOOD[2]

Preliminary experiments were made with rubbed joints using a well known liquid glue, dried without pressure for 38 hrs.; maple briquettes were employed as before. No difference could apparently be seen between the joints, which were about 0.002 in. in thickness. The results were 450, 574, 748, 776 and 1098

[1] By A. F. Nathan.
[2] By H. B. Chalmers.

lbs. breaking strength per sq. in. The work was repeated using a strong and a weak glue. Every attempt was made to have the results as uniform as possible. The briquettes were heated to 90° C., the glues to 95° C. and brought to the same consistency; the wooden surfaces were given five coats of thin glue sizing, finally glued and allowed to dry under 40 lbs. pressure for 37 hrs. The strong glue gave 553, 777, 789, and 1107 lbs. and the weak 324, 494, 656 and 903 lbs. The test was repeated using a very strong glue: 1234, 1776, 1897, 1920, 2168, 2244, 2393 and 2800 lbs. breaking strengths were obtained. Finally an experiment was made as in Table II, using a thick (6.5 in.) briquette, glued with the liquid glue already mentioned and dried for 96 hrs. in a testing machine under a load of 4000 lbs.; on being sawn apart, the breaking strengths were as follows, arranged in the order of the sections: 720, 804, 1060, 950, 742 and 524 lbs., the middle ones being the strongest.

These results being so unsatisfactory, substances other than wood were sought: porcelain lacked in porosity, tiling broke at 400 to 500 lbs., while glass, like wood glued with the grain, breaks elsewhere than at the joint.

Weidenbusch, in 1859, used rods of plaster of Paris mixed with glue; the method has the reputation of being uncertain, owing perhaps to the setting of the plaster. Following this example, briquettes of fuller's earth, diatomaceous earth, quartz sand and sawdust were made, using solutions of the various glues as binders. These in some cases were dried at 80° for 6 days. It was difficult to dry them completely, and the resulting briquettes were full of blow-holes rendering difficult an accurate measurement of the broken area. Some showed little or no strength, while others gave 1320 and 1480 lbs.; these were reglued and the fracture took place at a new point at 840 and 800 lbs.; on again being reglued they broke in still different places at 1216 and 1212 lbs.

Setterberg[1] employed strips of paper dipped in the glue solution and afterwards dried to determine the strength of glue; this was not found in our hands to give good results. Instead of finding the increase in tensile strength of the paper, it was thought that the bursting strength as shown by the Mullen paper tester might afford more reliable results. The tests were conducted as follows: strips of filter paper 2 in. wide were dipped into 25 per cent solutions of the glue and allowed to dry in the air for 36 hrs. The

TABLE IV—BREAKING STRENGTHS OF GLUE ON FILTER PAPER
LBS. PER SQ. IN. PER 100 MGS. OF GLUE

| | | | | | | | | | | | | | Average |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| C | 26.6 | 28.7 | 26.3 | 26.1 | 26.8 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| D | 35.5 | 36.5 | 35.2 | 35.0 | 35.6 | 34.7 | 32.6 | 33.2 | 35.1 | 34.8 | 34.6 | 33.5 | 34.7 |
| E | 16.9 | 20.2 | 20.4 | 20.0 | 18.5 | 19.3 | 23.6 | 17.3 | 19.4 | 20.1 | 19.9 | 20.1 | 19.6 |

paper was cut into 2-in. squares and weighed; these weighed before treatment from 499 to 618 mg. and carried from 86 to 195 mg. of glue. They broke at from 17 to 39 lbs. per sq. in. per 100 mg. of glue upon the 4 sq. in. of surface.

Table IV shows the variations with different glues. The results, while showing nothing as to the actual tensile strength of the glue, readily enable the strongest glue to be selected; furthermore, they are much more concordant than any that have so far been obtained. Considering Glue B as 100, the other glues rank as shown in Table V by the various tests.

TABLE V—COMPARISON OF VARIOUS TESTS UPON THE DIFFERENT GLUES

| GLUE | B | C | D | E |
|---|---|---|---|---|
| Cup test | 100 | 68 | 76 | 60 |
| Viscosity | 100 | 97 | 99 | 96 |
| Tensile strength | 100 | 40 | 80 | 60 |
| Sized paper | 100 | 81 | 94 | 67 |

## IV—BEARING SURFACES, JOINTS AND GLUE SOLUTIONS[1]

Careful consideration of the causes of error in the strength tests with wooden briquettes revealed one which so far had been overlooked. This was the bearing surface between the wood and the bronze clamp of the testing machine; if there were inequalities in the wood caused by irregularities in the grain or the hardness of the wood, these would produce eccentric loading. To obviate this it was proposed to use round blocks 1 in. in diameter with lag screws at each end, which could be suitably clamped; the lag screws were to be center-marked on their heads and the blocks turned down upon these centers, thus ensuring proper alignment. The blocks were to be sawn apart for gluing. While a $^{7}/_{16}$ inch lag screw required 5800 lbs. to pull it out of the block, yet it was found that this procedure was too tedious and troublesome.

On suggestion of Professor Schwamb, rectangular prismatic blocks were used of the dimensions shown in Fig. I-A, and sawn apart with a special saw. These were blocked up with bronze blocks to fit in the briquette holder of the testing machine. The depth of the slot was found by determining the compression strength of the maple (which was 11580 lbs. per sq. in.) and using a sufficient area to give a strength of at least 2000 lbs.; this would be about $^{3}/_{32}$ in. on each side. The method of preparing the joint and glue was as follows: the blocks were placed in a form and center punched on the ends, two numbers were placed on each for identification of each end and the block carefully sawn in two. This is one of the most important parts of the whole operation. The blocks are securely clamped in a "fence" and this sets upon the "rest" of the saw table; the saw used must be carefully trued upon the mandrel upon which it fits and is frequently filed. The blocks should be sawn at a definite rate. When done they should fit together perfectly and not "rock"—showing inequalities of surface; the surfaces should be smooth but not glassy.

One hundred and twenty grams of glue were weighed out into a beaker, covered with 150 cc. of water, allowed to soak over night, when it was warmed to dissolve the softened glue, allowed to stand again, and finally water added to make the weight 300 g., warmed on the steam-bath to a temperature not exceeding 65° and stirred until it was homogeneous. Thus nearly two days were required to make the glue solution and care was taken to heat it neither higher nor longer than necessary since such over-treatment causes a decomposition which diminishes the strength of the glue. A properly glued joint after breaking



By P. V. Estep.

should not show "glazed" spots—places where the light is reflected, showing that the glue has not filled in the space between the ends of the fibers; the broken surface on a strong joint is rough and irregular and of a frosted appearance. Besides the preparation of the glue and joint, the manner in which the joint is dried is of importance: this is ordinarily done in practice under pressure of screw clamps. As this pressure is very variable, the machine shown in Fig. I-B was devised. This enables any pressure up to 100 lbs. per sq. in. to be applied.

It consists of a frame carrying a dozen round, pointed steel pins in the top row: opposite them in the bottom row is an equal number of pointed screws; bent levers, *l*, 10 in. long with *f* as a fulcrum rest in holes in the top of the pins *p*, and carry a weight of 1 to 3 lbs.

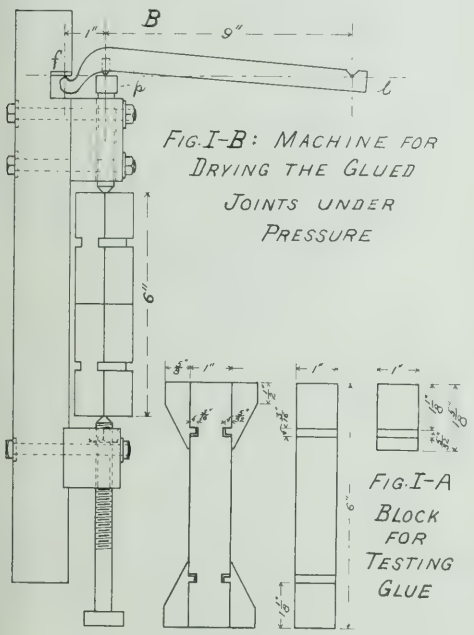


FIG. I

at the end, which is thus multiplied ten times. The pointed pins and screws fit into the center marks on the ends of the blocks, the screws being adjusted until both ends of the lever and its middle pin are in the same line. The pressure upon each block was determined by a spring balance rather than by calculation.

The pieces were glued as follows: The blocks were dried in a water oven at 65°, the glue solution made as previously described and heated to 65°; the halves of the block were held vertically over the glue, which was applied thoroughly with a brush; the blocks were then fitted together and the excess of glue allowed to drip away. The glued block was placed in a V-shaped form and the alignment completed by pressing another V-shaped form upon the block. While still in this holder the block was put in position in the drying machine, the weights applied and the form removed. The blocks were kept under a pressure of 31 lbs. for 1 hr., then heated to 50° C. for 3 hrs. and dried 2 or 3 days at room temperature. The results obtained and a comparison of the various tests made so far are shown in Tables VI and VII.

TABLE VI—TENSILE STRENGTH (LBS. PER SQ. IN.) OF VARIOUS GLUES

| Glue No. | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 1594 | 1627 | 1729 | 1820 | 1905 | 2081 |
| 2 | 1782 | 1878 | 1901 | 1942 | 1952 | 1953 2011 |
| 3 | 1938 | 2098 | 2168 | 2285 | 2299 | 2310 2553 |
| 4 | 1358 | 1495 | 1573 | 1658 | 1762 | 1809 1927 |
| 5 | 1582 | 1635 | 1755 | 1878 | 1963 | 1993 |

TABLE VII—COMPARISON OF TENSILE STRENGTH, JELLY TEST AND VISCOSITY OF VARIOUS GLUES

| Glue No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Average 3 highest in Table VI, lbs | 1935 | 1982 | 2387 | 1866 | 1928 |
| Jelly test, grams | 1223 | 145 | 358 | 171 | 281 |
| Viscosity at 104° F., grams sugar | 18.2 | 13.8 | 16.2 | 13.9 | 14.3 |

DESCRIPTION OF GLUES 1–5

No. 1—Made from the last runs or cookings of imported cattle hide fleshings that had been previously dried.

No. 2—Made by cooking carefully washed packer bones under pressure.

No. 3—A cattle hide glue.

No. 4—Made from packer bones and pieces of calfskin.

No. 5—Made from the liquors obtained in boiling bones in a packing house.

From Table VII it is evident that the three tests are independent of each other—perhaps because not dependent upon the same constituent.

V—DRYING PERIODS AND PRESSURES VARIED[1]

The previous investigation was continued using the same apparatus and glues but varying the conditions, making some 500 tests in all. Test specimens were dried 3 and 24 hrs. under pressures of 10, 20, 30, 40, 50 and 100 lbs. It was found in every case that the 24-hr. joint was about 3 per cent stronger and that 30 lbs. per sq. in. pressure gave a joint about 15 per cent stronger than either the 10 or 100 lbs. pressure. The exact behavior is shown in the curves of Fig. II. A summary of the results is given in Table VIII. The glued blocks were heated to 65° for several hours. This was shown by later work to diminish the strength very materially. It is much better to let them dry in the open room for 100 hrs.—the humidity seems to be without influence upon them.

TABLE VIII—AVERAGE TENSILE STRENGTHS OF GLUES IN LBS. PER SQ. IN.

A—Average of about 100 tests for each glue from 10–100 lbs. pressure and from 3–100 hours' drying.

B—Average of tests which are considered the most trustworthy.

| GLUE | 1 | 2 | 3 | 4 | 5 | Liquid glue |
|---|---|---|---|---|---|---|
| A | 3338 | 2443 | 2950 | 2336 | 1696 | 2093 |
| Average of 3 highest in A | 3791 | 3231 | 3253 | 2624 | 2095 | 2175 |
| Highest in A | 4829 | 5025 | 4170 | 3486 | 3067 | 2540 |
| Lowest in A | 1893 | 1399 | 1775 | 1761 | 1308 | 1631 |
| B | 3361 | 3212 | 2972 | 3624 | 2182 | 2085 |

VI—REVIEW AND CONCLUSION[2]

This consisted in verifying the work of the last two observers and in making definite directions for the gluing process, which requires practically a week for its execution.

GLUE SOLUTION—120 g. of glue are covered with

[1] By C. S. Redfield.

[2] By A. H. Whittlesey.

150 cc. of water (*e. g.*, on Monday night). The next morning the blocks to be glued are heated in an air bath to 60° C. for 2 hrs. Meanwhile the glue is warmed in a water bath and sufficient water added to make 300 g. of glue and water. When the 2 hrs. have nearly expired the 40 per cent glue solution is warmed in a water bath to 60° C., melted, and thoroughly stirred. Hot water should be at hand to add to the water bath for heating the glue in order that its temperature may be kept at 60° C.

SIZING—The hot blocks are taken from the air bath two at a time; the ends are dipped in hot water and rubbed together. This is repeated until the blocks are thoroughly moist, when they are dipped in the solution, the ends rubbed together, and set aside to dry in the air of the laboratory for 2 days. Sized joints are found to be stronger than unsized.

GLUING—The sized blocks are again heated to

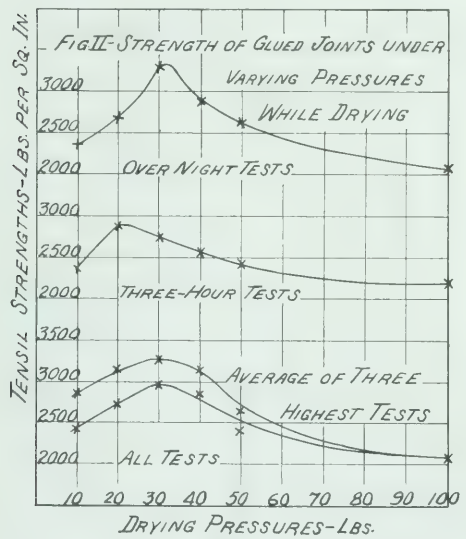


FIG. II

60° C., and the hot 40 per cent glue solution prepared as above. This should be close to the frame where the blocks are to be dried under weights. The blocks are taken from the air bath in pairs and the ends dipped in glue until there is a fairly thick layer on each block. They are then placed together by *sliding* the end of one across that of the other in order to avoid entangling air bubbles, and with due regard to the grain of the wood. The excess of glue around the joint is removed with a penknife. The blocks are placed in the V-shaped frames to secure alignment, put into the rack, and a weight of 30 lbs. per sq. in. is applied before the glue has a chance to peel or dry. Thus one block is glued before the next is taken from the air bath. The blocks are allowed to stay under pressure for 24 hrs., when they are removed, laid on their sides and dried in the air of the laboratory for at least 100 hrs. before breaking.

The results upon some of the preceding glues were as given in Table IX in lbs. per square inch.

TABLE IX—COMPARISON OF RESULTS BY VARIOUS WORKERS

| GLUE NO. 2 | | | Whittlesey | | | GLUE NO. 5 (Bone-glue) | | |
|---|---|---|---|---|---|---|---|---|
| Bone-glue | Esten | Red field | (*a*) | (*b*) | (*c*) | Esten | Red-field | Whitlesey |
| Average of all | 2443 | 2792 | 3056 | 2358 | 3888 | 1696 | 2730 | |
| Av. of 3 highest | 1982 | 2721 | 3630 | 3902 | 3206 | 5026 | 1928 | 2095 3562 |
| Highest | 2011 | 5025 | 3704 | 4000 | 3440 | 5920 | 1993 | 3067 3880 |
| Lowest | 1782 | 1399 | 1840 | 2040 | 1020 | 2140 | 1775 | 1308 1760 |

(*a*) Dec., 1912. (*b*) Dec., 1913. (*c*) Glued in April and broken 6 mos. later.

## SUMMARY

The preceding work seems to justify the following conclusions:

I—That the tensile strength, jelly test and viscosity of glue bear no relation to each other.

II—That the method followed for tensile strength may be expected to give results with a variation of 10 per cent.

III—That the method of testing the strength of glue by measuring the strength which it imparts to bibulous paper is dependable and gives fairly concordant results.

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# A COMPARISON OF VARIOUS MODIFICATIONS OF THE KJELDAHL METHOD WITH THE DUMAS METHOD OF DETERMINING NITROGEN IN COAL, WITH NOTES ON ERRORS IN THE DUMAS METHOD DUE TO NITROGEN EVOLVED FROM THE COPPER OXIDE[1]

BY ARNO C. FIELDNER AND CARL A. TAYLOR

The experiments described in this paper were undertaken to ascertain which modifications of the Kjeldahl method are best adapted to the determination of nitrogen in coal, and to check the results if possible with the Dumas gas-volumetric method. The latter method, although difficult and tedious to operate, is generally regarded as fundamental and applicable to almost all classes of organic compounds.

A series of determinations, using some of the best known of the various modifications of the Kjeldahl method, was made on the following eight coals chosen to represent various types and to range in nitrogen from 0.8 to 1.8 per cent:

TABLE I—DESCRIPTION OF COALS

| COAL NO. | LOCALITY | BED | CLASS |
|---|---|---|---|
| 1 | Morton Co., N. D. | ..... | Lignite |
| 2 | Mussellshell Co., Mont. | ..... | Sub-bituminous |
| 3 | Bureau Co., Ill. | No 3 | Bituminous |
| 4 | New River field, W. Va. | Sewell | Semi-bituminous |
| 5 | McDowell Co., W. Va. | Pocahontas No 3 | Semi-bituminous |
| 6 | Allegheny Co., Md. | Davis 6-ft. | Semi-bituminous |
| 7 | Fayette Co., W. Va | Sewell | Semi-bituminous |
| 8 | Campbell Co., Tenn. | Rex | Bituminous |

## GENERAL PROCEDURE

A considerable quantity of each sample was prepared by pulverizing the air-dried coal in a porcelain ball-mill to 60 mesh and finer; in fact, most of the material would pass through a 100 mesh sieve.

The general procedure in all of the Kjeldahl methods was essentially as follows: A 1 gram sample was digested in a 550 cc. Kjeldahl flask with 30 cc. concen-

[1] Presented at the Spring Meeting of the American Chemical Society, Cincinnati, April 7–10, 1914, by permission of the Director of the Bureau of Mines.

trated sulfuric acid and the other reagents required in that particular modification. The flask was first heated over a low flame till frothing subsided and then at a temperature sufficient to cause gentle ebullition. The digestions were continued for definite periods of time—2, 3, 4, and 7 hours in the various series. In those cases where potassium permanganate was used, it was added in the form of powder or small crystals, about 10 minutes after turning out the flame. The mixture had then cooled enough to avoid the violent local action that takes place on adding permanganate to the boiling mixture. Adding permanganate under these conditions several times during digestion did not cause appreciable loss of nitrogen, which confirms the results obtained by Siegfried and Weidenhaupt.[1] After cooling and diluting the solution to 250 cc., a few grams of granulated zinc and an excess of sodium hydroxide solution containing potassium sulfide were added and the flask at once connected to a block-tin condenser. To avoid mechanical carrying over of alkali the distillation was conducted very slowly, at the rate of 150 cc. in $1^1/_2$ to 2 hours. The ammonia was collected in standard sulfuric acid solution and titrated with a standard ammonia solution using cochineal indicator. The solutions were carefully standardized by several methods. Blank determinations were made in all cases, using 1 g. of pure sucrose in place of the coal sample.

## EXPERIMENTAL RESULTS

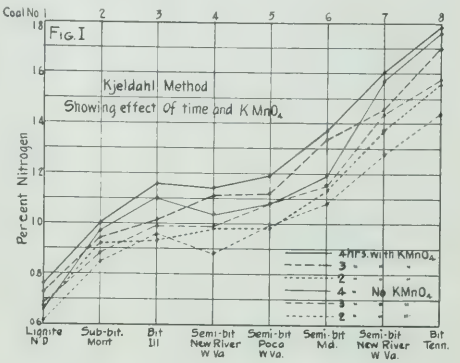
SERIES 1: KJELDAHL METHOD—Table II and the curves in Fig. 1 show the results obtained by digesting the samples

TABLE II—SERIES 1: KJELDAHL METHOD
Digestion with 0.7 g. Hg and 30 cc. $H_2SO_4$

| Coal No. | No $KMnO_4$ added at end of digestion: Per cent N after digesting 2 hrs. | 3 hrs. | 4 hrs. | $KMnO_4$ added at end of digestion: Per cent N after digesting 2 hrs. | 3 hrs. | 4 hrs. | No. hrs. digested before liquid became colorless |
|---|---|---|---|---|---|---|---|
| 1 | 0.63 | 0.68 | 0.65 | 0.65 | 0.70 | 0.75 | $1^3/_4$ |
| | 0.60 | 0.68 | 0.63 | 0.66 | 0.75 | 0.75 | |
| | | | 0.66 | 0.65 | | | |
| | | | 0.68 | 0.70 | | | |
| Av., | 0.61 | 0.68 | 0.65 | 0.66 | 0.73 | 0.75 | |
| 2 | 0.83 | 0.89 | 0.98 | 0.91 | 1.01 | 1.01 | 2 |
| | 0.85 | 0.88 | 0.97 | 0.93 | 0.93 | 1.01 | |
| | | | | | 0.93 | | |
| | | | | | 0.91 | | |
| | | | | | 0.92 | | |
| Av., | 0.84 | 0.88 | 0.97 | 0.92 | 0.94 | 1.01 | |
| 3 | 0.93 | 1.03 | 1.13 | 0.95 | 1.02 | 1.16 | 2 |
| | 1.00 | 0.95 | 1.08 | 0.90 | 1.04 | 1.15 | |
| | | | | | 1.00 | | |
| Av., | 0.96 | 0.99 | 1.10 | 0.93 | 1.02 | 1.16 | |
| 4 | 0.91 | 1.01 | 1.04 | 0.99 | 1.10 | 1.15 | $1^3/_4$ |
| | 0.89 | 0.98 | 1.04 | 0.98 | 1.16 | 1.13 | |
| | 0.86 | | | | 1.09 | | |
| | | | | | 1.12 | | |
| Av., | 0.88 | 0.99 | 1.04 | 0.98 | 1.12 | 1.14 | |
| 5 | 0.98 | 1.10 | 1.10 | 1.00 | 1.10 | 1.18 | 2 |
| | 1.00 | 1.05 | 1.08 | 0.95 | 1.15 | 1.20 | |
| Av., | 0.99 | 1.08 | 1.09 | 0.98 | 1.13 | 1.19 | |
| 6 | 1.09 | 1.19 | 1.21 | 1.16 | 1.35 | 1.36 | $2^1/_4$ |
| | 1.08 | 1.13 | 1.18 | 1.08 | 1.36 | 1.38 | |
| | 1.06 | 1.15 | | 1.15 | 1.33 | | |
| | | | | | 1.31 | | |
| Av., | 1.08 | 1.15 | 1.19 | 1.13 | 1.34 | 1.37 | |
| 7 | 1.26 | 1.45 | 1.55 | 1.39 | 1.48 | 1.58 | 2 |
| | 1.29 | 1.43 | 1.60 | 1.36 | 1.45 | 1.63 | |
| Av., | 1.28 | 1.44 | 1.58 | 1.37 | 1.46 | 1.60 | |
| 8 | 1.40 | 1.53 | 1.75 | 1.56 | 1.75 | 1.79 | $2^1/_4$ |
| | 1.47 | 1.58 | 1.78 | 1.54 | 1.67 | 1.78 | |
| | 1.45 | 1.63 | | 1.58 | 1.65 | | |
| | | | | | 1.78 | | |
| | | | | | 1.65 | | |
| Av., | 1.44 | 1.58 | 1.76 | 1.56 | 1.70 | 1.78 | |

with 30 cc. concentrated sulfuric acid and 0.7 g. of mercury for periods of 2, 3, and 4 hours, both with and without the addition of permanganate after completing the digestion. An inspection of the plotted results shows clearly that the amount of nitrogen obtained increases with the time of digestion and with the addition of permanganate. Apparently this method requires more than 4 hours' digestion to secure the maximum yield of nitrogen.

SERIES 2: KJELDAHL-GUNNING METHOD—Table III and the curves in Fig. 2 show the results obtained by digesting the samples with 30 cc. concentrated sulfuric acid, 0.7 g. of mercury, and 7 g. of potassium sulfate for periods of 2, 3, 4, and 7 hours with and without the addition of permanganate at the end of digestion.




The addition of potassium sulfate to the sulfuric acid and mercury accelerated the rate of oxidation of the coal, the digestion mixture becoming colorless approximately $^1/_2$ hour sooner than in Series 1. In those cases where permanganate was used at the end of the digestion, practically identical results were obtained in the 3-, 4-, and 7-hour periods. The same results were obtained on digesting 4 hours without adding permanganate

TABLE III—SERIES 2: KJELDAHL-GUNNING METHOD
Digestion with 0.7 g. Hg and 30 cc. $H_2SO_4$

| Coal No. | No $KMnO_4$ added: Per cent N after digesting 2 hrs. | 3 hrs. | 4 hrs. | $KMnO_4$ added at end of digestion: Per cent N after digesting 2 hrs. | 3 hrs. | 4 hrs. | 7 hrs. | No. hrs digested before liquid became clear |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.61 | 0.66 | 0.71 | 0.68 | 0.78 | 0.78 | 0.80 | $1^1/_4$ |
| | 0.64 | 0.69 | 0.76 | 0.71 | 0.77 | 0.76 | 0.78 | |
| | | | | 0.71 | 0.71 | | | |
| | | | | | 0.74 | | | |
| Av., | 0.63 | 0.68 | 0.74 | 0.70 | 0.75 | 0.77 | 0.79 | |
| 2 | 0.91 | 1.05 | 1.05 | 0.99 | 1.05 | 1.07 | 1.05 | $1^1/_2$ |
| | 0.91 | 1.03 | 1.04 | 1.03 | 1.04 | 1.05 | 1.07 | |
| | | | | | 1.04 | | | |
| Av., | 0.91 | 1.04 | 1.04 | 1.01 | 1.04 | 1.06 | 1.06 | |
| 3 | 1.12 | 1.12 | 1.13 | 0.98 | 1.15 | 1.15 | 1.18 | $1^1/_4$ |
| | 1.10 | 1.10 | 1.15 | 1.07 | 1.13 | 1.15 | 1.16 | |
| | | | | 1.04 | 1.12 | | | |
| Av., | 1.11 | 1.11 | 1.14 | 1.03 | 1.13 | 1.15 | 1.17 | |
| 4 | 1.08 | 1.19 | 1.19 | 1.15 | 1.16 | 1.18 | 1.15 | $1^1/_2$ |
| | 1.06 | 1.16 | 1.19 | 1.14 | 1.22 | 1.20 | 1.16 | |
| | | 1.14 | | 1.17 | 1.24 | 1.18 | | |
| | | | | 1.12 | 1.19 | | | |
| | | | | | 1.17 | | | |
| Av., | 1.07 | 1.16 | 1.19 | 1.14 | 1.20 | 1.19 | 1.16 | |
| 5 | 1.19 | 1.29 | 1.31 | 1.26 | 1.31 | 1.31 | 1.20 | $1^3/_4$ |
| | 1.23 | 1.31 | 1.30 | 1.21 | 1.31 | 1.31 | 1.33 | |
| | | | | | | | 1.25 | |
| Av., | 1.21 | 1.30 | 1.31 | 1.24 | 1.31 | 1.31 | 1.27 | |
| 6 | 1.28 | 1.33 | 1.40 | 1.33 | 1.36 | 1.38 | 1.35 | $1^1/_4$ |
| | 1.32 | 1.33 | 1.38 | 1.32 | 1.38 | 1.40 | 1.36 | |
| | 1.28 | | | 1.33 | | 1.38 | | |
| | | | | 1.32 | | | | |
| | | | | 1.34 | | | | |
| Av., | 1.29 | 1.33 | 1.39 | 1.33 | 1.37 | 1.39 | 1.36 | |
| 7 | 1.62 | 1.67 | 1.73 | 1.57 | 1.72 | 1.77 | 1.66 | $1^1/_2$ |
| | 1.51 | 1.65 | 1.75 | 1.49 | 1.71 | 1.75 | 1.63 | |
| | | | | | | | 1.61 | |
| | | | | | | | 1.70 | |
| Av., | 1.57 | 1.66 | 1.74 | 1.53 | 1.72 | 1.76 | 1.67 | |
| 8 | 1.85 | 1.83 | 1.86 | 1.75 | 1.76 | 1.83 | 1.87 | $1^1/_2$ |
| | 1.80 | 1.85 | 1.84 | 1.75 | 1.84 | 1.85 | 1.86 | |
| | | | | 1.78 | 1.85 | 1.82 | 1.89 | |
| | | | | | | 1.80 | | |
| | | | | | | 1.83 | | |
| Av., | 1.83 | 1.84 | 1.85 | 1.76 | 1.82 | 1.83 | 1.87(a) | |

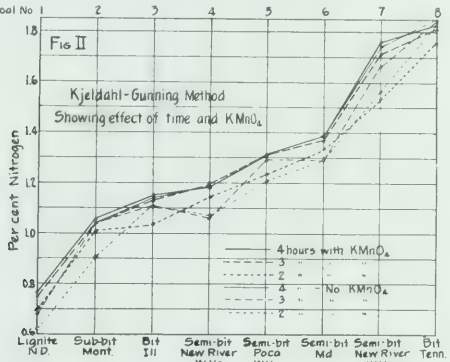
(a) Coal No. 8 digested in the same set for 4 hours gave 1.86, 1.88 and 1.86 per cent N.

[1] Siegfried, Max, and Weidenhaupt, O., "Kjeldahl Nitrogen Determination," *Z. physiol. Chem.*, **76** (1912), 238.

at the end; however, on digesting 3 hours without permanganate several low yields were obtained. Hence, adding permanganates according to the method previously described in this paper proved a positive aid to complete oxidation in those cases where the time of digestion was not quite sufficient. In no cases did the addition of permanganate seem to cause any loss of nitrogen.

The greater efficiency of the Kjeldahl-Gunning method as compared with the Kjeldahl method is graphically shown in Fig. 3 which gives a comparison of the nitrogen yields obtained by the two methods on digesting 2, 3, and 4 hours.

SERIES 3: EFFECT OF VARIOUS CONCENTRATIONS OF POTASSIUM SULFATE—Self[1] and Carpiaux[2] have recently called attention to the danger of volatilization of ammonia during digestion when the composition of the residue approximates that of acid potassium sulfate ($KHSO_4$). Losses of this nature were avoided by using a large excess of sulfuric acid, *i. e.*, 30 cc. acid to 7 g.




of potassium sulfate. As shown in the results of Table IV, no appreciable diminution in the yield of nitrogen occurred on increasing the potassium sulfate to 15 g. On digesting 4 hours with 22 g. potassium sulfate, losses of from 0.04 to 0.13 per cent nitrogen took place. Apparently the ratio of grams potassium sulfate to cubic centimeters sulfuric acid should not exceed 0.5.

TABLE IV—SERIES 3. EFFECT OF VARYING AMOUNTS OF $K_2SO_4$ IN KJELDAHL-GUNNING METHOD

30 cc. $H_2SO_4$, 0.7 g. Hg, $K_2SO_4$ as shown, and $KMnO_4$ at end of digestion

| Coal No | 3 hours 7 g. $K_2SO_4$ | 3 hours 10 g. $K_2SO_4$ | 3 hours 15 g. $K_2SO_4$ | 4 hours digestion 22 g. $K_2SO_4$ |
|---|---|---|---|---|
| 1 | 0.77 | 0.79 | 0.79 | |
| 2 | 1.04 | 1.04 | 1.05 | |
| 3 | 1.13 | 1.14 | 1.14 | |
| 4 | 1.20 | 1.18 | 1.15 | |
| 5 | 1.31 | 1.31 | 1.32 | 1.21(*a*) 1.19 |
| 6 | 1.37 | 1.40 | 1.40 | |
| 7 | 1.72 | 1.72 | 1.72 | 1.66(*a*) 1.68 1.68 |
| 8 | 1.82 | 1.82 | 1.82 | 1.76 |

(*a*) Coal No. 5 digested in the same set, with 7 g. $K_2SO_4$ gave 1.32 per cent N; coal No. 7 digested in the same set, with 7 g. $K_2SO_4$ gave 1.72 per cent N.

SERIES 4: MODIFICATION FOR NITRIC NITROGEN; KJELDAHL-GUNNING-JODLBAUER METHOD—Table V and Fig. 4 give the results obtained by digesting the coal with 30 cc. sulfuric acid, 7 g. potassium sulfate, 0.7 g. mercury, 2 g. zinc dust, and 2 g. salicylic acid, according to the Jodlbauer modification for nitric nitrogen. The time of digestion was necessarily longer on account of the slow and gradual heating required by this method. The results on digesting 4½ hours were approximately the same, within the experimental error, as obtained in the standard Kjeldahl-Gunning method;[1] as anticipated, the samples showed no nitric nitrogen.

TABLE V—SERIES 4. KJELDAHL GUNNING JODLBAUER METHOD

30 cc. $H_2SO_4$, 7 g. $K_2SO_4$, 0.7 g. Hg, 2 g. zinc dust, and 2 g. salicylic acid
All determinations became colorless after digesting 2 hours

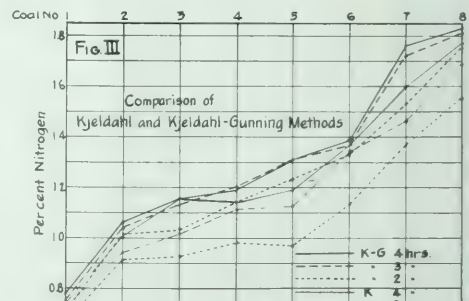
| Coal No | Per cent N after heating 3 hrs. | 4 hrs. | 4.5 hrs. | Per cent N by standard Kjeldahl-Gunning method | Difference |
|---|---|---|---|---|---|
| 1 | 0.78 | 0.75 | 0.78 | | |
| | 0.78 | 0.75 | 0.78 | 0.77 | +0.01 |
| | Av. 0.78 | 0.75 | 0.78 | | |
| 2 | 0.94 | 0.98 | 0.98 | | |
| | 0.93 | 0.98 | 0.98 | 1.06 | −0.08 |
| | Av. 0.93 | 0.98 | 0.98 | | |
| 3 | 1.12 | 1.15 | 1.17 | | |
| | 1.07 | 1.12 | 1.16 | 1.15 | +0.02 |
| | Av. 1.10 | 1.13 | 1.17 | | |
| 4 | 1.18 | 1.25 | 1.20 | | |
| | 1.25 | 1.23 | 1.18 | 1.19 | 0.00 |
| | Av. 1.21 | 1.24 | 1.19 | | |
| 5 | 1.24 | 1.34 | 1.37 | | |
| | 1.27 | 1.39 | 1.34 | 1.31 | +0.04 |
| | Av. 1.25 | 1.37 | 1.35 | | |
| 6 | 1.15 | 1.28 | 1.30 | | |
| | 1.15 | 1.25 | 1.33 | 1.39 | −0.08 |
| | Av. 1.15 | 1.26 | 1.31 | | |
| 7 | 1.62 | 1.74 | 1.77 | | |
| | 1.64 | 1.74 | 1.75 | 1.76 | 0.00 |
| | Av. 1.63 | 1.74 | 1.76 | | |
| 8 | 1.60 | 1.78 | 1.80 | | |
| | 1.65 | 1.80 | 1.82 | 1.83 | −0.02 |
| | Av. 1.62 | 1.77 | 1.81 | | |

SERIES 5: GUNNING METHOD—Table VI and Fig. 4 show the results obtained by digesting the coal 4 hours with 30 cc. sulfuric acid and 7 g. potassium sulfate, according to the Gunning method, and adding potassium permanganate at the end of digestion. This mixture oxidized the coal very slowly; from 3 to 4 hours of digestion were required before the solutions became colorless. All the results were low.

TABLE VI—SERIES 5: GUNNING METHOD

30 cc. $H_2SO_4$, 7 g. $K_2SO_4$; $KMnO_4$ added at end of digestion

| Coal No | Per cent N after digesting 4 hrs. Duplicates | | Av. | Per cent N by standard Kjeldahl-Gunning method | Difference |
|---|---|---|---|---|---|
| 1 | 0.65 | 0.65 | 0.65 | 0.77 | −0.12 |
| 2 | 0.78 | 0.75 | 0.76 | 1.06 | −0.30 |
| 3 | 0.88 | 0.93 | 0.90 | 1.15 | −0.25 |
| 4 | 0.90 | 0.95 | 0.93 | 1.19 | −0.26 |
| 5 | 1.03 | 1.00 | 1.01 | 1.31 | −0.30 |
| 6 | 1.10 | 1.15 | 1.13 | 1.39 | −0.26 |
| 7 | 1.25 | 1.20 | 1.23 | 1.76 | −0.53 |
| 8 | 1.55 | 1.48 | 1.51 | 1.63 | −0.32 |




SERIES 6: COPPER-SULFATE MODIFICATION—Table VII and Fig. 4 show the results obtained by digesting coal 3 hours with 30 cc. sulfuric acid, 7 g. potassium sulfate, 1 g. copper sulfate, and adding potassium permanganate at the end of digestion.

[1] Self, P. A. W., "An Unrecognized Source of Error in the Kjeldahl-Gunning Method for the Determination of Nitrogen," *Pharm. Jour.*, **88** (1912), 384–5.

[2] Carpiaux, Em., "A Source of Error in the Kjeldahl-Gunning Process," *Bull. Soc. Chim. Belg.*, **27** (1913), 13–14.

[1] Results by standard Kjeldahl-Gunning method refer to the average percentages of nitrogen obtained for each coal in Series 2, digesting 4 hours with 30 cc. concentrated $H_2SO_4$, 0.7 g. Hg, 7 g. $K_2SO_4$, and adding $KMnO_4$ at the end of the digestion.

The copper sulfate proved a less effective catalytic agent than mercury, about 45 minutes more time being required to attain a colorless solution. The percentages of nitrogen obtained on digesting 3 hours were from 0.02 to 0.37 per cent less than by the use of mercury. Longer periods of digestion would probably have given the full yield of nitrogen.

TABLE VII—SERIES 6. COPPER SULFATE MODIFICATION
30 cc. $H_2SO_4$, 7 g. $K_2SO_4$, 1 g. $CuSO_4$, adding $KMnO_4$ at end of digestion

| Coal No. | Per cent N after digesting 3 hrs. Duplicates | | Av. | Per cent N by standard Kjeldahl-Gunning method | Difference |
|---|---|---|---|---|---|
| 1 | 0.69 | 0.68 | 0.68 | 0.77 | —0.09 |
| 2 | 1.02 | 0.99 | 1.00 | 1.06 | —0.06 |
| 3 | 1.04 | 0.97 | 1.00 | 1.15 | —0.15 |
| 4 | 1.10 | 1.08 | 1.09 | 1.19 | —0.10 |
| 5 | 1.24 | 1.27 | 1.25 | 1.31 | —0.06 |
| 6 | 1.22 | 1.22 | 1.22 | 1.39 | —0.17 |
| 7 | 1.69 | 1.72 | 1.70 | 1.76 | —0.06 |
| 8 | 1.50 | 1.53 | 1.51 | 1.83 | —0.32 |

SERIES 7: WILFARTH'S MODIFICATION USING $P_2O_5$—Table VIII and Fig. 4 show the results obtained by digesting the samples 3 hours with 30 cc. sulfuric acid, 6 g. phosphorus pentoxide,

TABLE VIII—SERIES 7: WILFARTH'S MODIFICATION, USING $P_2O_5$
Using 30 cc. $H_2SO_4$, 6 g. $P_2O_5$, 0.7 g. Hg, with $KMnO_4$ at end

| Coal No. | Per cent N after digesting 3 hrs. Duplicates | | Av. | Per cent N by standard Kjeldahl-Gunning method | Difference |
|---|---|---|---|---|---|
| 1 | 0.73 | 0.71 | 0.72 | 0.77 | —0.05 |
| 2 | 1.01 | 0.98 | 0.99 | 1.06 | —0.07 |
| 3 | 1.11 | 1.06 | 1.08 | 1.15 | —0.07 |
| 4 | 1.13 | 1.16 | 1.14 | 1.19 | —0.05 |
| 5 | 1.28 | 1.33 | 1.31 | 1.31 | 0.00 |
| 6 | 1.33 | 1.28 | 1.31 | 1.39 | —0.08 |
| 7 | 1.68 | 1.73 | 1.71 | 1.76 | —0.05 |
| 8 | 1.63 | 1.63 | 1.63 | 1.83 | —0.20 |

0.7 g. mercury, and adding potassium permanganate at the end of digestion, according to one of the Wilfarth modifications of the Kjeldahl method.

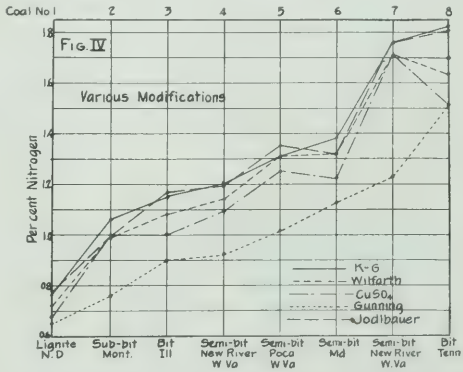
Using the above proportions of reagents, the phosphorus pentoxide was slightly less effective than potassium sulfate, and, furthermore, it is a less convenient material to use.

SERIES 8: DUMAS METHOD—The Dumas gas volumetric method of determining nitrogen is generally regarded as fundamental and applicable to most classes of organic compounds. So, in making an investigation of various modifications of the Kjeldahl method of determining nitrogen in coal, it seemed desirable to check the results by this method.

PROCEDURE—In general, the procedure followed was that given by Gattermann[1] and H. Meyer,[2] using an open tube and generating pure $CO_2$[3] by $K_2CO_3$ solution and dilute $H_2SO_4$.[4] The combustion tube was of fused silica and the nitrogen was collected in a Schiff nitrometer and transferred, for measurement over water, to a water-jacketed gas burette. The tube was charged in the usual manner with a roll of reduced copper gauze 8 cm. long, about 40 cm. coarse CuO, followed by 50 g. fine CuO mixed with the sample. In filling the silica tube, it was found more satisfactory to pour the fine CuO around a glass rod, then remove the rod holding the tube horizontally, thereby leaving a channel across the fine material, than to open the channel by tapping the tube as this tended to form a canal over the coarse oxide also. The fine oxide was reoxidized by heating in the air in an iron dish after each determination. The coarse oxide was so treated as often as it showed any appreciable signs of reduction.

TESTING THE METHOD—To test the method a blank determination was made, using 1 g. of the pure sucrose which is supplied by the Bureau of Standards for calorimeter standardization. There was little difficulty in clearing the cold tube of air so that the $CO_2$ was completely absorbed. However, on heating the copper oxide and especially that portion of the tube containing the fine oxide and sucrose, fine bubbles of a non-absorbable gas began to collect in the nitrometer. At the end of 2 hours' heating 2 cc. of gas had collected and after 4 hours there were over 4 cc. and the gas was coming slowly but steadily. As the sucrose and $CO_2$ were both free from nitrogen, the CuO was regarded as the probable source of error.

After cooling the furnace, the CuO was removed and ignited in the iron dish over a Chaddock burner for several hours. (The Chaddock burner gave a more general heat than the Meker, so that the iron dish was not oxidized sufficiently to scale off iron oxide.) The tube was recharged as before except that no combustible material was used. As before, the tube was cleared of air with little difficulty, but on heating the copper oxide a non-absorbable gas was given off. At the end of 6 hours 6.6 cc. had collected. The tube containing $CO_2$ was allowed to cool overnight, and again heated 7 hours the next day, yielding an additional 1.4 cc. At the end of the second day the evolution had practically ceased. An analysis of this gas showed 5.41 per cent oxygen, a trace of combustible material, and 94.6 per cent of nitrogen. These experiments were repeated using




several different brands of copper oxide but giving essentially the same results. However, oxidized copper wire seemed better than other forms as it was then easier to clear the tube of air. Repeated evacuation of the cold tube with a Geryk pump and refilling with $CO_2$ aided in removing the air, but failed to materially reduce the gas obtained on heating.

It appeared that copper oxide prepared by igniting and cooling in the air as usually directed retained air which could not be removed by evacuating the cold tube, and which was slowly but persistently given off on heating in an atmosphere of $CO_2$.

A review of the literature on this subject disclosed the following references: In speaking of the Dumas method, H. Meyer[1] states: "The chief source of error lies in the impossibility of freeing the fine copper oxide from air, and, therefore, most of the results are too high by 0.1 to 0.2 per cent." Fresenius[2] states: "The results are generally somewhat too high, *viz.*, by about 0.2 to 0.5 per cent;" and that in a blank experiment with sugar the quantity of unabsorbed gas "should not exceed 1 or 1.5 cc."

Abegg and Auerbach[3] state that "black copper oxide has the

[1] Gattermann-Schober, "Practical Methods of Organic Chemistry," p. 85.

[2] Meyer, H., "Analyse und Konstitutionsermittelung organischer Verbindungen," 2 Auflage, Julius Springer, Berlin, 1909, S. 185.

[3] Blau, Fritz, "Verfahren zur Bestimmung des Stickstoffes in organischen Substanzen," M. 13 (1892), S. 277.

[4] Young, G., and Caudwell, B., "An Improved Apparatus for Generating $CO_2$," *J. Soc. Chem. Ind.*, **26** (1907), 184.

[1] Meyer, H., "Analyse und Konstitutionsermittelung organischen Verbindungen," 2 Auflage, Julius Springer, Berlin, 1909, p. 187.

[2] Fresenius-Cohen, "Quantitative Chemical Analysis," 6th ed., Vol. II, p. 68 (1904).

[3] Abegg, R., and Auerbach, Fr., "Handbuch der anorganische Chemie," Vol. [illegible], p. 664

power of holding gases such as carbon dioxide, oxygen, nitrogen, carbon monoxide, water vapor, etc. This may be by adsorption, solubility in the amorphous phase, or perhaps by chemical combination."

Morse[1] prepares both coarse and fine copper oxide for use by first heating them for $1^1/_2$ hours or more at a full-red heat in a combustion tube through which is passed a current of oxygen or air. Without cooling, carbon dioxide is then passed through the tube for an hour or more. The oxide is allowed to cool in $CO_2$.

Phillips[2] in describing the Dumas method for the determination of nitrogen in natural gas states that "some difficulty was experienced in expelling air from copper oxide when the apparatus was being prepared for work. In beginning a series of determinations several days were often required for the purpose. The porcelain tube was strongly heated, while a slow stream of carbon dioxide was maintained; the CuO was not considered to be in proper condition until the escaping $CO_2$ was absorbed without residue. It was found that the CuO when once impregnated with $CO_2$, while strongly heated, could be reoxidized by air current with little tendency to occlusion of air, but if the copper oxide was allowed to cool in contact with air much time was lost in removing the air by carbon dioxide even when strong heat was applied."

As the preliminary determinations confirmed Phillips' observations in regard to the long time necessary to expel the air from copper oxide by merely heating it in a current of $CO_2$, it seemed desirable to try to shorten the time by heating the CuO in a vacuum to prepare it for the analyses. Experiments were made to see the advisability of this procedure and to obtain some data tending to show how the nitrogen is held.

EXPERIMENT 3*a*—Heating *in vacuo* was continued for several hours, $CO_2$ was then admitted and the tube allowed to cool. When cool the CuO was exposed to air for 2 hours in an open dish and the experiment repeated as in Experiment 1*a*, giving 1.9 cc. of non-absorbable gas or nitrogen.

EXPERIMENT 4*a*—The CuO from Experiment 3*a* was cooled in $CO_2$, then removed from the tube, mixed with sucrose, replaced in the tube, and largely reduced to metallic copper by heating. It was then removed from the tube, again oxidized in the air as usual, replaced in the tube, and treated as in Experiment 1*a*. 3.5 cc. of nitrogen were collected after 2 hours' heating.

EXPERIMENT 1*b*—A fresh sample of the same brand of copper oxide was taken and treated exactly as in Experiment 1*a*, giving 2.3 cc. of nitrogen.

EXPERIMENT 4*b*—The CuO from Experiment 1*b* was reduced with sucrose and treated exactly as in Experiment 4*a*, giving 3.9 cc. of nitrogen.

In order to show the effect of the size of CuO on the amount of nitrogen retained, a sample of Baker's CuO in "wire form" was pulverized to pass through a 40 mesh screen and remain on 100 mesh.

EXPERIMENT 1*c*—Using 100 grams of this CuO and treating exactly as in Experiments 1*a* and 1*b*, 0.9 cc. of nitrogen was obtained.

EXPERIMENT 2*c*—This oxide from Experiment 1*c* was treated exactly as in Experiment 2*a*, and gave 0.7 cc. of nitrogen.

EXPERIMENT 4*c*—The oxide from Experiment 2*c* was reduced with sucrose and treated exactly as in Experiments 4*a* and 4*b*, and gave 2.7 cc. of nitrogen.

EXPERIMENT 5*c*—The oxide from Experiment 4*c* was treated as a fresh sample as in Experiments 1*a*, 1*b* and 1*c*, giving 0.7 cc of nitrogen.

EXPERIMENT 6*c*—The CuO from Experiment 5*c* was again reduced with sucrose and further treated as in Experiments 4*a*, 4*b* and 4*c*, and gave 3.2 cc. of nitrogen.

EXPERIMENT 7—60 grams of the 40–100 mesh material that had been reduced and reoxidized in air were tested in a special apparatus of glass and quartz with mercury seals at the joints. The CuO was placed in a quartz tube, which was then completely evacuated with a mercury pump. Heat was applied by an electric furnace and the temperature of the CuO raised to 800° C. Over 150 cc. of gas were collected. This was analyzed, showing 89.60 per cent $CO_2$, 8.34 per cent air, and 2.06 per cent excess nitrogen. The CuO was then removed from the apparatus and heated in air in the open dish for 3 hours and again tested just as described, giving less than 1 cc. of gas under the combined heat and vacuum. The same CuO after being reduced by sucrose and cooled in $CO_2$ was again heated in the special apparatus *in vacuo* to about 500° C., when such a large quantity of gas was suddenly evolved that the apparatus was broken and further tests discontinued.

A study of the results of Experiments 1 to 6, inclusive, as shown in Table IX, tends to show that the nitrogen given off on heating CuO *in vacuo* or $CO_2$ is held by the oxide in two ways:

(1) In some form of chemical combination which takes place on oxidizing reduced copper in air.

TABLE IX EXPERIMENTS SHOWING NITROGEN GIVEN OFF FROM COPPER OXIDE ON HEATING UNDER VARIOUS CONDITIONS

Cc. N at 25° C. and 740 mm. pressure, given off on heating 100 g. copper oxide at approximately 850° C. for a period of 2 hours

| Experiment No | Method of Treatment | Baker and Adamson 200 mesh CuO Sample A | Baker and Adamson 200 mesh CuO Sample B | J. T. Baker's CuO, "wire form," 40–100 mesh Sample C |
|---|---|---|---|---|
| 1 | Copper oxide placed in silica tube, evacuated and replaced with $CO_2$ repeatedly until no further nitrogen was evolved. It was then heated for 2 hours | 2.5 | 2.3 | 0.9 |
| 2 | Copper oxide from previous experiment, subjected alternately to vacuum and $CO_2$ while heated to 850° C. for several hours, then cooled in $CO_2$, exposed to air 18 hours, and tested as in Experiment 1 | 2.2 | ... | 0.7 |
| 3 | CuO from previous experiment treated as in Experiment 2, except exposed to air only 2 hours | 1.9 | ... | ... |
| 4 | CuO from preceding experiment cooled in $CO_2$, reduced to metallic Cu, re-oxidized, cooled in air, and treated as in Experiment 1 | 3.5 | 3.9 | 2.7 |
| 5 | CuO from preceding experiment treated as in Experiment 1 | ... | ... | 0.7 |
| 6 | CuO from preceding experiment treated as in Experiment 4 | ... | ... | 3.2 |

### EXPERIMENTAL WORK ON NITROGEN HELD BY CuO

As a basis of comparison the gas volume was reduced in each case to the corresponding volume at 25° C. and 740 mm. pressure, that being about the average temperature and pressure at which the experiments were made.

EXPERIMENT 1*a*—100 grams of Baker and Adamson's CuO of 100 mesh or finer (86 per cent passed through 200 mesh), followed by a reduced copper spiral for removing oxygen, were placed in the silica tube of a combustion furnace. The tube was connected with a nitrometer, an apparatus for generating pure $CO_2$, and a Geryk pump. The air was removed by the Geryk pump and replaced by pure $CO_2$ several times, till there was complete absorption on passing $CO_2$ through the tube. The CuO was then heated to a full-red heat for 2 hours, giving 2.5 cc. of non-absorbable gas.

EXPERIMENT 2*a*—Heating of CuO in Experiment 1*a* was continued several hours, applying vacuum repeatedly and replacing the gas by $CO_2$ until no further non-absorbable gas was liberated. The CuO was cooled in $CO_2$, then removed from the tube and let stand overnight in the air. It was then replaced in the tube, the air replaced by $CO_2$ by use of vacuum until there was complete absorption in KOH solution. After heating the CuO 2 hours 2.2 cc. of gas were collected.

[1] Morse, H. N., "Exercises in Quantitative Chemistry," p. 276.

[2] Phillips, F. C., "Fluctuation in the Composition of Natural Gas," *Proc. Eng. Soc. Western Pa.*, **14** (1898), 309.

(2) By adsorption.

Experiments 4 and 6 show that both coarse and fine copper oxide, when partly reduced and reoxidized in air, retain nit ogen which is not completely removed at room temperature by evacuation and replacement with $CO_2$, 2.7 to 3.9 cc. of nitrogen being given off from 100 g. oxide on subsequently heating it 2 hours at 850° C. in an atmosphere of $CO_2$.

On the other hand, when the CuO was subjected to alternate vacuum and $CO_2$ for several hours at 850° C. instead of room temperature, until no further nitrogen was evolved, and was then cooled in $CO_2$, exposed to air and again heated as in Experiments 4 and 6, the 40–100 mesh "wire" oxide gave off only 0.7 to 0.9 cc. of nitrogen, while the 200 mesh material gave off 1.9 to 2.2 cc.

It seems, then, that adsorption may account for this residual nitrogen which varies in amount with the fineness of the oxide, and that the larger quantity of nitrogen which is obtained on the first vacuum-and-heat treatment subsequent to reoxidation in air of reduced copper is present in some form of chemical combination. The larger error due to the so-called chemically combined nitrogen can be eliminated from the Dumas method by first preparing the copper oxide which is subsequently mixed with the sample, by heating it *in vacuo* for several hours and cooling it in $CO_2$. The smaller, but more persistent error, due to adsorbed nitrogen can be reduced by using as coarse an oxide as possible.

Using 50 g. of the 40–100 mesh CuO and coarse oxidized wire, both prepared as above, the sucrose and picric acid gave the following results under the usual conditions of determining nitrogen:

TIME OF HEATING, 2 HOURS

| Sample Gram | Nitrogen cc. | Temperature ° C. | Pressure mm. Hg | Nitrogen Mg | Nitrogen Per cent |
|---|---|---|---|---|---|
| SUCROSE: | | | | | |
| 1.0000 | 0.4 | 25 | 740 | 0.43 | 0.04 |
| 1.0000 | 0.1 | 26 | 745 | 0.11 | 0.01 |
| 1.0000 | 0.14 | 30 | 744 | 0.15 | 0.02 |
| PICRIC ACID: | | | | | |
| 0.2000 | 34.2 | 27 | 745 | 37.1 | 18.55 |
| 0.2000 | 33.7 | 26 | 740 | 36.4 | 18.18 |
| 0.2000 | 32.8 | 20 | 746 | 36.8 | 18.41 |
| 0.2000 | 33.4 | 23 | 746 | 36.9 | 18.46 |

Since the theoretical nitrogen content of picric acid is 18.34, both of hese series show that the error is within the limits of the errors of manipulation for most work. In further corroboration, the explosive chemical laboratory of the Bureau has made many nitrogen determinations on various nitrogen compounds with uniform success, by using these precautions in the preparation of the CuO.

In Table X and Fig. 5 are given the percentages of nitrogen obtained by the Dumas method in the previously described eight samples of coal. The procedure was the same as in the sucrose and picric-acid determinations. The average values by the Dumas method check the Kjeldahl-Gunning values to within the total experimental error of the two methods. The larger

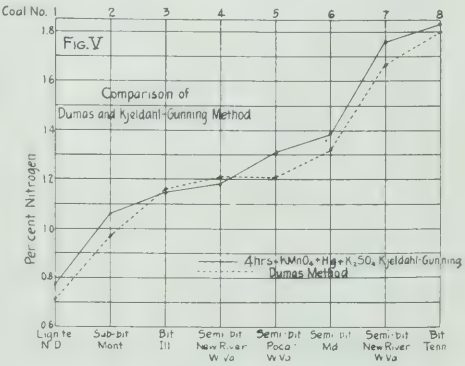
TABLE X—SERIES 8. COMPARISON OF RESULTS BY DUMAS AND BY KJELDAHL GUNNING METHOD

| Coal No | Percentage N by Dumas method | Av | Kjeldahl-Gunning method | Diff. | Coal No | Percentage N by Dumas method | Av | Kjeldahl-Gunning method | Diff. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.73 | | | | 5 | 1.39 | | | |
| | 0.61 | | | | | 1.10 | | | |
| | 0.80 | 0.71 | 0.77 | —0.06 | | 1.23 | 1.21 | 1.31 | —0.10 |
| 2 | 1.03 | | | | 6 | 1.44 | | | |
| | 0.90 | | | | | 1.19 | | | |
| | 0.97 | 0.97 | 1.06 | —0.09 | | 1.32 | 1.32 | 1.39 | —0.07 |
| 3 | 1.15 | | | | 7 | 1.61 | | | |
| | 1.28 | | | | | 1.65 | | | |
| | 1.07 | 1.16 | 1.15 | +0.01 | | 1.76 | 1.67 | 1.76 | —0.09 |
| 4 | 1.21 | | 1.19 | +0.02 | 8 | 1.61 | | | |
| | | | | | | 1.86 | | | |
| | | | | | | 1.83 | | | |
| | | | | | | 1.91 | 1.80 | 1.83 | —0.03 |

deviations of the individual Dumas values are due to the experimental difficulty in burning a relatively large quantity of carbon as compared to the nitrogen present, without having the nitrogen contaminated with combustible gases, or leaving some unburned coal in the tube. These sources of error are not common to definite nitrogen compounds.

The volatile hydrocarbons of coal including large amounts of methane are given off readily on heating. These are but slowly oxidized by CuO in the presence of $CO_2$,[1] thereby giving the possibility of too high results.

Furthermore, coal and coke[2] are oxidized very slowly by CuO in the presence of $CO_2$, leaving a possible residue of unburned




carbon even after 2 or 3 hours heating. So without examining the evolved nitrogen for combustible gases and the CuO residue for unburned carbon, there would always be some doubt, in the case of coals, of the accuracy of the individual determinations.

## SUMMARY

1—In comparative nitrogen determinations by various modifications of the Kjeldahl method on 7 different coals and 1 lignite, the highest and most concordant results in the shortest time of digestion were obtained by the combined Kjeldahl-Gunning method, using both mercury and potassium sulfate as proposed by Dyer.[3] This confirms the results obtained on other organic materials by Sherman and Falk,[4] Gladding,[5] Wedemeyer,[6] Trescot,[7] and the Committee[8] on Fertilizer Analysis of the American Chemical Society.

2—When 22 g. of potassium sulfate were used with 30 cc. of acid, no losses occurred between limits of 7 and 15 g. $K_2SO_4$ per 30 cc. $H_2SO_4$.

3—As a catalytic agent mercury proved more effective than copper sulfate, and for raising the boiling point of the mixture, $K_2SO_4$ was superior to $P_2O_5$ from every standpoint.

[1] Dunstan and Carr, "Note on a Difficulty in the Determination of Nitrogen by the Absolute Method," *Proc. Chem. Soc.*, **1896**, pp. 48–49.

[2] Schmitz, G., "Zur bestimmung des Stickstoffes in Steinkohle und Koks," *Z. anal. Chem.*, **25** (1886), 314–318.

[3] Dyer, B., "Kjeldahl's Method for the Determination of Nitrogen," *Jour. Chem. Soc.*, **67** (1895), 811–817.

[4] Sherman, H. C., and Falk, M. J., "The Determination of Nitrogen in Organic Compounds," *J. A. C. S.*, **26** (1904), 1469–74.

[5] Gladding, T. S., "Comparative Work on Nitrogen Estimation by the Kjeldahl and Gunning Methods and by a Combination of the Two Methods," *Proc. Assoc. Off. Agr. Chem.*, **1906**, 85.

[6] Wedemeyer, K., "Ein Wort zur Stickstoffbestimmung nach Kjeldahl-Gunning," *Chem. Zeit.*, **22** (1898), 21.

[7] Trescot, T. C., "Comparison of the Kjeldahl-Gunning-Arnold Method with the Official Kjeldahl and Official Gunning Methods of Determining Nitrogen." THIS JOURNAL, **5** (1913), 914.

[8] "The Determination of Nitrogen in Commercial Ammoniates of High Nitrogen Content," First Report of the Committee on Nitrogen Division of Fertilizer Chemists, *Amer. Chem. Soc.*, THIS JOURNAL, **3** (1911), 691.

4—The official Gunning method did not prove applicable to coal as the results on digesting 4 hours were 0.2 to 0.3 per cent low.

5—Modifications for nitrates or nitro compounds did not give results appreciably different from the ordinary Kjeldahl-Gunning method.

6—In no cases could low results be ascribed to the addition of potassium permanganate in the manner described. On the other hand, it seemed to promote higher results in cases of incomplete digestion.

7—In all cases it was found necessary to digest coal approximately 2 hours after becoming colorless, to secure maximum yield of nitrogen.

8—An independent check on the absolute accuracy of the Kjeldahl-Gunning method was obtained by determining the nitrogen in the same samples by the Dumas gas-volumetric method. The greatest difference in the average values was 0.10 per cent and the mean difference was 0.05 per cent.

9—Errors in the Dumas method due to nitrogen from the fine CuO were minimized by previously heating the oxide for several hours *in vacuo*, cooling it in $CO_2$, and using "wire form" oxide pulverized to pass through a 40 mesh screen and remain on 100 mesh.

The authors desire to acknowledge their obligations to G. A. Hulett, Chief Chemist, for valuable suggestions and criticisms, to G. A. Burrell and his associates for making gas analyses and to G. B. Taylor for making the special vacuum tests of Experiment 7.

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## THE DETERMINATION OF GASOLINE VAPOR IN AIR

By G. A. Burrell and I. W. Robertson

Received November 10, 1914

In this report are shown results obtained by the Bureau of Mines in determining gasoline vapor in air. One of the methods presented is essentially the same as that used by the authors in determining benzene in artificial illuminating gas[1] except that lower temperatures were used. Briefly stated, this method consists in introducing the gasoline vapor-air mixture into a glass vessel at atmospheric pressure, cooling it by means of liquid air, then withdrawing the air with a vacuum pump, next closing the stopcock on the liquefaction bulb, next removing the liquid air, thereby allowing the gasoline to vaporize and reading its pressure on a manometer attached to the liquefaction bulb.

Dr. G. A. Hulett, Chief Chemist of the Bureau of Mines, first suggested this scheme of analysis to the authors for the determination of water vapor in air. It was a simple matter to apply it to benzene vapor, gasoline vapor, or other vapors in air. The chief requirement is that the vapor be cooled at a temperature where its pressure is practically nil. It was found that the temperature of solid carbon dioxide and acetone (about —78° C.), although low enough to retain benzene (boiling point 80° C.), was not low enough to retain the gasoline the authors worked with. This gasoline had a specific gravity at 15° C. of 0.689 = 73.2° Bé.

[1] Burrell, G. A. and Robertson, I. W. "The Separation of the Illuminants in Mixed Coal and Water Gas." THIS JOURNAL, 7 (1915), 17.

The following fractionation analysis made by Dr. E. W. Dean of the petroleum laboratory of the Bureau shows the fractions obtained at different temperatures: 200 g. of the gasoline were distilled in an unjacketed glass flask at the rate of 2 to 3 drops per sec.

TABLE I—FRACTIONATION ANALYSIS OF GASOLINE

| Temperature ° C. | Percentage by weight | Temperature ° C. | Percentage by weight |
|---|---|---|---|
| 50 | 0.9 | 110–120 | 7.3 |
| 50–60 | 9.0 | 120–130 | 4.9 |
| 60–70 | 14.5 | 130–140 | 3.2 |
| 70–80 | 14.4 | Residue | 2.7 |
| 80–90 | 13.8 | | |
| 90–100 | 12.9 | Total | 94.5 |
| 100–110 | 10.9 | Loss | 5.5 |

As stated before, experiments by the authors have shown that although benzene (boiling point 80° C.) can be retained at a temperature of —78° C., the gasoline vapor could not. The above fractionation analysis explains why. It will be observed that a considerable portion of the gasoline distilled at temperatures lower than 80° C., hence a temperature that would retain benzene vapor would not necessarily retain the gasoline vapor. Since a temperature lower than that of liquid carbon dioxide had to be used, the authors found it expedient to use the temperature of liquid air, because the latter has to be used, and time is consumed, in obtaining temperatures between those of liquid carbon dioxide and liquid air.

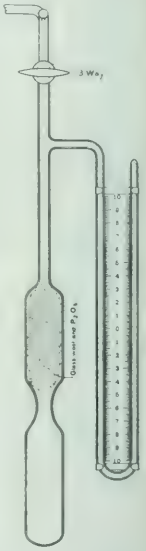

FIG. 1—APPARATUS FOR THE DETERMINATION OF GASOLINE VAPOR IN AIR

At Fig. 1 is shown the apparatus for the gasoline vapor or benzene-vapor determination. The bulb contains phosphorus pentoxide for removing water vapor. If the latter were not removed it would also be retained at low temperatures and its pressures subsequently measured along with the pressure exerted by the gasoline vapor.

To start a determination the apparatus is connected to a vacuum pump and exhausted of its air. The mixture of gasoline vapor and air is then introduced at atmospheric pressure, the barometer read, and the two bulbs immersed in liquid air contained in a Dewar flask. After waiting about 10 minutes the air is removed from the apparatus with a vacuum pump. The stopcock on the apparatus is then closed, the liquid air removed, the gasoline allowed to vaporize and its pressure read on the mercury manometer attached to the apparatus. The ratio of this pressure to the pressure of the atmosphere gives the percentage of gasoline vapor originally in the air.

The first work of the authors in analyzing gasoline vapor-air mixtures was performed by burning the gasoline vapor with air or oxygen, measuring the contraction in volume and the carbon dioxide produced, and from these data calculating the percentage of gasoline vapor by assuming that it was all pentane vapor. This assumption is wrong because gasoline

TABLE II—COMPARISON OF LIQUID-AIR SEPARATION AND COMBUSTION ANALYSIS METHODS FOR GASOLINE VAPOR IN AIR

| Sample Number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| LIQUID-AIR SEPARATION | Mm. Hg | Mm. Hg | Mm. Hg | Mm. Hg | Mm. Hg |
| Barometric pressure | 744 | 748 | 744 | 744 | 740 |
| Partial pressure of gasoline vapor | 8 | 19 | 23 | 67 | 110 |
| PER CENT GASOLINE VAPOR | $\frac{8 \times 100}{744} = 1.08$ | $\frac{19 \times 100}{748} = 2.40$ | $\frac{23 \times 100}{744} = 3.09$ | $\frac{67 \times 100}{744} = 9.04$ | $\frac{110 \times 100}{740} = 14.85$ |
| COMBUSTION ANALYSIS | Cc | Cc. | Cc | Cc. | Cc. |
| Volume of sample taken | 50.60 | 46.80 | 34.58 | 28.89 | 40.96 |
| Oxygen added | 40.10 | 46.80 | 51.16 | 72.44 | 69.08 |
| Total volume | 90.70 | 93.60 | 85.74 | 101.33 | 110.04 |
| After combustion | 88.55 | 88.65 | 81.42 | 90.75 | 84.94 |
| Contraction | 2.15 | 4.95 | 4.32 | 10.58 | 25.10 |
| After KOH absorption | 85.85 | 82.46 | 76.18 | 77.97 | 54.44 |
| $CO_2$ produced | 2.70 | 6.19 | 5.29 | 12.78 | 30.50 |
| PER CENT GASOLINE VAPOR | $\frac{2.70 \times 100}{5 \times 60.5} = 1.07$ | $\frac{6.19 \times 100}{5 \times 46.80} = 2.65$ | $\frac{5.29 \times 100}{5 \times 34.58} = 3.07$ | $\frac{12.78 \times 100}{5 \times 28.89} = 8.86$ | $\frac{30.50 \times 100}{5 \times 40.96} = 14.83$ |

is a mixture of liquid paraffin hydrocarbons including other paraffins than the pentanes. It was found, however, that the results obtained in the combustion analysis by calculating the data as pentane checked very well with the results obtained by separating the gasoline vapor with liquid air. In other words, the pentanes are distilled in largest quantity at first when gasoline is exposed to the air. Pentane reacts with oxygen as follows:

$$C_5H_{12} + 8O_2 = 5CO_2 + 6H_2O$$

The contraction is 4 volumes and the carbon dioxide 5 volumes. Hence the carbon dioxide produced by burning a sample of gasoline vapor can be divided by 5 to obtain the gasoline vapor present in air or the contraction can be divided by 4. The authors used the first method in the data presented in this paper.

The analyses in Table II show the data obtained by burning the gasoline-vapor-air-mixture in oxygen, and by separating the gasoline vapor with liquid air.

It will be observed that the combustion data, *i. e.*, the contraction and $CO_2$, agree very well with the reaction that occurs when pentane reacts with oxygen. In other words, the constituents that evaporated from the gasoline in greatest quantity were the pentanes.

SUMMARY

Two methods for the determination of gasoline vapor in air are shown. One has to do with the cooling of the sample with liquid air, the removal of the air with a vacuum pump, and the measurement of the partial pressure of the gasoline vapor. Another method has to do with the burning of the gasoline vapor with air or oxygen and calculating the percentage present from the carbon dioxide or contraction. One can tell closely enough for most purposes, how to calculate the combustion data from the ratio between the carbon dioxide and contraction.

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## THE COLORING PRINCIPLE OF MYRICA RUBRA -ITS AZO-, SULFIDE AND NITRO-DYESTUFFS

By SADAKICHI SATOW

Received November 28, 1914

In Japan, the bark of myrica rubra has been used for yellow or black dyeing from ancient times; it is found in the districts adjacent to warm-water currents and not in those influenced by cold currents. There are two varieties of it in Japan, one producing a larger sized fruit than the other; the larger fruit yields a greater quantity of coloring principle having the stronger tinctorial power.

While investigating the coloring principle of this variety, the author used a new process of separation of pure coloring principle which seems simpler and more effective than former processes. The method used was as follows: One pound of the extract of the bark of myrica rubra was crushed to bean size, boiled with 15 liters of water for several hours and set aside for four days; the brown solution was decanted off, the muddy precipitate once more boiled with 10 times its volume of water and filtered by suction while hot. After standing for a time, the glucoside of the coloring principle was deposited from the filtrate in rhombic crystals. The dark yellowish muddy residue was treated with twenty times its volume of acetone and filtered; to the brown filtrate a solution of lead acetate was added until the appearance of a reddish brown precipitate which was filtered off. The brownish yellow filtrate was distilled in a flask and the acetone evaporated off for the crystallization of the coloring principle. On concentrating the solution, fine greenish yellow needle crystals were easily obtained; these were washed several times in distilled water, then collected on a porous tile and recrystallized from acetone solution; the pure crystals were slightly greenish yellow and monoclinic in form. The yield thus obtained was nearly 5 per cent of the extract, or $1^1/_2$ per cent of the bark. The crystals analyzed as follows in percentages:

| No | G. OF SAMPLE As anhydride | $CO_2$ | $H_2O$ | C | H |
|---|---|---|---|---|---|
| 1 | 0.5463 | 1.1323 | 0.1623 | 56.53 | 3.30 |
| 2 | 0.2746 | 0.5701 | 0.0828 | 56.62 | 3.35 |
| 3 | 0.3477 | 0.7195 | 0.0960 | 56.43 | 3.06 |
| Theoretical for $C_{15}H_{10}O_5$ | | | | 56.60 | 3.14 |

The author determined the molecular weight of the coloring principle by both the cryoscopic and chemical methods. Anhydride of the coloring principle was dissolved in absolute alcohol and the rise of boiling point was determined by means of Beckmann's apparatus.

| No. | G. of anhydride | G. of alcohol | Rise of temperature | Molecular weight |
|---|---|---|---|---|
| 1 | 0.1712 | 21.4395 | 0.26° | 314 |
| 2 | 0.2176 | 26.6512 | 0.30° | 316 |

The sulfate of the coloring principle having been decomposed by boiling water, sulfuric acid was determined as barium sulfate, and the deposited coloring principle collected and weighed.

| No. | G. of the sulfate | G. of $BaSO_4$ | G. of coloring principle | Molecular weight |
|---|---|---|---|---|
| 1 | 0.3874 | 0.2167 | 0.2963 | 318.7 |
| 2 | 0.4886 | 0.2724 | 0.3740 | 319.8 |

The pure glucoside having been decomposed by sulfuric acid, the weights of coloring principle and rham-

nose were determined, and the molecular weight was calculated.

| G. of glucoside | G. of coloring principle | G. of rhamnose | Molecular weight |
|---|---|---|---|
| 2.2142 | 1.4068 | 0.8074 | 317.2 |

According to these results the molecular formula of the coloring principle is $C_{15}H_{10}O_8$ (mol. wt. 318). It has one molecule of water of crystallization, which is dehydrated partially in a desiccator and perfectly above 135° C. It is acetylated by acetyl chloride in its pyridine solution; the crystals of the acetyl derivative were obtained pure from its acetic acid solution.

To determine the number of hydroxyl groups, the author saponified the acetyl derivative with concentrated sulfuric acid and the deposited coloring principle was collected and weighed.

| No. | G. acetyl derivative | G. coloring principle | Per cent coloring principle |
|---|---|---|---|
| 1 | 1.0907 | 0.6049 | 55.46 |
| 2 | 0.7376 | 0.4102 | 55.61 |

Theoretical percentage requires for:

| | |
|---|---|
| $C_{15}H_5O_8(C_2H_3O)_5$ | 60.23 |
| $C_{15}H_6O_8(C_2H_3O)_4$ | 55.79 |
| $C_{15}H_7O_8(C_2H_3O)_3$ | 51.06 |

Hence the coloring principle has six hydroxyl groups. By alkali fusion, it decomposes into gallic acid, phloroglucinol, oxalic acid and carbon dioxide.

According to the above investigations, the yellow coloring principle separated by this process should be identical with "myricetin" which A. G. Perkin has already investigated; in fact, the two substances have both similar and dissimilar properties. For instance, the former dissolves partially in glacial acetic acid, and still its lead compound does not become yellower by boiling. The author also discovered it to react noticeably with nitrous acid. When an alcoholic solution of the coloring matter is added to a nitrous acid solution, a deep reddish purple coloration is produced, which, on standing, fades away gradually to a yellowish color.

It dyes brownish yellow, orange-yellow, orange-brown, and black, with alumina, tin, chrome, and iron mordants, respectively; on comparing their fastnesses, the black by iron (which is extraordinarily fast and resists practically all tests) ranks first; the chrome stands second. For brightness and deepness of color shades, the single-bath method is superior to the two-bath method, especially with alumina, tin, and chrome mordants.

The author prepared several new dyestuffs by introducing myricetin into azo-, sulfide-, and nitro-dyestuffs. Observing the constitution of the myricetin, it may easily be seen that it can be employed as a component of azo-dyes; many kinds of azo-dyes were prepared from myricetin and aromatic bases, all of which have hues varying from orange to brown.

Applying the formation of the ingrain colors, the author effected a new process of batik dyeing; *i. e.*, a piece of cloth was dipped into an alcoholic solution of myricetin and dried without washing. A mixture of resin and Japan-wax was then lacquered over both surfaces of the cloth; when cooled, it was cracked by the hands, and dipped into a diazotized solution to develop the color. In this way, any desired color may be obtained without any danger of melting either resin or wax. Besides this the author also discovered a process which enables the operator to dye several kinds of shades by a single process, never repeating the cracking and dyeing as in the usual batik process. This new process consists only of immersing a piece of fabric, which has already been cracked upon the resin surface, in dilute alcohol for a few seconds, before it is dipped into the diazotized solution. Then the whole surface of resin and wax is dissolved by alcohol deeply or thinly according to the condition of the cracking; and thus when the cloth is developed by a diazotized solution, several gradations or shades of color are produced after their respective degrees of dissolution by alcohol. In this way, by the art of cracking, there may be obtained very interesting depths of shades of color by a mere single process.

The author has also prepared three new sulfide dyestuffs by melting myricetin: 1—with polysulfide of soda and free sulfur; 2—by adding metallic salts to the polysulfide melting; and 3—by direct melting with sulfur.

1. POLYSULFIDE MELTING—One molecular weight of myrecitin was thrown into the solution of three molecular weights of $Na_2S_4$, and the mixture was heated in an oil bath for ten hours at 115–130° C., and then for seven hours at 150–180° C., under a reverse condenser. The syrupy mass was dissolved in hot water and sodium sulfide added; the filtrate was slightly acidified with dilute hydrochloric acid and an excess of sodium chloride added; thus the brown sulfide dyestuff was salted out, and then washed and dried. The dried dyestuff is a black powder which dissolves in hot water without the aid of sodium sulfide. It dyes cotton directly to a deep sepia color which does not require any after-treatments, and it may also be topped with basic colors with quite good fastnesses.

2. POLYSULFIDE MELTING WITH METALLIC SALTS—Copper sulfate, manganese sulfate and ferrous sulfate were added and the polysulfide melting was carried out under conditions quite similar to Case 1; the dyestuff containing copper sulfate has the stronger tinctorial power and a bluish brown shade; manganese sulfate and ferrous sulfate give dyestuffs of weaker dyeing power and of a bluish gray shade.

3. DIRECT MELTING WITH SULFUR—One part of flowers of sulfur and four parts of myricetin were thoroughly mixed and heated for five hours at 200–210° C.; the brown mass was dissolved in caustic soda and acidified with dilute hydrochloric acid; a brown-yellow precipitate of the dyestuff was produced which was collected and dried. It dissolves in hot water and dyes animal fiber yellowish brown, directly in its acid bath.

The author also prepared an interesting direct yellow dyestuff by nitrating the sulfonic acid of myricetin with fuming nitric acid. One part of myricetin was dissolved in twenty parts of fuming sulfuric acid and warmed to 80° C. on a water bath. To the deep brown-violet solution, kept cold by means of a freezing mixture, ten parts of fuming nitric acid were added slowly, drop by drop, while stirring the solution and keeping the temperature below 10° C. After ten hours,

it was diluted with water, neutralized with caustic soda and then shaken with ether to extract the nitro-dyestuff; a yellow needle crystalline mass was obtained after the ether had evaporated. The compound has explosive properties and readily dissolves in water. This aqueous solution dyes animal fibers directly a bright yellow with a remarkable tinctorial power and even appearance.

Thus, an insoluble, naturally yellow, mordant coloring matter, myricetin, was converted into several other useful soluble dyestuffs, that have many new and different hues by converting it into azo-dyes, sulfide-dyes, and nitro-dyes.

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## ON A STARCH-FORMING ENZYME FROM MALT: ITS ACTION ON HEMICELLULOSES AND ITS COMMERCIAL APPLICATION TO BREWING

By Charles B. Davis

Received December 2, 1914

The chemistry of enzymes or unorganized ferments teaches one to believe without seeing, for on account of reactions, and products of reactions, we have every reason to believe that enzymes exist, and yet—who has ever seen an enzyme? This "something" cannot be produced by chemical means and is of unknown chemical composition. Enzymes inhabit every part of the animal and vegetable organism, and in the vegetable world are employed to render insoluble matter soluble and diffusible. For example, starch is carried throughout the plant, building up its fabric, reappearing at different stages as cellulose, gum and lignin, and is again converted back to starch as reserve material in the seed.

E. Roux and L. Maquenne[1] have shown that at highly elevated temperatures, *e. g.*, 120–150° C., products were formed from hemicelluloses having cell structure similar to ordinary starch; these could not be gelatinized in hot water and reverted to hemicellulose on cooling the solution. All of this work has been disputed by Fernback. Roux and Maquenne do not claim that their results were brought about by an enzyme, nor could one have been present at the temperatures used in their experiments. H. C. Schellenberg[2] speaks of the action of fungi on hemicellulose, but since the writer's experiments were carried out in the presence of 1 per cent toluol or chloroform his results are due entirely to enzymic hydrolysis and not to vital organisms.

Ling[3] has shown by microphotographs that the cell walls of the endosperm of barley are not dissolved by the enzymes during malting.

Hemicelluloses together with mineral matter constitute the cell walls of yeast, also the envelopes or cellulosic skeletons of the endosperm and starch granules (Fig. I), and are at present converted to sugar either by boiling with dilute mineral acid or by heating under pressure to a temperature of 150° C., and then immediately converted to sugar by active diastase, since on standing cold they revert to hemicelluloses.

My attention was first called to the new enzyme which is the subject of this paper, on determining the yield of extract from barley malt between the temperatures of melting ice and boiling water as shown in Table I and Fig. II.

Table I—Yield of Extract from One Sample of Western Barley Malt

Malt was Crushed 25° Seck., Mashed with Three Times Its Weight of Water and Each Temperature Was Maintained 30 Min. in Water Bath. Highest Yield by Laboratory Method = 68.91 Per Cent.

| Temperature ° F. | ° C. | Total Yield Windisch | Temperature ° F. | ° C. | Total Yield Windisch |
|---|---|---|---|---|---|
| 32 | 0 | 14.35 | 140 | 60 | 51.67 |
| 50 | 10 | 17.28 | 149 | 65 | 65.80 |
| 68 | 20 | 18.45 | 158 | 70 | 70.59 |
| 86 | 30 | 19.16 | 167 | 75 | 71.50 |
| 104 | 40 | 20.60 | 176 | 80 | 72.15 |
| 113 | 45 | 24.50 | 185 | 85 | 71.50 |
| 122 | 50 | 26.60 | 194 | 90 | 70.60 |
| 126.5 | 52.5 | 31.01 | 203 | 95 | 68.80 |
| 131 | 55 | 35.61 | 212 | 100 | 67.00 |

Table I and Fig. II show that although diastase is coagulated and destroyed at 75° C., there is a marked activity and conversion between the temperatures

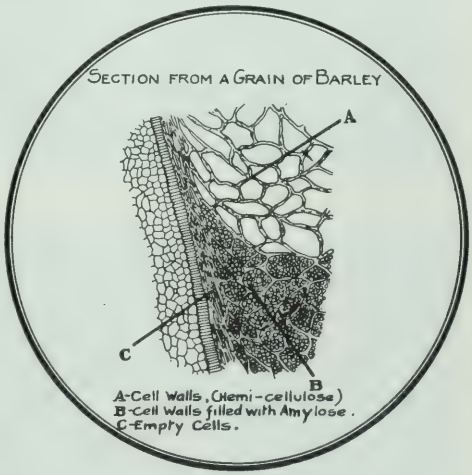



Fig. I × 250

75° and 85° C., and that the worts or extract show a blue starch reaction by iodine due to transformation of hemicelluloses to starch by the "hemicellutase."

### Separation of the Starch-Forming Enzyme from Malt

Three hundred grams of ground barley malt and 700 g. of water were macerated with 1 per cent toluene, an antiseptic, at 60° to 70° F. for 4½ hrs. The liquid pressed out was (450 g.) heated in a water bath to 81° C. to destroy the diastase, and the separated clots were filtered off after 5 min. heating. The resultant clear liquid, when cooled to 70° F., measured 375 cc., equivalent to about 150 g. of malt. This was precipitated with 15,000 cc. of 95 per cent alcohol and allowed to stand 24 hrs. The precipitate was filtered off, washed with alcohol and water (4 : 1), dissolved

[1] *Compt. rend.*, **1904**, 49–51, 213–4, 375–7 Also **1905**, 440–2, 943–6, 1259–61 and 1303–8.

[2] *Woch. fur Brau.*, **25** (1908), 539

[3] Roux and Maquenne, *Brewers' Journal*, **40** (1904), 741–1

in water, diluted to the original volume of 375 cc., and again filtered clear; 250 cc. of the clear liquid, or about 100 g. of malt, were again precipitated with 500 cc. of 95 per cent alcohol, the precipitate collected, washed with alcohol and ether and dried in a desiccator. This dry residue was extracted with water; the water extract, evaporated over calcium chloride, weighed 0.0574 g. and contained 21.37 per cent albumin. It possessed the activity on hemicelluloses described above, transforming about 1000 times its weight of these bodies to starch, did not coagulate on boiling, was not precipitated by zinc sulfate, but was thrown out of solution by sodium phosphotungstate in acid solution or by Tanret's reagent, thus showing the enzyme to be of a peptone nature.

cellulose, and amylopectin, pentosans and hexosans, transforming them *permanently* into *gelatinized starch* between the temperatures of 15° C. and 90° C., and transforming the jelly of hemicelluloses which react yellow to iodine (Fig. IV) to gelatinous insoluble starch giving an intense blue reaction with iodine (Fig. V); a partial transformation is shown in Fig. VI. The formation of starch, which is the first observable assimilative product of plants, is perhaps brought about by "hemicellutase" through a condensation or concentration of hemicellulose molecules; no cell structures are visible as in the Roux and Maquenne experiments; this would tend to indicate that starch is a hydrate of cellulose.

The transformation is accompanied by a generation

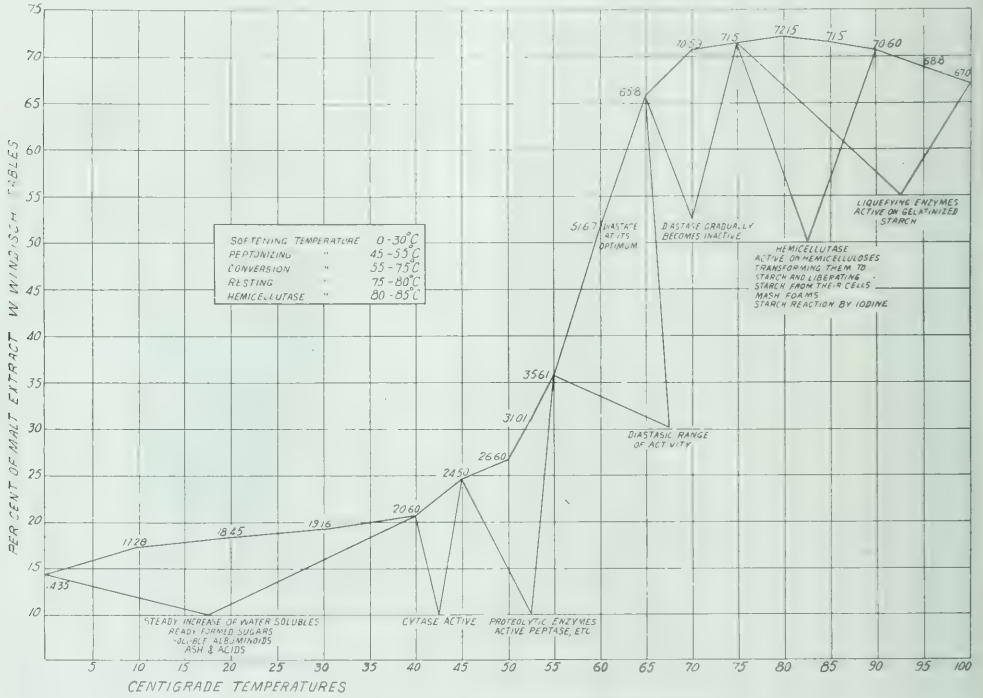



FIG. II ENZYMATIC ACTIVITY OF BARLEY MALT BETWEEN 0° AND 100° C

This new enzyme from malt the writer calls "hemicellutase" on account of its hydrolyzing action on the hemicelluloses of yeast and cereals, which in cereals constitute the reserve material for sustenance, while in embryo, it possesses all the characteristics of known enzymes, such as being a colloid incapable of dialysis, of albuminoid nature, soluble in water, active at 15° C. and having an optimum temperature, which is 82.5° C. Hemicellutase is precipitated by metals, metallic salts, alcohol and tannin. Its enzymatic action is destroyed at an elevated temperature above its optimum, 90° C., at which its action is irrevocably changed (see Fig. II). Its action is catalytic and hydrolytic on hemicelluloses, otherwise known as granulose, starch cellulose, amylo-

of gas, as seen in Fig. II and the following experiment:

TABLE II CARBOHYDRATES OF CEREALS

| STARCH | HEMICELLULOSES (Carbohydrates left insoluble after diastatic conversion, with the exception of the husk) | |
|---|---|---|
| Amylose | | |
| SUGARS | STARCH | PENTOSANS |
| Sucrose | | Araban |
| Dextrose | | Xylan |
| Levulose | | |
| Raffinose | CELLULOSES | |
| | Granulose | HEXOSANS |
| | Amylocellulose | Mannan |
| HUSK | Amylopectin | Galactan |
| Lignified (woody) cellulose | | Dextrosan |

When commercial starch or refractory starch products, such as coarse corn grits, cornmeal, barley, or rice, all of which contain upwards of 20 per cent of hemicelluloses (Table II), are boiled with water, a gelatinous mass results, consisting of soluble starch which is devoid

of gelatinizing qualities and a jelly of these hemicelluloses or insoluble carbohydrates. If this gelatinous mass is cooled to 60° C. and mixed with active diastase at this temperature the starch will pass into solution leaving the jelly undissolved. Repeating this experiment with malt extract and heating to 80–85° C., the most favorable active temperatures of hemicellutase, the hemicelluloses, are converted to starch and on cooling to 60° C. and adding active diastase, both the starch and the hemicelluloses pass into solution with generation of gas. Fig. VII shows only small particles of albuminoids left insoluble.

20 g. more of crushed malt added and the mixture heated to 50° C. for 30 min., to 65° C. for 30 min., and finally to 75° C. for 45 min. The cage was then removed, the contents washed and collected on a tared filter,

TABLE III

| Percentages | Coarse corn grits | Flaked corn | Rice | Commercial starch |
|---|---|---|---|---|
| Moisture | 12.00 | 10.00 | 11.00 | 10.90 |
| Fat | 0.70 | 0.40 | 0.50 | 0.07 |
| Fiber | 0.75 | 0.55 | 0.35 | 0.05 |
| Protein | 10.00 | 10.50 | 8.10 | 0.10 |
| Ash | 0.58 | 0.50 | 0.60 | 0.18 |
| Carbohydrates | 75.97 | 78.05 | 79.45 | 88.70 |
| Equivalent to sugar | 84.41 | 86.72 | 88.28 | 98.50 |
| Total yield of extract with hemicellutase and diastase | 84.50 | 86.68 | 88.50 | 98.80 |
| Yield with diastase alone | 79.00 | 81.00 | 82.10 | 92.50 |

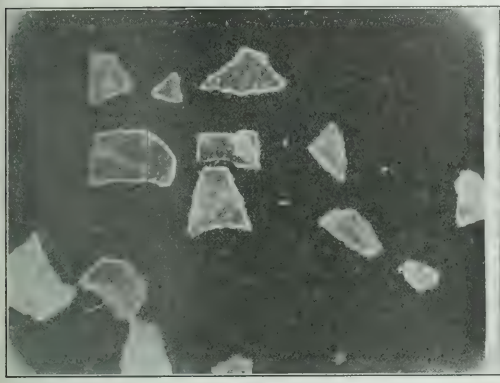


FIG. III × 250

FIG. IV × 250

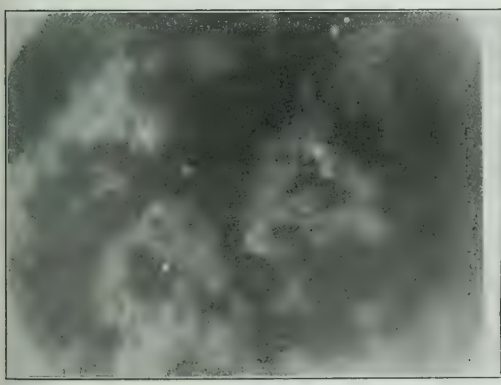


FIG. V × 250

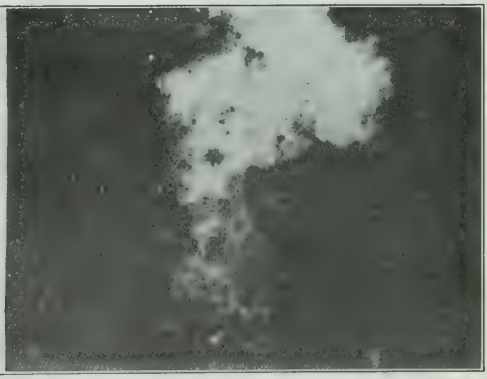


FIG. VI × 250

Corn products and rice analyzed by this method with "hemicellutase" showed the results given in Table III.

"Hemicellutase" is without action on nitrogenous compounds, such as proteids, albumin, peptone, etc., as is shown by the following experiment: Twenty grams of coarse corn grits contained in a cage of 200 mesh wire gauze were immersed in 100 g. of crushed malt and 250 g. of water at 85° C., and maintained at this temperature for one hour. The mass was then cooled, dried and weighed. Its weight was found to be 1.7523 g. and to consist of protein having a nitrogen content of 0.2795 g. or 1.7468 g. of protein equivalent to 8.73 per cent, thus proving that hemicellutase is not a proteolytic enzyme.

Diastase or other enzymes of malt known to scientists at present are incapable of affecting these hemicelluloses. "Hemicellutase" is capable of converting them to starch without pressure and at temperatures of 15 to 80–85° C., disintegrating the envelopes and liberating

their starch content, as was shown by the following experiments: 300 g. crushed malt and 900 cc. water were macerated at 70° F. for 5 hrs., filtered clear and used as "A" in Experiments I–IV.

TABLE IV—ACTION OF HEMICELLULASE ON HEMICELLULOSES

I—100 cc. "A" + 2 g. Commercial Starch Paste.
II—100 cc. "A" heated to 85° C. to Destroy Diastase, Cooled and Mixed with 2 g. Commercial Starch Paste.
III—"A" Heated to 85° C., Cooled and Mixed with the Hemicelluloses(*a*) from 2 g. Starch Paste.
IV—"A" Heated to 85° C., and All Enzymatic Action Destroyed by Boiling before Adding the Hemicelluloses from 2 g. Starch Paste.

| TEMP.(*b*) C | TIME Min | IODINE REACTIONS I | II | III | IV |
|---|---|---|---|---|---|
| 60 | 5 | Deep blue | Deep blue | Yellow | Yellow |
| 60 | 10 | Violet | Deep blue | Yellow | Yellow |
| 60 | 20 | Red | Deep blue | Yellow | Yellow |
| 60 | 30 | Yellow | Deep blue | Yellow | Yellow |
| 70 | 5 | Yellow | Deep blue | Yellow | Yellow |
| 80 | 5 | Yellow | Deep blue | Yellow | Yellow |
| 82.5 | 5 | Faint blue | Deep blue | Faint blue | Yellow |
| 82.5 | 10 | Blue | Deep blue | Blue | Yellow |
| 82.5 | 20 | Decided blue | Deep blue | Decided blue | Yellow |
| 82.5 | 45 | Deep blue | Deep blue | Deep blue | Yellow |

(*a*) The hemicelluloses are best employed in the moist gelatinous condition, and the hemicellulase in its peculiar organic combination and normal association as found in malt extract. The hemicelluloses on drying become horny and are acted on more slowly.
(*b*) When the hemicellulose is finely divided, the reaction takes place at 10–20° C.

## APPLICATION OF HEMICELLUTASE TO PRACTICAL BREWING

Brewers at present are employing expensive apparatus called "cookers" to gelatinize and burst the cell walls of the refractory corn and rice products. This is considered necessary, since, as stated above, diastase has no action on the hemicelluloses of starch granules of raw cereals, and is coagulated and destroyed at 75° C.; therefore when the brewer had reached this degree, he proceeded with unchecked rapidity to raise the mash to the boiling temperature, thus destroying the activity of the hemicellutase; this

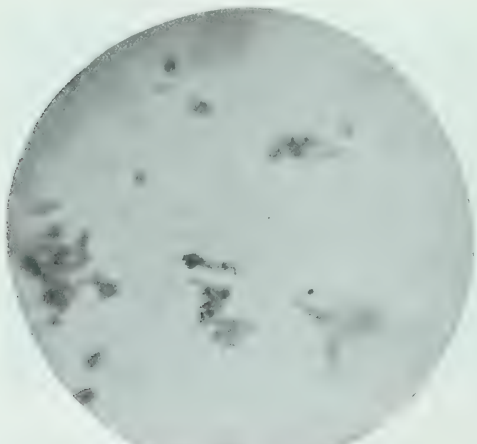


FIG. VII × 280

accounts for its not being detected up to the present time.

This heating of the mash under pressure or even to the boiling point caramelizes the starch and causes loss of extract. The cooker mash is at present run down into the cool malt mash, containing the active diastase, to effect a starch conversion temperature; the starch passes into solution but the hemicelluloses are left unaffected and are lost in the grains or by-product, with a great loss of valuable beer-making extract.

It has been observed by brewers that if they made a mistake in their temperature calculations and obtained a "striking heat" of 75° C., or above, that starch made its appearance in the worts. But this was attributed to the solution of unmodified starch rendered soluble by liquefying enzymes, and therefore a higher temperature than 72° C. is avoided. In reality the unmodified starch is sealed up in its envelope of hemicelluloses, and is incapable of solution at 75° C. and the starch reaction is due to steely malt which is composed of dried gelatinized starch.

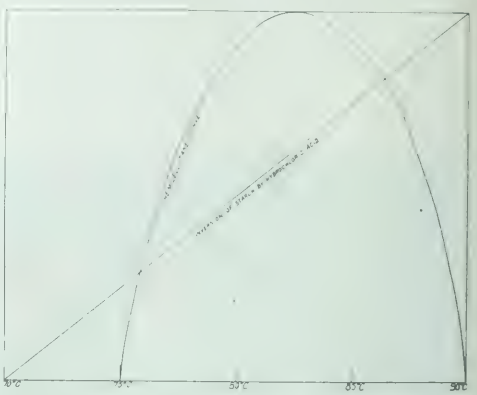


FIG. VIII—THE ACTIVITY OF HEMICELLULOSES ON HEMICELLULOSES TO FORM STARCH, AS COMPARED WITH INVERSION BY HYDROCHLORIC ACID

Manufacturers have gone to great expense to construct apparatus for gelatinizing and drying these refractory starch products which are sold under the trade names of: Cerealine, Corn Flakes, Flaked Rice, etc. These may be added directly to the malt, but the hemicelluloses are left insoluble and in a horny state to say nothing of the high cost of these materials adding to the price of the finished product.

The mashing process with "hemicellutase" is best carried out in practical brewing with indirect heating by radiation in a water-jacketed machine.

When a suitable quantity of cold water has run into the machine, the appropriate amount of crushed malt and raw grain (corn, barley, rice, etc.) are added, the agitators are set in motion and the mash is raised to 80° C., then cooled to below 75° C. and more malt added. The results by this method show at least three and one-half per cent more beer produced over the laboratory methods and at least eight per cent more beer over the quantity produced by the present methods. The grains are not pasty and the drainage is very rapid, due to the conversion of the cell walls.

The writer wishes to extend his thanks to Dr. George C. Fisher of the American Museum of Natural History for his kind help in making the microphotographs shown herewith.

402 WEST 23RD ST., NEW YORK

# LABORATORY AND PLANT

## THE USE OF HYDROMETALLURGICAL APPARATUS IN CHEMICAL ENGINEERING[1]

By John V. N. Dorr

This paper, although the title is somewhat general, will be devoted principally to a description of the apparatus with which my name is connected. It was prepared at the suggestion of your president who felt that it would interest chemical engineers to know of methods which have proved of definite value in metallurgical work where large quantities of material are handled with low costs.

### GENERAL METALLURGICAL TENDENCIES

Metallurgical engineering is really one department of chemical engineering in its broadest sense. Comparing metallurgical operations of to-day with the work of thirty years ago, we note that nearly everything is done on a much larger scale. One reason for this is the general development of engineering knowledge with improved materials and the substitution of exact scientific methods for the old "rule of thumb" ways. Another is the greatly increased demand for metallurgical products, the consumption of all the common metals having increased several times as fast as the growth of our population. A third and perhaps more important reason is that most of the smaller rich ore deposits have been worked out so that we have been forced to attack the large low-grade deposits which twenty years ago were considered of no value. This tendency is well shown by the treatment of the disseminated porphyry copper ores and the handling on a much larger scale of the lower grade ores at Butte and in the Lake Superior district.

The introduction of mechanical power in place of hand labor has, of course, been as important a factor in metallurgical progress as in all other lines of endeavor.

The introduction of continuous methods in the different steps of metallurgical processes in place of intermittent methods formerly used, has led to great advances. Continuous work invariably means lower labor costs and a high load factor, thus assisting in lower power costs and interest charges. Where the change does not sacrifice control of the operation it results usually in allowing a large output of uniform nature. As illustrations of this tendency towards continuous work in metallurgy may be noted the use of pan conveyors and rotary cylinder feeders in delivering ore to primary crushers, automatic weighing machines, and belt conveyors for the transport of dry material around a mill. The belt conveyor is also in use for stacking tailings from leaching tanks and has been used to stack slime tails from an Oliver filter and dewatered sand tails from a Dorr classifier. In smelting plants we see the use of mechanical roasters and sintering machines, such as the Dwight-Lloyd, with continuous removal of slag by granulation.

[1] Presented at the 7th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 2 to 5, 1914.

The change in cyanide practice has been quite marked. Where leaching was practiced the original means of removing slime was to collect the sand in tanks while overflowing the slime, and then shovel or otherwise transfer the sand so collected to other vats for leaching. Continuous separation, whether by cones or mechanical classifiers, has done away with this, and the sand usually passes directly to leaching tanks without coming to rest.

In slime treatment, whether of classified slime or the whole mill feed reground, Dorr continuous thickeners have made continuous settling feasible and continuous agitation has replaced the charge system for the dissolution of precious metals, with a very definite saving in power, attention and first cost of the installation required. The Oliver continuous filter has come into extensive use for that step in the process. It is interesting to note that the decantation process, the first method used for the recovery of dissolved gold from slimes, which was abandoned everywhere except in South Africa on the introduction of the modern type of filter, when made continuous by the use of the Dorr thickener, is coming into extensive use again and displacing in some instances intermittent types of filters.

Zinc dust precipitation, when first introduced as an intermittent process, could make no headway against continuous precipitation with zinc shavings, but since being made a continuous process by Merrill has come into extensive use in modern mills.

### INTERCHANGE OF APPARATUS IN INDUSTRIES

One characteristic of technological work in the last few years that was not in evidence in the centuries preceding, is the exchange of information among workers in different fields. Although the total knowledge in the world has increased so enormously, and this has been called very properly an age of specialization, the specialist is expected to have a general knowledge of progress outside his own field to such an extent that he can profit by it in advancing his own work. This has been made easier in metallurgy than in most other industries, I should say, by the greater freedom that exists among metallurgists in the exchange of data. A valid reason for this is that the metallurgist competes in a much greater degree with natural conditions than with other producers of the same product.

The price of gold is essentially constant whether more or fewer mines are operating, and, while the prices of silver and the base metals vary with the supply and demand, the profits made depend so greatly on other factors, such as richness of the ore and costs of mining and milling, that I doubt if any producer would hope to get an advantage over the other by secrecy. In fact, there is a general understanding among the larger copper companies to-day for an exchange of information which gives them all an advantage in the combat with Dame Nature.

In manufacturing, on the other hand, there is com-

petition for the purchase of the raw material and the sale of the finished product so that manufacturing costs and profits must come between the two, and any advance that can be made in reducing the former seems of no real benefit unless kept from competitors.

The cyanide process has been advanced by the adoption of methods and machinery from other industries and has made its own contribution in return. Fine grinding has been aided materially by the adoption of the tube mill from cement grinding, and when dry crushing and chlorination on Cripple Creek ores were in vogue the inclined traveling screens used in clay working were of great assistance as were the dust collectors taken from Minneapolis flour mills.

Our early paddle arm agitators came from chemical works and the air-lift agitator or "Pachuca" tank which succeeded them, was first used, I am told, in a powder plant in California. The plate and frame filter press so extensively used in Australian metallurgical practice was another adoption from chemical industries, and the rotary drum filter was used in Syracuse as a dewaterer of chemical precipitates before the cyanide process was known. As developed by Oliver with means for washing and blowing off the cake formed, it has been returned by the cyanide operator to several industrial uses.

Various forms of vacuum and pressure "cake" filters, such as the Moore, Butters, Kelly and Sweetland, might be said to have their prototype in the potters' method of making pitchers which is done by pouring "slip" into a plaster of Paris mould and when a solid deposit has been formed by the absorption of moisture, pouring out the remainder of the liquid "slip" and drying the vessel thus formed in the mould. From cyaniding they have found their way extensively into sugar refining, alkali works and many other lines. The Merrill sluicing press is being installed in a large aluminum plant in the South.

In closing this general discussion I will say that, while the basic principles for the mechanical treatment of analogous materials are the same, great caution should be used in proposing the substitution of any method or apparatus successful in some other field for that now used. It is safe to assume that the latter is in use as a result of much study and gradual development, and its replacement should be preceded by a most careful detailed study of all the conditions of operation and the purposes to be accomplished. Suggestions as to such substitutions may be advanced tentatively, but an actual demonstration is worth a lot of theorizing. In introducing new methods we usually find troubles come where they are not expected, and apparent difficulties do not prove real.

### THE DORR APPARATUS

The apparatus to which I wish to call your attention has been developed in the last ten years in the course of operating cyanide mills in the West. Each machine performs a certain useful function satisfactorily and economically, and I feel that you will agree with me that where similar work is to be done they are worthy of consideration. I do not mean, of course, that a machine adapted for handling a sandy pulp is necessarily the best type to handle an extremely light chemical precipitate, but I feel that, where the operations of washing, settling or agitation are required, they may be of service.

As a generalization, I believe I am safe in saying that machinery successful in operations where costs per *ton* are studied to a fraction of a cent, have possibilities where materials are handled on which cost per *pound* are watched. It is true on the other hand that the economies of continuous work decrease with a reduction in tonnage, so that each case has to be studied by itself. In discussing the apparatus I have of necessity quoted freely from my paper on the same read at the Salt Lake Meeting of American Institute of Mining Engineers in August, 1914.

### CLASSIFIER

This machine was devised in 1904 to replace hydraulic cones for the purpose of making a separation of sand and slime at the mill of Lundberg, Dorr & Wilson at Terry, South Dakota. The method of cyaniding the gold ore in use at that mill was crushing to pass

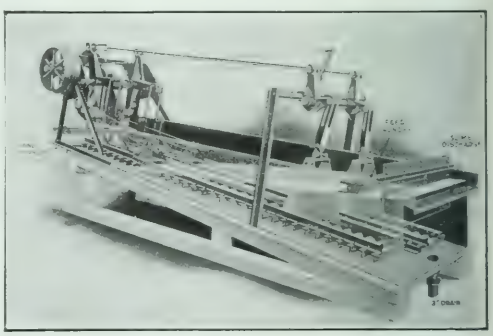


FIG. 1 THE DORR CLASSIFIER (PATENTED MODEL C)

a 20 mesh screen, separating the sand from the slime, leaching the sand in vats by percolation and treating the slime after agitation and thickening by the Moore filter process. The machine proved such an improvement over the cones in use at our plant and elsewhere that it was rapidly adopted and has come ito wide use. It has been improved from time to time to meet new conditions and as now manufactured is shown in Fig. 1, which illustrates the standard duplex machine. It consists of a settling box, in the form of an inclined trough with the upper end open, in which are placed mechanically operated rakes or scrapers for the purpose of removing the quick-settling material from the open end, the liquid and slime overflowing at the closed end. Each rake is carried by two hangers: one at the sand-discharge end suspended from an arm attachment to a rocker arm or lever, which terminates in a roller: the other depended from a bell crank connected by a rod to the same rocker. The roller is kept pressed against a cam on the crank shaft by the weight of the rakes. The rakes are lifted and lowered at opposite ends of the stroke by the action of the cams

transmitted through the rocker arms and bell cranks, and the horizontal motion is obtained directly from the crank.

The bell cranks at the slime end are carried by a second larger bell crank held in position by a chain attached to a spool on a worm gear at the head end of the classifier. By this means the rakes can be raised 10 inches at the lower end and operated in that position or any intermediate one. This allows the classifier to be started readily when nearly filled with sand after an unexpected shutdown, and the regulation of the depth of the settling box when in operation to vary the products being made.

The pulp is fed across the settling box as shown and a uniform flow to the lip at the end is maintained while the sand settles to the bottom and is advanced by the rakes until it emerges from the liquid and is discharged with from 20 to 30 per cent moisture.

The agitation near the bottom of the tank, caused by the reciprocating motion of the rakes, assists in keeping the slime in suspension, but is not normally sufficient to cause fine sand to overflow.

REGULATION OF PRODUCTS—The machine is intended of course to make only two products, and the point of separation can be varied by the following means:

1—The use of the baffle shown, which allows a reduction of the cross section of flow, so as to overflow more fine sand.

2—Raising the rakes and thus obtaining the effect of operating them in a shallower tank.

3—Increasing the speed of the rakes until the agitation keeps fine sand in suspension.

4—The attachment of perforated spray pipes to the rakes at a point where they remove the sand from the liquid, allowing a rewashing of the sand and removal of any slime that may be carried down with it.

This latter feature will probably be of more interest from the chemical engineer's standpoint as enabling him to discharge finely divided sandy material and give it a complete wash to free it from any dissolved material which adheres to it.

CAPACITY—The capacity of the Dorr classifier depends upon the dilution of the feed and the point of separation which it is desired to make. The rakes of the duplex machine, operating at normal speed, are able to discharge at least 150 tons of solids in 24 hours.

TABLE I—OPERATING DATA ON DORR CLASSIFIERS

| | Feed | | | | | Sand | | | Slime | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mill | Tons per 24 hrs | Dilution | +100 | +200 | −200 | +200 | +200 | 200 | +100 | +200 | 200 |
| Portland, Colorado | 145(a) | 5 to 1 | 38.3 | 13.4 | 47.1 | 75.3 | 16.2 | 7.4 | 0.9 | 5.8 | 94.7 |
| Golden Cycle, Colorado | 151(a) | 3.5 to 1 | 45.0 | 19.0 | 36.0 | 68.0 | 23.0 | 9.0 | .. | 11.0 | 89.0 |
| Cia. Benef. de Pachuca, Mexico | 144(b) | 4 to 1 | 42.7 | 25.1 | 32.5 | 43.6 | 40.1 | 16.8 | 0.1 | 3.8 | 96.8 |
| Tonopah Extension, Nevada | 73(c) | 6 to 1 | 65.0 | 11.1 | 23.9 | 70.0 | 18.3 | 11.7 | 0.6 | 8.5 | 90.9 |
| Amparo Mining Co., Mexico | 125(a) | 7.5 to 1 | 52.4 | 18.5 | 29.1 | 71.4 | 27.4 | 1.2 | ... | 6.5 | 93.5 |
| Tonopah-Liberty, Nevada | 85(c) | 7 to 1 | 30.5 | 41.9 | 26.3 | 75.7 | 24.0 | 0.1 | 2.5 | 14.3 | 81.4 |
| Goldfield Consolidated, Nevada | 264(d,b) | 3 to 1 | 40.0 | 12.0 | 48.0 | 74.0 | 19.0 | 7.0 | 2.6 | 19.5 | 79.1 |
| Tonopah-Belmont, Nevada | 70(e) | ... | 65.6 | 2.7 | 28.9 | .... | .... | .... | 0.4 | 6.6 | 93.0 |
| Alaska-Treadwell, Alaska | 89(c) | .. | 48.7 | 41.5 | 9.8 | 48.7 | 41.5 | 9.8 | .. | 2.0(f) | 98.0 |
| Nipissing, Canada | .. | .. | 78.7 | 3.6 | 16.8 | 85.8 | 7.2 | 6.9 | .. | 0.5 | 99.5(f) |

(a) New ore.
(b) Includes tube-mill return. Under normal conditions, with tube-mill in closed circuit with a Dorr classifier, 35 to 50 per cent of original feed returned.
(c) New ore; tube-mill product returned, but amount not stated.
(d) 168 tons come from the stamps, the rest being returned from the tube mill.
(e) Classifiers used in connection with the regrinding of concentrates; rakes operated 24 strokes per minute; 100 per cent of concentrates pass 200 mesh; the 2 per cent is silica from tube-mill pebbles.
(f) Of this 200 mesh product 15 to 20 per cent. is sand; crushing is done in two sets of tube mills; the sand from the first classifiers being reground in closed circuit with tube mills and other classifiers, the combined slime overflows giving the screen test shown.

Table I, showing results at different plants, will give the best idea of what may be expected.

COST OF OPERATION—Experience has shown that repair costs on these machines are extremely small. I know of one classifier which operated nearly four years with repair costs of less than $5.00, and half a mill per ton seems a safe figure. While the power taken will vary of course with the load, it appears that 1/4 H. P. is ample in most cases. With normal feed the attendance required is practically nothing, being limited only to an occasional oiling. All parts in reciprocal motion are removed from contact with the liquid so that there is no opportunity for wear starting at any point.

USES—Besides being used to separate a leachable sand product from slime, Dorr classifiers are in general used to-day in connection with fine grinding.

Fig. 2 shows the arrangement of classifiers and tube mills operating in closed circuit in the Tonopah-Belmont Mill. It is considered much more economical in power and equipment when a product of perhaps 150 mesh or finer is desired, to pass a large tonnage continually through a tube mill, return the discharge to a Dorr classifier and overflow the part which is ground fine enough, returning the balance to the same machines for further grinding together with the sand

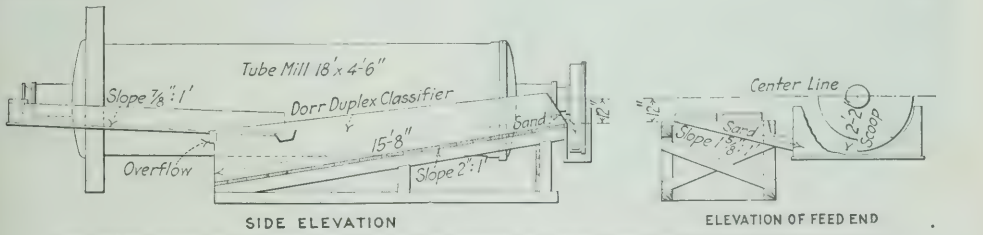



FIG. 2—ARRANGEMENT OF CLASSIFIERS AND TUBE MILLS OPERATING IN CLOSED CIRCUIT IN THE TONAPAH BELMONT MILL

coming from the new feed. This is considered much more efficient than to attempt to reduce the product to the size required in one passage through the tube mill. It seems more than probable that it will prove equally advantageous in connection with industrial pulverization of quartz, flint, barytes, cement material and other mineral products that require fine grinding. Some work has already been done on these lines, especially in connection with pigment grinding, but I have no data that are at present available.

Dorr classifiers are now in successful use as dewaterers of concentrates, both magnetic iron concentrates and sulfides, and at one plant are discharging the former with only 12 per cent moisture.

FIG. 3—TAILING DISCHARGE FROM THE LAST MACHINE OF A SERIES OF ACID PROOF CLASSIFIERS USED FOR LEACHING COPPER ORE BY THE BUTTE-DULUTH MINING CO.

LEACHING—The use of a series of classifiers for the purpose of leaching and washing was first suggested by Mr. Utley Wedge and some experiments were made along that line several years ago but not carried to a conclusion. Last year Captain Wolvin, of the Butte-Duluth Company, at Butte, who was leaching oxidized copper ores in vats there, brought up the same idea and we furnished him with five classifiers for trial, all parts subject to contact with the acid being made of hard wood. These machines proved very successful, increasing the extraction over the former leaching in vats at least 20 per cent, and we have since then furnished this Company with more machines for the same purpose. Fig. 3 shows the discharge of tailing from the last machine of a series. I have been unable to get reliable figures on these operations as they have been changing details from time to time, but Table II shows data obtained last summer from the Butte-Duluth Company, when the first installation consisting of six small classifiers was in use, and will give an idea of the operations at that time.

TABLE II—DATA ON CLASSIFIERS USED FOR LEACHING

6 Classifiers in series; five 15 in. × 4½ in. and one 30 in. × 4½ in. Ore crushed through 0.12 in., opening in inclined impact screens, giving a product about —10 mesh

| | |
|---|---|
| Value of heads | 2.14 per cent Cu |
| Average strength $H_2SO_4$ used | 7.33 per cent |
| Ratio of solution to ore | 2.25 : 1 |
| Moisture in discharged tails | 20.0 per cent |
| Extraction | 89.9 per cent |
| Value of solution going to cells | 1.8 per cent Cu |
| Value of solution from cells | 0.9 per cent Cu |
| Speed of Classifier rakes, strokes per minute | 6.0 |
| H. P. (Motor 80 per cent efficient) Total | 4.6 |

The average daily capacity for the month in which the above figures were obtained was about 150 tons. The limit to the capacity was the lack of electrolytic cell room.

Spent electrolyte after strengthening was added to the first two classifiers and water into No. 6. Most of the overflow from the latter went to scrap iron precipitation and an amount equal to the acid liquor brought out from No. 5 with the ore was carried through Nos. 5 and 4 to No. 3, thus effecting a counter-current washing. The overflows from Nos. 1, 2 and 3, after clarifying, were sent to electrolytic precipitation. The ore received about 40 minutes' contact while passing through the whole series.

TRIPLE-WASHING CLASSIFIER—Fig. 4 shows a machine which we have designed to wash a sandy material absolutely free from any trace of slime or to wash the same kind of material entirely free from any liquid in which it may be suspended. It will be noted that there are a number of opportunities to get rid of the liquid or slime. As the sand is raked up above the water level in each box it is sprayed with any solution, or water, and as it is washed into the following box it is diluted with the same liquid, so that in all it gets a very thorough treatment.

POSSIBLE USES OF THE CLASSIFIERS—Several of my classifiers are now in operation at one of the mid-western chemical works, used, I believe, for draining a granular chemical precipitate and washing it. Its use in the preparation of a high-grade kaolin is now being considered in place of the settling boxes which require a great deal of labor for removing the sand from them, and its use for dewatering granular material from any liquid will be apparent.

## CONTINUOUS THICKENER

This apparatus was developed in 1906, when, in remodeling a mill in the Black Hills, I desired to thicken the slime pulp from classification, continuously, in large units and avoid the use of the large cones which accumulated solid slime on the sides and gave much trouble. The trial machine was operated in a tank 35 ft. in diameter by 12 ft. deep at a speed of 1/20 R. P. M. and gave excellent results, continuing in operation until the mill burned five years later.

DESCRIPTION—The Dorr continuous thickener, Fig. 5, consists of a slow-moving mechanism placed in a suitable tank, by means of which the operation of settling may be made continuous through the removal of the settled material to a point of discharge and the prevention of its accumulation as a solid in the tank. As usually furnished, it consists of a central vertical shaft with radial arms equipped with scrapers to bring the thickened material to a discharge opening at the center by the slow rotation of the mechanism. The thick material may be discharged by gravity at this point into a launder, or piped to the side of the tank and raised by air lift or pump to the level of the overflow or higher.

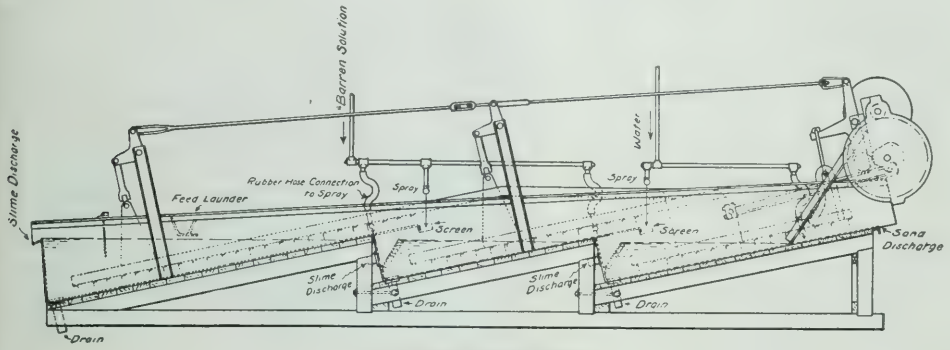



FIG. 4 TRIPLE-WASHING CLASSIFIER

The machine is arranged for raising the shaft so that the arms will not be embedded in the thick material if the power should be shut off for any length of time. The shaft can be lowered again gradually while running. Shaft and gear bracket are supported by a bridge over the tank or suspended from the roof trusses. At the Liberty Bell Mill, thickeners have been installed driven from below the tank through a mercury bearing, and have proved efficient although they cannot be raised.

The thin pulp is delivered near the center of the tank in a suitable well with a float to cause minimum disturbance, and the overflow is taken off by a peripheral launder. The thickened pulp can be accumulated and withdrawn at intervals or a continuous discharge maintained as desired. Nozzle discharge is in use in some concentrating mills where a comparatively thin pulp is desired, and also in one case where a product of only 30 per cent moisture is being obtained. Many are using diaphragm pumps for this purpose. They have the advantage of ready regulation and require little attention. Having a positive displacement they tend to regulate automatically the amount of solids withdrawn, for, when the pulp becomes thicker, more solids are pumped with each stroke. A pet cock to admit air into the suction has proved most satisfactory as a means of regulation.

SPEED—The thickener has been operated at speeds ranging from 1 revolution in 2 minutes to 1 in 40 minutes. A quick-settling sandy material will offer great resistance unless a comparatively high speed is maintained, while colloidal slime will give a slightly thicker underflow, at a very slow speed. It will be found when handling sandy material that if the sand accumulates so that it is being moved around the tank by the channel arms as well as being advanced toward the center by the plows the resistance increases rapidly and the speed should be increased.

POWER varies with the size of the tank and the nature of the feed. Of course the motor input is much larger than the actual power consumed, owing to the low load factor commonly used, as it is essential to have power enough to meet an unusual strain. Spring measurements have shown approximately 1/20 H. P. being transmitted to the worm shaft of a 44-ft. thickener handling a classified slime. It would not be advisable, however, to instal less than a 1 H. P. motor on a single machine, but 1/2 H. P. each can be allowed when several are driven from one lineshaft.

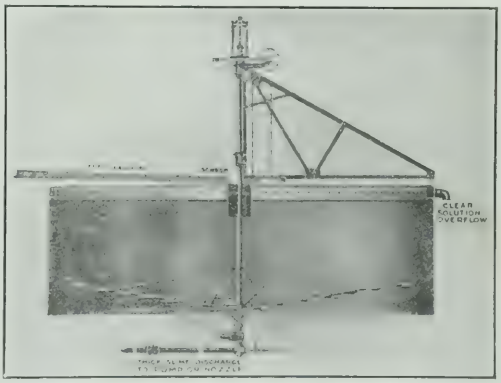



FIG. 5 THE DORR CONTINUOUS THICKENER (PATENTED)

REPAIRS—Normal operation of the thickener causes no wear except on the worm, and many machines are running to-day that have not cost a cent for several years. On the other hand, if started after a shutdown without raising, a strain of any amount may be given so that the "weakest point" would have to yield.

TABLE III—OPERATING DATA ON DORR THICKENERS

| MILL | Sq. ft. settling area per: Ton of solids thickened per 24 hrs. | Sq. ft. settling area per: Gallon overflowed per minute | REMARKS |
|---|---|---|---|
| San Rafael, Mexico | 4.5 | | Tube-mill product, 75 per cent —200 mesh, discharge 48.5 per cent solids |
| Liberty Bell, Colorado | 15.0 | 12.6 | Tube-mill product, much light argillaceous slime. Discharge 33 per cent solids, —100, 87 per cent; +200, 13 per cent; —200, 70 per cent. Feed 9: 1. Solution fed at capacity; solids not. Large area per gallon overflowed per minute due to density of underflow and nature of the slime. |
| Mogul, South Dakota | 3.92 | | Tube-mill product; ore silicious: +60, 0.6 per cent; +100, 7.8 per cent; +200, 26 per cent; —200, 65.6 per cent. Discharge 56 to 59 per cent solids. Continuous decantation. |
| Batopilas, Mexico | 0.6 to 0.9 | ... | 40 mesh product; 90 per cent passing 100 mesh. |
| Zambona, Mexico | 3.1 | | Tube-mill product. Discharge 40 per cent solids. |
| Dominion, Ontario | 5.4 | | Tube-mill product, 88 per cent —200 mesh, ore diabase. Discharge 40 per cent solids. Feed 6: 1. |
| Porcupine-Crown, Ontario | 4.25 | | Tube-mill product, 75 per cent —200 mesh. Discharge 65 per cent solids. Quartz ore. Continuous decantation. With 5.1 sq. ft. settling area per ton settles to 71 to 83 per cent solids. |
| El Palmarito, Mexico | 4.5 | | Tube-mill product; pure quartzite, 97 per cent —200 mesh. Feed 7: 1. Discharge 65 to 70 per cent solids. Continuous decantation. |
| Amparo, Jalisco, Mexico | 4.9 | 1.4 | Tube-mill product, silicious: 93.5 per cent —200 mesh. Feed 24.5: 1. Discharge 23.5 per cent solids; used to feed vanners. |
| Veta Colorado, Parral, Mex | 5.0 | 3½(*a*) | Tube-mill product, rather argillaceous: 71 per cent —200 mesh. Feed 11: 1. Discharge 33 per cent solids for agitator. Have settled to 65 per cent solids. |
| Smuggler-Union, Telluride, Colo | | | Very clayey slime with classified sand. Screen test: +40, 1.48 per cent; +60, 7.27 per cent; +100, 14.81 per cent; +200, 11.63 per cent; —200, 65.81 per cent. |
| | 30.0 | 26.0 | Settling from cold water, slightly alkaline. Feed 8: 1. Discharge 50 per cent solids, 1.429 sp. gr. |
| | 10.0 | | Settling from cyanide solution. Feed, 2.5: 1. Discharge 40 per cent solids, 1.316 sp. gr. |
| A large copper company, Arizona | 11.6 | 8.11 | Considerable argillaceous slime. Feed 10.4 per cent solids. Discharge 25.3 per cent solids. |
| Pennsylvania Steel, Lebanon, Pa | 14.2 | 2.48 | Thickening ahead of vanner concentration. Feed 2.8 per cent solids. Discharge 10.6 per cent solids. Overflow 0.4 per cent solids, extremely fine, which does not interfere with using water again. |
| Nevada Consolidated, Ely, Nev | ... | 1.25 | "Each 17-ft. thickener supplies wash water for 20 Wilfley tables and occasionally for wash on vanners. One thickener has a greater capacity than twelve 8-ft. cones. Area of 17-ft. tank is 226 sq. ft., of the twelve 8-ft. cones, 525 sq. ft. |
| Broken Hill, Proprietory, Australia | | 1.80 | Dewatering slime from lead-zinc concentration mill. Feed 100: 1. Discharge 55 per cent solids. |
| Anaconda Copper, Mont | ... | 5.95 | Dewatering slime from concentrator. Forty 4-deck thickeners, each 28 ft. in diameter by 3 ft. 3 in. deep, handle about 26,000,000 gal. of pulp per day which contains approximately 2 per cent solids. A clear overflow obtained, the underflow containing about 15 per cent solids, which is fed to buddles. |

(*a*) Not up to capacity of overflow.

The Overload Alarm, Fig. 6, is arranged to indicate the resistance offered by the mechanism as shown by the thrust on the worm shaft and to ring an alarm when the load becomes excessive. A solenoid or other means can be used to correct automatically the conditions causing the excessive load, by reducing the feed or increasing the underflow. The alarm has proved very valuable, especially on quick-settling pulp, when it is desired to obtain the thickest discharge.

LABOR—The attendance required varies with the regularity of conditions maintained and is usually confined to lubrication once a shift, so that the care of the thickeners is included in the duties of some man employed principally on other work.

CAPACITY—The capacity of my thickener on any pulp has been found to be primarily a function of area, although the depth of the tank has an influence depending on the dilution of the feed and the dilution of the underflow desired. With a given area and depth and a very dilute feed and underflow the capacity depends on the amount of liquid that can be clarified, *i. e.*, additional solids, but no additional liquid can be added to a tank already fed to capacity, without overflowing slime. On the other hand, with a feed of perhaps 8 of liquid to 1 of solids and a thick discharge of 2 to 1 or less, it will be found usually that additional liquid can be added to a thickener operating at capacity without overloading it, but any addition of solids will cause slime to overflow.

If a plant requires more settling capacity, raising the temperature of the solutions may prove an economical way to add 10 to 20 per cent. The capacity of any filter can also be increased by this means.

Table III presents data given me from time to time. It shows the settling area in use per ton in different mills which in many cases were not feeding their thickeners at capacity. The figures show that when pulp is carried in cyanide solution a provision of 5 to 6 sq. ft. per ton for a silicious tube mill product is ample and from 7 to 15 sq. ft. for a clayey material or classified slime product. When very dilute products are handled the area required is determined usually by the gallons per minute to be overflowed.

DENSITY OF UNDERFLOW—This depends on the nature of the pulp to be settled and the size of the particles. An argillaceous pulp, such as that at the Liberty Bell in Colorado, although containing a large percentage of reground silicious material, will not settle thicker than 60 per cent moisture, while a finely ground quartz will give as low as 27 per cent moisture. At the Porcupine-Crown plant, handling a quartz product of 75 per cent minus 200 mesh, the average final pulp discharged contained 30 per cent moisture with the feed at the rate of 1 ton of solids per day for each 4.7 sq. ft. of tank area.

We have no reason to think that the use of the Dorr thickener will increase the amount of water that can be clarified in a given settling area at the beginning of the flow into the tank, but the removal of the pulp as rapidly as it settles certainly avoids the decrease in the settling rate which would follow when a tank is filling up in intermittent settling. At one plant where reground ore pulp was thickened from 10 to 1 to approximately 2 to 1, actual experience indicated that the change from intermittent to continuous settling enabled three tanks equipped with Dorr

thickeners to do the work of five used intermittently.

TRAY THICKENER—The original thickener was installed in a tank 12 ft. deep and we adhered to approximately that depth, varying from 6 to 16 or 20 ft., for a number of years. One reason for this was that it early showed itself to be an advantage to have ample storage capacity for thickened slime at the bottom of the tank. It not infrequently happens that the flow of slime to the settling tank will vary during the day and the settling qualities of the slime vary as well so that if the feed is light a large quantity of clear liquid accumulates on the top of the thickener which, when more slime comes, flows away together with the freshly clarified water and partly thickened slime takes its place, thus giving a great reserve capacity. In 1913, however, I had occasion to go into the question of securing large settling capacity with small floor space and developed what I have called a tray thickener. There are two types of this. The first, which would seem to be the simplest, has been installed by the Anaconda Copper Company and in the Coeur d'Alenes. It consists of two or more shallow tanks, each carrying thickening apparatus attached to a common shaft and acting as an independent unit with its own feed, clear water overflow and thick slime discharge. Tests made by the Anaconda Copper Company indicated that with their material, tanks 28 in. × 3 in. would handle approximately 90 per cent of the material that tanks 28 in. × 9 in. would handle, so that this gives them a great economy in plant construction. Fig. 7 shows this type and represents one of forty tray thickeners installed in their settling plant which is handling 26,000,000 gallons of water a day and separating from it 2,600 tons of extremely colloidal slimes.

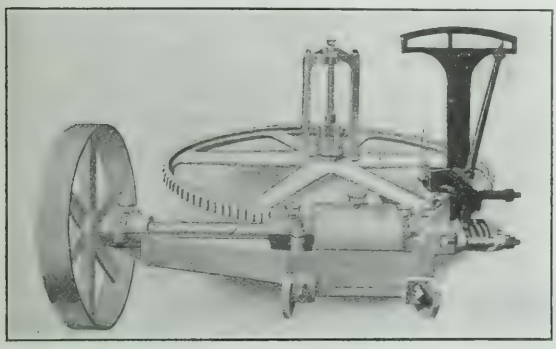


FIG. 6—OVERLOAD ALARM AND RESISTANCE INDICATOR ON THICKENER WITH ARRANGEMENT FOR RAISING SHAFT WHILE OPERATING

The second type of tray thickener, which I have called the submerged type, was tested first at the Homestake Mill at Lead, South Dakota, and consisted as tried there essentially of a shallow thickener and tank entirely submerged in a cone-bottom settling tank. The space below the small thickener had its own feed and discharge and the clear water overflowing from it joined the overflow of the shallow thickener tank. The latter has its own feed and discharge as well.

The drawings shown in Fig. 8 give the result of tests made there to show comparative capacities of tanks with and without the tray. Applying the idea to thickeners already installed, Fig. 9 shows the installation of a tray in a standard deep thickener. It gives in effect two tanks each with its own feed and discharge and a combined overflow, and in practice has resulted in enabling us to add 70 to 100 per cent to the capacity of plants already in operation. It has been found unnecessary to make this tray strong enough to support these tanks filled with liquid if the space below it is empty as by means of an automatic float we have arranged to make connections between the upper tank and the lower in case the level of the liquid drops in either. It will be evident, I think, that these trays will afford means of obtaining a large amount of settling capacity with comparatively small floor space, and we are working now on their further development.

LARGE THICKENERS—For a long time the largest thickeners in use were in tanks 50 ft. in diameter by 20 ft. deep at the Nevada Consolidated Company. Within the last year, Mr. David Cole, the constructing engineer of the Arizona Copper Company, designed and installed a Dorr thickener in a tank 130 ft. in diameter:

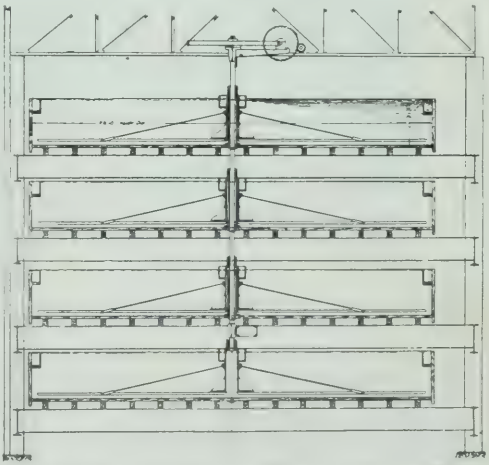


FIG. 7 THE DORR TRAY THICKENER PATENTED SUPERPOSED TYPE

Fig. 10 shows the machine in operation. It has proved entirely successful and indicates the possibility of furnishing very large units which will cost less per sq. ft. of settling area than the smaller ones. The tank in this case is merely a ring of concrete erected on a slag dump, the settled slime forming its own bottom. Tanks built along these lines with dirt bottom and walls of concrete or wood will aid materially in re-

ducing costs of installation. It is probably as large as we would care to build, but we anticipate building up to 100 ft. using the bridge and central shaft, which we now use on our standard machine. This large thickener has handled over 1200 tons of solids per day and Mr. Cole estimates that it would take care of 2000 tons of material 40 mesh and finer. Its overflow has been over 3,000,000 gallons per day and its limit of

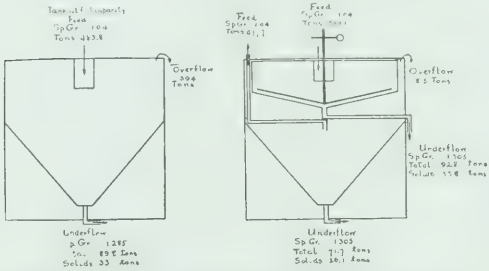



FIG. 8—TEST OF TRAY THICKENER AT HOMESTAKE MILL, LEAD, S. D.

capacity has not yet been reached. The net saving in water by the use of this machine with the mill at capacity is $120 per day.

USES—The thickener was originally introduced in cyaniding for thickening slime or reground pulp previous to agitation and filtration and came into general use for that purpose. Within the last few years it has proved a means for recovering the dissolved values as well by continuous counter-current decantation, which will be spoken of later. Its use in thickening ahead of slime concentration has become very general, nearly all the large copper and lead companies having adopted it within the last few years. The development of flotation has also found a new use for it at most of the plants that have been installed recently in this country and in Australia.

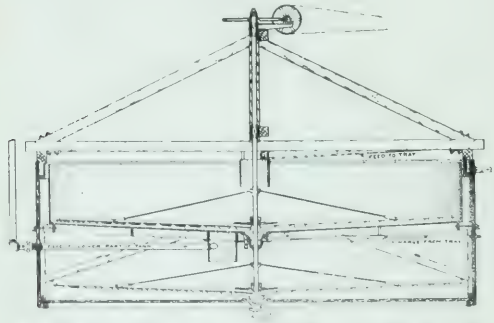


FIG. 9—THE DORR TRAY THICKENER (PATENTED) SUBMERGED TYPE

INDUSTRIAL USES—The thickener presents great opportunities for the recovery at an extremely small expense of all kinds of finely divided residues that go to waste or are recovered intermittently from settling ponds. The expense, including interest on equipment, amounts in one case to one mill and in another two mills per thousand gallons clarified. In both cases the solids removed are colloidal ore slimes. One plant recovering a finely divided organic material from settling ponds substituted the Dorr thickeners for them and, I am advised, save the labor of 12 men per day. Its use for removing heavy silt in water purification seems possible with the large units now feasible.

Its use for sewage sedimentation and for the prevention of stream pollution looks promising. A plant is now planned for the recovery of precipitated ferric hydrate from mine water. In all industrial work its use to furnish a much thicker product to a filter press will mean great increase in the capacity of the press with diminished costs.

### CONTINUOUS COUNTER-CURRENT DECANTATION

Continuous counter-current decantation consists of so operating a series of settling vessels that the solids to be treated continuously pass through them in succession, being diluted after each thickening by solution from the overflows passing in the opposite direction. The objects to be attained are the dissolution under most favorable conditions of a portion of the solids, the separation of a solution from a finely divided solid with minimum dilution, or both combined. The last result is that usually obtained in metallurgical work as the separation of most of the dissolved material from the solids always occurs and even when apparently adequate means for dissolution are provided ahead of the system the favorable conditions afforded usually give an additional extraction.

HISTORY—The principles of continuous counter-current decantation are very old and have been applied in many ways in chemical technology as well as in metallurgy. The first cyanide plant using this method in the United States was erected by John Randall in the Black Hills in 1902, using large cones for settlers, and was operated for a year. The invention of the Dorr thickener in 1906 gave an opportunity to avoid the troubles inherent in cones, and in 1910 the first modern plant was started. Since that time a large number of plants have been installed, several of them replacing vacuum filters, so that it may be regarded to-day as one of the well-established methods of cyaniding. Several years ago Dr. R. Gahl successfully operated an experimental plant with cone settlers leaching copper ore slimes with sulfuric acid, treating seven or eight tons daily, to which he referred in a paper read before the American Electrochemical Society, April, 1914. A test plant of 75 tons capacity is now starting, using thickeners.

The following description of a typical flow sheet of a continuous counter-current decantation cyanide plant will undoubtedly explain the process further and also show the method we have used to determine the results that may be expected from any conditions assumed.

The square marked MILL, Fig. 11, represents the grinding machinery, and we assume the ore is crushed in cyanide solution which brings the fine pulp continuously into thickener V from whence the solids pass through the agitators and thickeners W, X, Y and Z until discharged from Z as tailings.

The following conditions are assumed:

1—The thick pulp underflows are thoroughly mixed with the clear overflows before entering the next tank so that the dissolved gold is uniformly distributed through the liquid.

II—100 tons of ore are milled per day.

III—$8.00 is dissolved per ton; 75 per cent in the mill, the balance in the agitators.

IV—The pulp from all thickeners is discharged at a ratio of 1:1, or 50 per cent moisture.

V—300 tons of solution are precipitated to a value of $0.02 per ton.

To determine the value of the solution from any thickener, if V, W, X, Y and Z equal the value in dollars per ton of the solution leaving each thickener, we get the following equations, as the same amount of gold and solution will enter and leave each tank:

$$400\ W + (\$6.00 \times 100) = 300\ V + 100\ V \quad (1)$$

That is, the gold in W plus the additional gold assumed to be dissolved in the mill equals the overflow and underflow of V.

$$100\ V + (\$2.00 \times 100) + 400\ X = 400\ W + 100\ W \quad (2)$$

The ($2.00 × 100) represents additional gold dissolved in the agitators.

$$100\ W + 400\ Y = 400\ X + 100\ X \quad (3)$$

$$100\ X + 100\ Z + (300 \times \$0.02) = 400\ Y + 100\ Y \quad (4)$$

$$100\ Y + 100 \text{ water (no value)} = 100\ Z + 100\ Z \quad (5)$$

In (4) the $0.02 represents the value of the precipitated solution returned to Y.

Equation (5), representing a simple dilution with water, means that Z will have one-half the value of Y.

Solving these equations we get the values,

$$V = 2.656\ W = 1.156\ X = 0.286\ Y = 0.076\ Z = 0.038$$

which may be checked as follows:

| | |
|---|---|
| The gold precipitated ($2.656 — $0.02) × 300 | $796.80 |
| Lost in tailings ($0.038 × 100) | 3.80 |
| TOTAL | $800.60 |
| Total assumed dissolved (100 × $8.00) | 800.00 |
| Discrepancy due to decimals | .60 |

From the above we deduce:

| | |
|---|---|
| Assay value of solution precipitated | $2.656 |
| Dissolved loss per ton solution | 0.038 |
| Dissolved loss per ton ore | 0.038 |
| Percentage dissolved gold recovered | 99.6 |

Similar calculations have shown that if one thickener is omitted from the flow sheet and no other conditions are changed the dissolved loss is increased to $0.133. Using the same four thickeners and precipitating 400 tons, instead of 300, the loss is cut to $0.08, while if the pulp can be discharged with 60 tons of solution, instead of 100, making it contain 37 per cent moisture, the amount precipitated can be reduced to 240 tons and the loss will be only $0.76 per ton of ore, although the solution precipitated will assay $3.321.

I should explain that the reason the precipitated solution is added at Y, instead of Z, where it would obviously be more effective in increasing the extraction of gold, is that we have also a mechanical loss of cyanide to contend with. The 100 tons of water which can be added at Z to replace the liquid discharged with the tails reduces the strength of the solution lost to one-half when added to 100 tons of cyanide solution, whereas if added to 400 tons of solution it would reduce it to only four-fifths. A further saving in cyanide can be made by adding the barren solution at X, but this usually means adding an additional thickener on account of excessive gold losses.

It will be noted from these figures that the loss in gold can be regulated at will by increasing the solution precipitated or the number of thickeners in the series, and also that pulp settling to 30–40 per cent moisture can be treated much more efficiently than pulp settling to 50–60 per cent. If pulp cannot be settled to 50 per cent or thicker it will usually be profitable to use a filter merely for dewatering at the end of the series.

FIG. 10—THE DORR THICKENER IN TANK 130 FEET IN DIAMETER AT ARIZONA COPPER CO.'S MILL

DETAILS OF PLANT—Fig. 11 and what has already been said about Dorr thickeners will give a clear idea of the construction of a continuous counter-current decantation plant. The tanks in the series are either arranged on a level, in which case both the overflow and underflow must be elevated before being transferred into the next tank or in a series of steps so that the overflow goes by gravity from tank to tank and only the smaller quantity of underflow is raised each time. Each method has its advantages.

TRANSFERAL OF PULP is preferably done by a diaphragm or other pump of fixed displacement as thereby a certain amount of automatic regulation is obtained.

STORAGE TANKS—The more a flow sheet and the actual conditions of mill operations are studied the less additional storage capacity is felt necessary.

RESULTS—I realize that details of the technical results obtained in cyaniding will not be of great interest to chemical engineers so will say only that when working on a hard, quick-settling ore ground to pass an 80 mesh assayers' screen or finer, which can be settled to a thick product containing 35 to 50 per cent moisture, it has proved a most efficient means for the recovery of dissolved gold and silver from the pulp. Compared with the usual filtration methods it has shown lower operating costs in spite of a higher mechanical loss in cyanide, and a higher recovery due to a lower loss of dissolved values and often to an additional extraction being made that could not be made commercially by direct agitation.

The following quotation from an article on continuous counter-current decantation in the *Engineering and Mining Journal* of October 31, 1914, sums up the conclusions reached at the Gold Road Mill where continuous counter-current decantation was installed to replace a vacuum plant:

"The operators state that the principal disadvantage they found with the vacuum-filtration system upon their ores was that it was almost impossible to wash satisfactorily the cakes on the leaves. Cakes of uniform resistance could not be formed. They would crack badly and large sections would fall from them, making satisfactory washing impossible. Besides, the expense of labor, repairs and power is considerably more than is necessary in following the counter-current decantation system. They find practically no difference between the two systems in the amount of cyanide and lime consumed; perhaps a slightly greater quantity, amounting to about 0.1 lb. of cyanide, is being consumed in the decantation system.

"An advantage found with counter-current decantation is that the dissolution of gold is so perfect, due to the longer contact between the solutions and the pulp. The difference, considering all things, between leaf filtration and counter-current decantation is at least 60 cents per ton of ore treated in favor of the latter."

This figure is higher than could be expected under usual conditions, but we have also had definite statements of savings from the other plants that have changed. Information received from a number of plants operating indicates that on quick-settling ore from which $5.00 to $20.00 is recovered the mechanical loss in gold varies between 4 and 10 cents per ton of ore.

GENERAL CONSIDERATIONS

DISSOLUTION AND RECOVERY—From the nature of the process it is apparent that its use for dissolution is antagonistic to its use for recovery of the dissolved material, and although some have proposed the alternation of agitators and thickeners I have always advocated, where a high per cent of recovery in a concentrated form was required, as in cyaniding, that all dissolution possible should be made ahead of the system. In other cases, as in that described by Dr. Gahl, where it was essential to make the dissolution in stages so as to end with a nearly neutralized liquid and have the copper pulp when nearly finished meet fresh acid, alternation is of course necessary, but it calls for one series on dissolution and another on washing.

SCALE OF OPERATIONS—It will be seen that any continuous method of treatment of materials has greater relative advantages with an increase in size of operations and a continuous counter-current decantation plant with 50-ft. tanks will require no more labor, and, in fact, less than one with 10-ft. tanks, although it will have 25 times the capacity. As the actual labor cost for operating a series of thickeners is less than one man a shift, it will be seen that if any washing or leaching operation is requiring the full time of one or more men this method can be considered if other conditions are favorable.

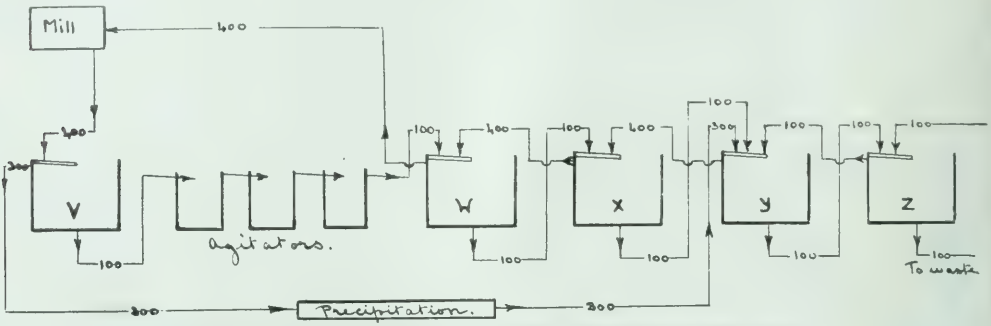



FIG. 11—EXAMPLE OF CONTINUOUS COUNTER-CURRENT DECANTATION FOR CYANIDE PLANT
Figures Refer to Solution Tonnages

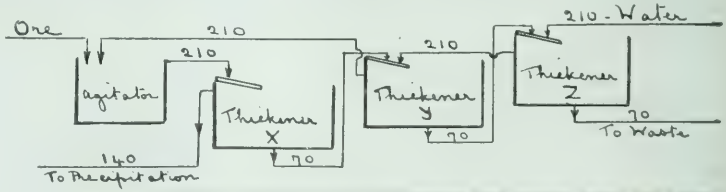



FIG. 12—EXAMPLE OF CONTINUOUS COUNTER CURRENT DECANTATION WITH WASHING LIQUID NOT REUSED

OTHER APPLICATIONS—Fig. 12 is intended to show a copper problem which I think will correspond to many problems that may occur in chemical industries, *viz.*, the complete washing of finely suspended solids and the obtaining of the dissolved material in as concentrated a form as possible from which it is to be re-

| Number of Thickeners Used | 3 | | 4 | | 3 | | 4 | |
|---|---|---|---|---|---|---|---|---|
| Tons of solution sent to precipitation | 140 | | 140 | | 210 | | 210 | |
| | Lbs. per ton | Per cent | Lbs. per ton | Per cent | Lbs. per ton | Per cent | Lbs. per ton | Per cent |
| Copper in the solution for precipitation | 27.5 | 1.37 | 28.2 | 1.41 | 18.7 | 0.93 | 18.0 | 0.94 |
| Copper in the solution wasted with the residues | 2.7 | 0.13 | 0.7 | 0.03 | 0.9 | 0.04 | 0.2 | 0.01 |
| Lbs. of dissolved copper lost per ton of slimes | 1.48 | | 0.49 | | 0.63 | | 0.16 | |
| Per cent of dissolved copper sent to precipitation | 96.3 | | 98.8 | | 98.5 | | 99.6 | |

covered by evaporation or complete precipitation or by any other method, so that none of the liquid has to be returned to the system as in cyaniding.

EXAMPLE OF CONTINUOUS COUNTER-CURRENT DECANTATION WITH WASHING LIQUID NOT REUSED

The following conditions are assumed in Fig. 12:

I—100 tons of oxidized copper ore slimes treated per day.

II—Slimes contain 2 per cent soluble copper or 40 lbs. of copper per ton.

III—Pulp is discharged from all thickeners with 41.2 per cent moisture.

IV—The inflow to each thickener is thoroughly mixed before entering same.

V—210 tons of wash water added to Thickener "Z." The total overflow from Thickener "X," 140 tons, sent to precipitation and 70 tons sent to waste with the discharged residues from Thickener "Z."

VI—Let X, Y and Z represent the pounds of copper per ton of solution discharged from the respective thickeners.

If we equate the inflow and outflow of each thickener in terms of tonnage and copper content we have:

$$70X + 140X = 210Y + (100 \times 40 \text{ lbs.}) \quad (1)$$

$$70Y + 210Y = 70X + 210Z \quad (2)$$

$$70Z + 210Z = 70Y + 210 \text{ tons of water} \quad (3)$$

Simplifying and solving we obtain:

X = 27.5132 lbs. copper per ton of solution.

Y = 8.4656 lbs. copper per ton of solution.

Z = 2.7164 lbs. copper per ton of solution.

From the above the following results are deduced:

1—Overflow to be precipitated, "X", contains 1.37 per cent copper or 27.5 lbs. per ton of solution.

2—Solution wasted with the residues, "Z," contains 0.13 per cent copper or 2.7 lbs. per ton of solution.

3—Copper sent to precipitation = 96.3 per cent of that dissolved.

4—Copper lost per ton of slimes = 1.48 lbs.

Varying the number of thickeners used and solution tonnage sent to precipitation and assuming conditions I to IV to remain constant, we obtain the results given at the top of this page.

It is apparent from this that the enriched solutions, which contain 96.3 per cent of the soluble copper, will carry 1.37 per cent copper per ton and that you get no weak liquors at all for further handling. The additional tabulations above show the results of changing various factors. You can see that, precipitating 140 tons of solution, but adding a fourth thickener, increases the percentage recovered from 96.3 to 98.8 per cent with an enrichment of the solution from 1.37 to 1.41 per cent. Precipitating 210 tons of solution, on the other hand, shows a solution to be precipitated carrying 0.93 per cent copper with three thickeners and 0.94 per cent with four thickeners, while the percentage of recovery is 98.5 and 99.6 per cent.

In other words, it is easy to see that by using the proper number of thickeners you can make practically any recovery desired and get any concentration you wish.

This method could be applied as readily to the manufacture of caustic from soda ash and lime, and I can say that a plant to use it to some extent has been purchased abroad, but its installation has been delayed by the war. As the reaction between the soda and the lime requires a definite time it is possible that it might be necessary to do it in charges, but the same was believed true in cyaniding until it was demonstrated that continuous agitation with a series of agitators was better.

AGITATOR

This machine, Fig. 13, I designed in 1910, but it did not come into actual use until 1912, when about a half dozen machines were put out for trial purposes on a working scale at several different plants. The results obtained were so good that last year many more were installed in this country and abroad. During 1914, although mining in general has been very quiet, the use of them has increased greatly and from all installations made we have had nothing but satisfactory reports. The illustration will give a good idea of the machine, which is very much like the Dorr thickener, the central shaft being replaced by a pipe at the top of which distributing launders are arranged to distribute the pulp which is raised through the pipe by means of air. A worm and sheaves pro-

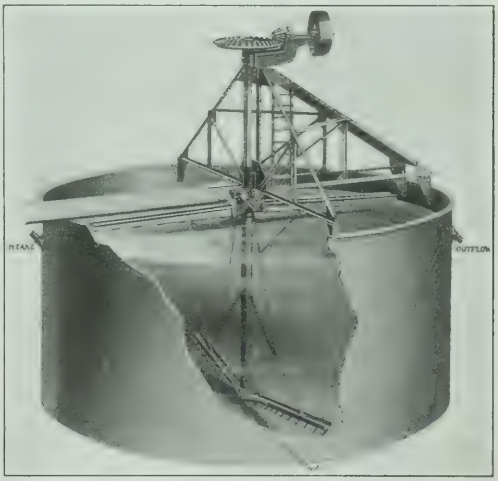


Fig. 13—The Dorr Agitator (Patented)

vide means for raising or lowering the hinged arms at will. In cyanide metallurgy mechanical sweeps in flat-bottomed tanks were first used for agitating the pulp, but the great difficulty experienced in most cases with these, including breakages and the power required, made the use of a high cone tank with a central air lift seem most attractive, and when it was introduced into this country and Mexico from Australia a very large percentage of the mills installed it. At this time agitation was done in charges, but when continuous agitation became the established practice a few years ago it was found that there was a great tendency for the coarser material in the pulp being agitated to build up on the sides of the 60° cones used

so that eventually the major portion of the agitating area became filled up with solids and the agitation took place only in a small cylinder in the center. It was also found necessary to give a much more violent agitation than the chemical treatment of the ore required in order to keep the pulp in suspension as much as possible. The Dorr agitator, by the use of mechanical arms with the thickener plows on, which prevents settling of solids and brings the material from the bottom to the central uplift pipe, allows the regulation of the intensity of the agitation given to suit the chemical need of the ore and not the necessity for keeping everything in suspension.

EFFICIENCY—The value of an agitator depends on the cost of making the maximum economic extraction by its use. This will be determined by its cost of agitation per ton per hour and the time required to obtain dissolution. All the data I have been able to obtain indicates that the cost of agitation per hour is extremely low. Extraction tests that have been made indicate that the rate of dissolution on both gold and silver ores in Dorr agitators, with a uniform although less violent agitation, is at least as rapid as in any other agitators with which they have been compared.

The most favorable conditions for the dissolution of gold and silver in cyanide solution vary with each ore treated. The maintenance of an excess of dissolved oxygen throughout the whole mass of pulp and the free movement of all particles of solids in the liquid immediately adjacent seem to be the only conditions that can be generally specified.

Definite work both in milling and the laboratory indicate that many ores will give a more rapid extraction and allow the use of a weaker solution when agitated as a dilute pulp of 3 to 1 or 4 to 1, and also cause less chemical consumption of cyanide.

The Dorr agitator with its combination of air and mechanical agitation gives a flexibility that is apparent and it insures keeping all the solids in suspension all the time whether the pulp is subjected to a gentle or a violent movement. This is essential especially in continuous agitation.

SELECTIVE AGITATION—The question of selective agitation was discussed by Mark R. Lamb in the Transactions of the *American Institute of Mining Engineers* **11** (1909), 775. As used here the expression is taken to mean continuous agitation under conditions which cause the coarser particles of the ore to remain in the agitator longer than the average time of treatment and thus give them the longer exposure they may require to obtain the best extraction.

This can be accomplished readily with the Dorr agitator by agitating at a dilution which allows the coarser material to classify out and discharging the raised pulp near the center while the outflow is taken from near the periphery. It will be seen that if a segregation takes place and the agitator is fed a pulp carrying 10 per cent plus 100 mesh, the discharge may be only 5 per cent plus 100 mesh at first. With twice as much inflow as outflow of 100-mesh material it will concentrate in the agitator while gradually increasing in the outflow until an equilibrium may be reached in which the feed and discharge will both be 10 per cent and the average pulp in the tank 20 per cent, so that the exposure of coarse sand would be approximately double the average. While this is theoretical, enough work has been done to indicate that the idea can be put to practical use.

My agitators have been installed in tanks of various sizes, the largest being those in use at the Desert Mill at Tonopah, Nevada, in tanks 36 ft. in diameter by 20 ft. deep. The Company estimate that the total power required to operate one of these large machines including mechanical horse power and the air required for maintaining agitation, is not over 5 H. P., so you will see that it is extremely small. A recent measurement in a 20 ft. by 12 ft. agitator showed that only 10 cu. ft. of free air at 15 lbs. pressure were needed. The application of Dorr agitators in the chemical industry has not been investigated to any extent, but it would seem that with finely divided materials from which it is desired to dissolve one constituent they should perform as useful a function as they are now doing in metallurgy.

ACID-PROOF MACHINERY

As all the submerged portions of classifiers, thickeners and agitators have no reciprocal motion, it has not been found difficult to manufacture them so as to resist ordinary acid liquors, and acid-proof machines of all three kinds are now in use.

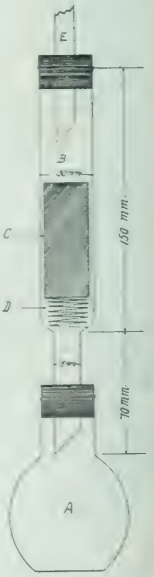
30 CHURCH STREET, NEW YORK

## A SIMPLE FAT EXTRACTION TUBE

By C. A. BUTT

Received December 22, 1914

The cost of fat extraction tubes has long been a source of much expense to laboratories doing work requiring the use of Soxhlet's apparatus, owing to their fragileness and the necessity of importing them. It occurred to me that in place of the rather elaborate tube now in general use, one constructed similar to the ordinary filter tube, with the stem enlarged so that the vapors from the solvent may pass upward, permitting at the same time the downward flow of the condensate, would answer the purpose.




Accordingly, I have had some of these tubes made and they have proved in several tests, using cottonseed meal and extracting with petrolic ether, to be even more efficient than the usual form. The results of these tests will be found on the following page.

It will be noticed that the new tube shows a more rapid extraction than the Smalley tube.

The illustration shows the approximate dimensions of the tubes we now have in use. The vapors from the solvent pass from flask "A" through the small part of tube "B" and around thimble "C,"

| Sample of cottonseed meal No. | Tube | Percentage of oil extracted in varying lengths of time 30 min. | 45 min. | 60 min. | 90 min. | 120 min. | 135 min. | 180 min. | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | New | .... | .... | .... | .... | .... | .... | 6.92 | Sample in poor mechanical condition |
| | Smalley | .... | .... | .... | .... | .... | .... | 6.90 | |
| 2 | New | .... | .... | 6.57 | .... | 6.64 | .... | 6.72 | |
| | Smalley | .... | .... | 5.92 | .... | 6.63 | .... | 6.66 | |
| 3 | New | 5.68 | .... | 7.42 | 7.48 | 7.52 | .... | .... | Made to pass 60-mesh screen |
| | Smalley | 3.76 | .... | 7.14 | 7.48 | 7.54 | .... | .... | |
| 4 | New | .... | 7.60 | .... | 7.78 | .... | 7.85 | .... | Good mechanical condition |
| | Smalley | .... | 7.30 | .... | 7.78 | .... | 7.85 | .... | |

which is raised by the use of a wire coil, spring or gauze "D," to allow free passage of vapors to the condenser tube "E." They have proved satisfactory for the extraction of hulls as well as meal; they are made of thick glass, and are, therefore, very durable.

LABORATORY INTERNATIONAL AGRICULTURAL CORPORATION
EAST POINT, GEORGIA

# ADDRESSES

## THE WAR AND THE CHEMICAL INDUSTRY[1]

By Wm. H. Nichols

Philadelphia was the cradle of Chemistry in this country. What was possibly the first Chemical Society in the world was founded here in 1792. A few years later one of its members addressing the Society said: "The only true basis on which the independence of our country can rest is agriculture and manufactures. To the promotion of these, nothing tends in a higher degree than Chemistry. It is this science which teaches man how to correct the bad qualities of the land he cultivates by a proper application of the various species of manure, and it is by means of a knowledge of this science that he is enabled to pursue the metals through the various forms they put on in the earth, separate them from substances which render them useless, and at length manufacture them into various forms for use and ornament as we see them. If such are the effects of Chemistry, how much should the wish for its promotion be excited in the heart of every American! It is to a general diffusion of knowledge of this science, next to the virtue of our countrymen, that we are to look for the firm establishment of our independence. And may your endeavors, gentlemen, in this cause, entitle you to the gratitude of your fellow citizens!" Considering the time when these words were spoken, we must marvel at the vision of the future which must have illumined the mind of the speaker. If in the last clause quoted he had said "ladies and gentlemen" it would have been complete.

But Philadelphia was also the cradle of the chemical industry in this country, and up to the present day occupies a very important part of that field. Some of the pleasantest recollections of my earlier life are associated with those fine men then prominent here, but now mostly passed on, who made this city respected wherever chemical products were concerned, and no insignificant part of my youthful enthusiasm was imbibed from them.

Therefore, when I was asked to talk to you on the subject of the war and the chemical industry, I accepted with the hope that I might add something to the general knowledge on the subject and, in a modest way, pay a portion of an old debt. In the interval which has elapsed, however, the ground has been covered by many men on many occasions, and I find myself in the position of talking to you on a subject as well understood by most of you as it is by myself. There may be certain phases, however, which will repay further thought, and possibly there may be deductions worth considering. I shall, therefore, ask your indulgence if I ramble somewhat, and talk largely about what we have not done, avoiding dry statistics as far as possible.

Some of us may be old enough to remember our own Civil War. Most of us remember the so-called Spanish War. Any knowledge or experience gained from these wars, intimate as the former was, gives no data on which to base any calculation as to the world-wide results of the present devastating struggle. Even our imaginations are unable to satisfy our judgments, which are more or less consciously or unconsciously influenced by our point of view. It is simply impossible to forecast the results, industrial, geographical or moral. The world has never seen anything like it before, and, therefore, reasoning from analogy is entirely out of the question. We know this, however, that where such an enormous number of men are withdrawn from ordinary pursuits, many never to return, and such incalculable damage is done to property, the world must feel for many years to come the effects which this impoverishment must produce. We might just as well accustom ourselves to the thought that before us lie years of painful toil and reconstruction, so that prudence, that great virtue of our forebears, may become more and more a part of us, and drive out the vice of extravagance which has become such a prominent characteristic of our people.

Judging from what we read in the papers, we might conclude that the chemical industry in the U. S. is in an infantile condition, and hardly worthy of serious consideration. Those not acquainted with the subject are ready to admit without argument that almost any European country is far and away ahead of us in volume and ability to produce economically. A glance at the 13th U. S. census will dispel at least some of these views, and is well worth taking. It includes under the heading "Chemicals and Allied Products" nine principal divisions, and gives the value of the output of each.

| | Value |
|---|---|
| 1—Paint and varnish | $125,000,000 |
| 2—Chemicals (general) | 117,000,000 |
| 3—Fertilizers | 104,000,000 |
| 4—Explosives | 40,000,000 |
| 5—Dyestuffs and extracts | 16,000,000 |
| 6—Sulfuric, nitric and mixed acids | 10,000,000 |
| 7—Wood (except rosin and turpentine) | 10,000,000 |
| 8—Essential oils | 2,000,000 |
| 9—Bone, carbon and lampblack | 2,000,000 |

The above values were produced by 2,140 establishments, having a capital of $483,000,000, and employing 88,000 persons. The census does not state, however, what is probably the fact, that the U. S. produces more sulfuric acid by catalysis than any other country in the world, and possibly more than all other countries combined. This fact has a bearing on what will be alluded to later, namely, the possible manufacture of coal-tar dyes and other products, for which fuming sulfuric acid is often an absolute necessity.

The census furthermore shows that the return on capital invested in the chemical and allied industries is not so great as in other branches of manufacturing endeavor. This is due to the high initial cost of plant, frequent alterations and reconstructions made necessary by the advance of knowledge, and I imagine by a somewhat senseless competition, which has seemed to affect chemical manufacturers for as long as I can remember.

Owing to the enormous territory covered, the conditions governing the industry are quite different from those existing in other countries. Like all industries, the greatest economies can be practiced in the largest units, but this fact of extensive territory which is served makes numerous small units necessary. The products usually are bulky and low-priced, and railroad freights play an important part in the problem. This fact must be borne in mind constantly when comparing the industry in this country with that in any other.

We Americans are apt to pride ourselves on the progress which we have made along manufacturing lines, and take to ourselves

[1] Address before the American Association for the Advancement of Science, Philadelphia, December 30, 1914.

great credit for what has been accomplished. In view of the enormous supply of various raw materials which this country has at its disposal, an analysis of what we have done, I fear, would show that instead of taking undue credit to ourselves we should be very humble because we have not done much better. Of course, I realize that this is a comparatively new country and that it took time to get things into working order. Lines of communication had to be constructed, factories had to be built and rebuilt and all the necessary impedimenta of industry had to be evolved from a condition which, at the time the Philadelphia chemist quoted in the beginning spoke, consisted of little more than forests, prairies and prospects of mines. If during this period of development a good deal of waste occurred, and a number of abuses crept in, it is not so much to be wondered at. We have, however, arrived at a period when it is borne in upon us from all sides that conservation of natural resources, as well as human energy, is absolutely essential, if we are to go forward with anything like the strength and certainty to which our resources entitle us.

Of raw materials for the chemical industry, without going into unnecessary voluminous details, we have an abundance—cheap phosphate rock, salt, copper, sulfur, coal, wood, bauxite, zinc. In addition to raw materials, and among our most valuable assets, are our college professors of chemistry who, I am sure could, if called upon, render additional priceless services to the lasting benefit of the world and of themselves.

On the other hand we must import much of our sulfur in the form of pyrites, nearly all of our potash, all of our tin, nickel and nitrate of soda. We have large supplies of nitrogen, available from animals and coal. But the great supply of the future is still in the air. This source of supply, however, has up to the present time proved rather difficult of access. Of course, it must be secured, but just how is not altogether clear in spite of the good work already accomplished. This is one of the problems which the chemist, chemical engineer and electrical engineer must solve, however, within a comparatively few years, as the nitrate beds of Chili, while still very large, will some time come to an end.

With the Allies in command of the sea, the war has not affected any of these raw materials very greatly, except potash. This salt is widely enough disseminated in various forms in this country but where of hopeful strength it is inaccessible, and where accessible it cannot be produced without expensive plant construction which would probably be useless as soon as the German supply is once more obtainable. In arriving at this conclusion due note must be made of the German costs and not of the German selling prices. The Stassfurt salts can be produced very cheaply indeed and the price which they have been able to bring in the markets of the world have yielded an enormous profit. This fact, of course, is a determining one when we talk of producing our own potash.

One of the most important of the chemical industries is the manufacture of fertilizers for the soil. We have in this country enormous deposits of phosphate rock, easily accessible and cheaply mined. This rock has been exported in large quantities to Europe and the Orient and is in sufficient quantity to last a number of years even in the careless way in which it has been used. A complete fertilizer, however, requires potash and, as noted above, we have been in the habit for a number of years of getting our potash from Germany and there is every reason to expect that we will continue to do so for many years to come. If, as one of the results of the war, while it lasts, enough potash cannot be obtained to make the fertilizers to which we have been accustomed, I feel that this will not be an absolutely hopeless misfortune. It is quite possible that the propaganda for the use of potash has been carried too far, and that less could be used on the soil without any great disadvantage. At any rate, we shall be quite able to furnish an abundance of fertilizers in this country containing phosphoric acid and nitrogen, and if for a while we have to rely more or less upon the soil to furnish its own potash I imagine we shall not suffer beyond redemption. From some quarters in the south and elsewhere I have heard rumors that a smaller cotton crop would be looked upon as a blessing, and it is quite likely that without government or other assistance the natural laws of supply and demand will produce a smaller crop next year simply because there may not be enough potash to supply the requirements of a large one.

With here and there an exception, the only effect the war has had upon the chemical industry is the effect which it has had upon those industries which consume its output, and I think this can be taken as a general statement covering all articles Of course, there are notable exceptions, such as smokeless powder and other products required for war purposes.

Some heavy chemicals, the receipt of raw material for which has been very much curtailed or stopped altogether, have advanced sharply in value, but generally speaking the chemical industry has not profited by advanced prices as a result of the war. Owing to reduced home consumption the result in some cases has been a great falling off in profit, a condition which I trust will not be of long duration. I believe that the manufacturing industries of this country will before very long be on the up-grade and all of the chemicals produced, speaking generally, will be needed.

More has been talked and printed lately about a portion of the chemical industry which has not taken very deep root in this country, than about all the rest of the industry put together. I refer to the organic chemicals resulting from products of the distillation of coal tar. Many have wondered why the American chemist has not stepped up and taken the place of the foreign manufacturer in supplying the textile and other industries with colors, evidently not understanding the size and complexity of the question. I think it worth while, therefore, to discuss this at some length as it is probably the most pressing question before the chemical world in this country today and I fear the one least likely to receive a favorable reply. A few years ago every coke oven in this country was what is known as a bee-hive oven, and all the by-products of the distillation of coal were lost. It is only in comparatively recent years that by-product furnaces have been constructed and various by-products saved. The ammonia was naturally first utilized and the products of the distillation of tar have been among the last. In fact, a theory existed in the minds of many people that the tar produced by American coal did not possess the necessary constituents to make it useful as a basis for the production of organic chemicals. I have been myself told by one of the large producers in Germany that it was absolutely certain that American coal did not possess the necessary qualities. The object of this information was probably to put out of my mind any latent ambition along forbidden lines, but as it was given by the commercial manager and not by one of the scientific staff, I believed him, but wondered if it were true.

In a lecture delivered to the Board of Directors of the General Chemical Company on October 23, 1914, the subject and its difficulties were outlined by Dr. B. C. Hesse. Owing to the immensity of the subject, only a small part of it was treated. This able lecture has since been published in the December number of THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY[1] but I cannot do better than quote from it freely, as I consider it the best exposition of the case that has come to my attention. He says, "At the very beginning, it should be pointed out that the world's market in coal-tar dyes as it stands today, comprises, in round numbers, 900 distinct and different chemical substances which are made by the aid of 300 products of transformation, them-

[1] THIS JOURNAL, 6 (1914), 1013.

selves not dyes, of 10 products obtained or obtainable from coal-tar by distillation, refrigeration, expression or the like. Therefore, actually and in reality the present coal-tar dye industry comprises no fewer than 1,200 different products and as many or more different processes of manufacture and requires many hundred different sets of apparatus of varying capacity and of differing kind for many hundred different operations. A manufacturing problem comprising so many independent and yet interlaced units of manufacture and production has, therefore, within it many elements of complexity.

"World's figures are not available. The fullest, best, most dependable and most recent figures are those dealing with Germany. In the year 1913 the total export value of Germany's coal-tar industry, including dyes and products of chemical transformation or intermediates, amounted to $55,264,522 distributed over 33 countries and shared in by 22 factories; on June 30, 1912, 21 of these factories had a combined capitalization of $36,700,000 and declared and paid dividends of $11,600,000, or 21.74 per cent of the capitalization, for that year.

"Of the 5369 active corporations in Germany on June 30, 1912, 1004 or 18.69 per cent are divided into 19 groups of the chemical and allied industries. Arranged in the order of their income-producing effects these 19 groups are, in part, as follows:

| | Per cent | No. of corporations |
|---|---|---|
| Coal-tar dyes | 21.74 | 21 |
| Metallurgy | 11.78 | 61 |
| Soaps and candles | 11.65 | 21 |
| Glass | 11.61 | 38 |
| Heavy chemicals | 11.51 | 104 |
| Explosives | 11.22 | 28 |

The remainder range between 5 and 10 per cent except mining which is at the foot of the list with 0.51 per cent return.

"Therefore, any attempt to take away the coal-tar dye business from Germany means attacking the best equipped and the best income producer of Germany's entire chemical and allied industry."

Dr. Hesse estimates as follows on the entire world production:

| | |
|---|---|
| "Germany | $68,222,846 |
| Great Britain | 5,982,675 |
| Switzerland | 6,452,651 |
| France | 5,000,000 |
| United States | 3,750,000 |
| | $89,408,172 |

with Russia, Holland, Austria and Belgium to be added. Allowing $10,000,000 for these, which is clearly very high, it makes the absolute maximum production all over the world substantially $100,000,000.

"The development of the coal-tar dye industry called for 8062 German patents in the years 1876–1912, or 224 per year; corresponding patents have been taken out in other countries, *e. g.*, 2432 in the United States.

"But it is authoritatively said that only 1 in 100 of the German patents is a money-maker and as a matter of fact in the case of the 921 dyes in the world markets at the end of 1912, only 485 U. S. patents and 762 German patents were involved, or 19.94 per cent of the total U. S. and 9.46 per cent of the total German patents. Of these 921 dyes, 50 per cent were never patented in the United States; the U. S. patents on 26 per cent have now expired, leaving 24 per cent still covered by existing U. S. patents and many of those expiring in 1915.

"Broadly speaking, the entire coal-tar dye industry is a complicated maze and network of interlocking and interlacing products and by-products; these are great in number but, in most cases, small in volume individually. In numerous instances the very existence of the by-products was the sole directing cause for the invention of new dyes and classes of dyes.

"The average annual unit gross per year of the 900 coal-tar dyes, exclusive of alizarin and indigo, all over the world outside of Germany has previously been shown to be about $41,000. Add to this fact the interlocked and interlaced dependence of intermediates and finished dyes, and further that the German works have long ago fully paid for their plant, their experience and their sales organization and the result is what seems to be a complete answer why Germany controls the world's coal-tar dye market. In fact, the whole industry, taking everything into account, is just about a one-nation business. It is a business made up of a large number of small units with all the units essential to success.

"Germany has this business established in 33 other countries; it is evident that any country starting in now would be greatly handicapped thereby if it attempted to enter the race for the full distance.

"Although Germany has relied upon Great Britain for its crudes, *i. e.*, its benzol, its toluol, its naphthalene and its anthracene up to the middle of the '90's, and perhaps later, yet England has not been able to make any headway, but on the contrary has always lost ground. Many of these non-patented world's dyes are also non-patented in England, yet most of Great Britain's requirements of these materials have always been supplied by Germany.

"The answer to the question as to why Great Britain has not succeeded against Germany cannot be that Great Britain is not a nation with highly developed chemical industries. A German chemist as well equipped as any other living man to express an opinion and to compare German industries with British industries has said the following: 'To be sure, we know that several of the European countries, *e. g.*, England, are still ahead of us in many branches of the chemical industry, especially in inorganic manufacture. But in no country on earth are those branches of the chemical industry which demand versatility of thought, and particularly a large body of scientifically trained employees, so well developed as with us. Our synthetic dye, synthetic drug, and perfumery industries are foremost throughout the world, and there is probably no country in which the heads of factories are so imbued with the conviction that their employees must needs cast a glance beyond domestic boundaries.'

"Each one of the large chemical manufacturing countries of Europe, without exception, buys more intermediate products from Germany than it sells to Germany and all of the countries but one, namely, Switzerland, buy more dyestuffs from Germany than they sell to Germany. In other words, and broadly speaking, all the rest of the world, outside of Germany, merely assembles intermediates purchased from Germany, into finished dyes; Germany alone makes all its own intermediates; that is, Germany makes all the dye-parts and the rest of the world assembles these dye-parts into finished dyes. Needless to say, the one who controls the manufacture of dye-parts actually controls the manufacture of dyes.

"Where Austria, Belgium, France, Great Britain, Italy, Russia and Switzerland singly and combined have failed, in spite of their large other chemical industries, to take away this business from Germany, the American chemist should not be blamed or found fault with because he has not succeeded, nor should it be assumed that transplanting of the whole industry can be done at once and is a perfectly easy thing to do, as so many seem to think. The transplanting of that industry out of Germany is an undertaking properly and fitly to be described as titanic.

"Why the other countries have failed is probably due to the fact that they contributed little or nothing to the real upbuilding of the business and to its creation, for the coal-tar dye business is a *created* business; those who aided in its creation were in a position first to reap the benefits—an advantage they have no doubt earned and deserved through the effort they expended and the risks they assumed.

"In 1913, Germany had for sale to foreigners $3 worth of these products as against every dollar's worth that it needed at home.

"Nine hundred different dyes were on the United States markets of which 100 were made or assembled in this country from

intermediates purchased from Germany. Yet these one hundred do not seem to be enough for American dye-users. How much less than the full nine hundred will satisfy American users is known to them and to the importers; the latter cannot be expected to divulge that information; if the former want substantial help from American chemical makers *they* must divulge it, no other way of ascertaining being available.

"In 1909 the United States produced $3,462,436 worth of artificial dyes which are probably aniline dyes in the strict sense. Compared with Switzerland's $3,200,000 production, *i. e.*, assembly in 1896, this is an achievement of which Americans need not be ashamed. The wonder is not that we have not done more but that in the face of the well-organized manufacturing plants of Germany and of Germany's very much superior facilities for foreign trade, both banking and carrying, that we have done as much as we have. Blame should not be parceled out for what American chemists have not done, but credit, which has been so far withheld, should be given for what has been done in spite of obstacles abroad and obstacles at home. The users of dyestuffs have invariably opposed any tariff enactment that would substantially encourage a domestic production of coal-tar dyes. That so many are produced in this country as are being produced is due to no coöperation of dyestuff users but was accomplished in spite of their obstruction and if today the users are in serious difficulty through a lack of dyestuffs they have their own shortsightedness to blame and cannot, by any argumentation whatever, shift the blame to American chemists. With proper help and encouragement the American chemist will be able to increase the domestic production of coal-tar dyes and to inaugurate the making of intermediates; in the course of time this country may then ultimately look forward to a substantial share of the world's coal-tar dye business.

"Hardly any of the valuable or useful intermediates ever were patented. A considerable number of non-German chemists have invented and patented finished dyes made from non-patented intermediates. These inventors had perfect freedom to make the needful intermediates and an *exclusive* right to make, sell and use their new dyes therefrom, yet they bought their intermediates from Germany rather than make them themselves. The patent situation is, therefore, really, that Germany excelled the rest of the world in making patentable combinations from non-patented and non-patentable intermediates and further in making those non-patented and non-patentable intermediates in open competition with the rest of the world. So, from one point of view, it appears that the rest of the world, inclusive of the United States, lay back, let the Germans do all the hard work and when the rest of the world finally woke up to the value of what the Germans had accomplished they became very busy making excuses and explaining instead of making a determined, directed, united and effective attempt to recover the ground so lost. That such a recovery will require the hardest kind of work on the part of all, users, capitalists, consumers and makers alike, is self-evident and obvious and the question is: do we want to pay the price? It can be done, if the price be paid."

At the conclusion of Dr. Hesse's lecture the Directors were called upon for remarks. One well qualified arose and simply quoted from Mrs. Stowe's "Old Town Folks:"

"One of the characters, Sam Lawson, had gone to 'meetin house' to hear the new preacher, and returning shortly afterwards to the kitchen, where the 'women folks' were preparing the meal, they inquired of him why he happened to come so soon—'surely, meetin' couldn't be out'."

He replied: "No, meetin' isn't out, but the preacher said how by a state of natur' we were all down in a deep well, and the sides of the well were glar ice. There warn't one in ten, warn't one in one hundred, warn't one in a thousan' 'd ever get out, and yet it war the partickler duty of every one of us to get out. At that pint in the discourse, I rose and went out, thinkin' any one was welcome to my chance."

From the foregoing it will appear as if the opportunity to produce colors and other articles and products in a large way in this country, while open, are not likely to be availed of to any great extent during the existence of the present war, unless the war should last much longer than even the most pessimistic fear.

I might say, however, in this connection that I remember distinctly being told by one of the best authorities on the subject that it was absolutely impossible to manufacture Portland cement in this country and it might just as well be put aside as one of the things for which this country was not adapted. I have also heard exactly the same statement regarding soda ash and caustic soda, and yet these materials somehow or other have become rather important articles of our manufacture and for a long time we have not been obliged to call loudly for outside help.

In spite of the difficulties, however, some feeble steps have been taken here, partly, I confess, out of curiosity to learn if it were really true that our coal lacked the self-respect to hold all the treasures it should possess when, strange to relate, out came aniline oil of the best quality. What happened then is worthy of note, as it shows at least one state of affairs which it is necessary to correct if we are ever going to escape from the dilemma which discouraged Sam Lawson. As soon as American aniline oil was offered for sale, down went the price below cost. A tariff of 10 per cent put upon it by Congress as a compromise between judgment and party was immediately absorbed by the foreign makers, and the price here became lower still. You see on the other side of the Atlantic they believe in coöperation. Here our legislators think we believe in destructive competition, and have made coöperation one of the seven deadly sins. Nothing but demonstration by the ballot box will prove the contrary. A man with his ear to the ground does not always hear the "music of the spheres." The low price of aniline oil had no relation to its cost. It was simply dumped, by agreement, to discourage the American infant. And it did.

Many devices have been suggested to encourage the coal-tar dye industry in this country, such as a high protective tariff and changes in the patent law.

The former does not seem likely to be evolved, although a good deal can be said on the side that a high tariff in these articles would either result in the establishment of the industry or else produce a considerable revenue, either one most desirable to attain. The latter is such a complex subject that it is not so clear that good results would ensue on changing the patent laws. While it is important to establish a coal-tar dye industry as far as is practicable, we must not be selfish enough to forget that there are other important industries already established, and the American people must learn more and more to consider the rights and needs of the individual in their relation to the rights and needs of all.

Another obstacle besides the patent laws and the absence of tariff protection, to the establishment in this country of any new industry strongly intrenched abroad, is to be found in the inadequacy of the anti-trust laws to protect American industry against systematic dumping of goods from abroad at prices substantially less than foreign prices with intent to injure or destroy the local industry.

Much has been done by the present Congress in the creation of a Trade Commission and in the statutory condemnation of certain specific practices to render those laws more efficient; but, taken as a whole, the efficiency of those laws, so complete for domestic commerce, is quite unsatisfactory when applied to imports from abroad, and that despite the very real help to be expected from the new Trade Commission.

The trouble lies partly in the inherent difficulty of the subject and partly in the inadequacy or ambiguity of previous legislation. First of all, our anti-trust laws can have no extra-terri-

torial force. Cartels and trusts that would be invalid here are lawful abroad, and in so far as these operate on their own soil even to our detriment, the individuals concerned can with difficulty be reached so long as the acts done are lawful in the country where they are done. But these unfair practices must express themselves in imports into this country, and this implies the existence of importers or agents who must either be, or occasionally come, within the jurisdiction of our laws.

And so we find that in 1894 our Congress partially legislated on this very subject—and by the anti-trust sections of the Wilson Tariff law (Secs. 73–77) visited upon importers who should combine in importing to restrain trade in this country all the pains and penalties of the Sherman Law of 1890; namely: fines, imprisonment, forfeiture of goods in transit, triple damages, injunction and dissolution.

But this Wilson Bill, which may well be deemed to be the exclusive expression of Congressional purpose on this subject of imports, is confined to restraint of trade by two or more—and it does not, like the Sherman Law, prohibit monopolizing, nor acts done by one person or corporation alone, nor does it prohibit unfair methods as such.

Now the unfair methods here complained of are precisely those which tend to monopoly by the destruction of competitors, and they can as well be employed by a single powerful concern as by a combination.

Viewed merely as "unfair methods," it is probable that they would not have been held by the courts to have fallen under the Sherman Law so long ago as 1894; but would have been classed among those acts which the Supreme Court has lately characterized as "no more than ordinary acts of competition or the small dishonesties of trade."

But in the last few years ideas on this subject have undergone a complete change, and many methods formerly thought legitimate have passed under the ban of the law. Railway rebates are a notable example of this; and now with the legislation of this year we find legislative authority for the condemnation of unfair methods of competition generally, and notably discrimination in prices with intent to injure.

Admirable as are these provisions, there is nothing in the new statutes which extends their scope by way of amendment to the Wilson Bill and to imports—and there is much to indicate the legislative intent to confine those provisions to domestic commerce alone. The word "commerce" both in the unfair methods clause (Sec. 5 Commission Bill) and in the price discrimination clause (Sec. 2 Clayton Bill) is defined as commerce among the States or between this country and a foreign country, and this definition excludes the idea of its including also commerce within a foreign country.

The practices that we complain of involve commerce not in the restricted sense as defined, but a commerce that includes foreign countries as well as our own. But if these practices of foreigners and importers are nevertheless to be deemed unfair methods within the Commission Bill (Sec. 5), the only remedy for them is an order of the Trade Commission to desist. They are not expressly prohibited by the Act itself, nor made punishable in any way. If, however, these practices are to be deemed price discrimination within the Clayton Bill (Sec. 2), which seems impossible, then the only remedy besides an order to desist is a right to sue for triple damages. The difficulty in estimating any damages at all is obvious enough in any case, especially so in the case of the destruction of a small *new* industry, and still more so in the case of an embryo industry that has never raised its head.

Even if Sec. 2 of the Clayton Bill apply, we must assume that it creates a new offense not included in either the Sherman or the Wilson Bills; hence, that there would be no authority of law for any remedy except those alluded to as given in the act creating the offense, especially so inasmuch as the Wilson law stands out unrepealed as the sole legislative expression on the subject of imports and is silent and unamended upon the subject of price discrimination.

If this conclusion be correct (and it is almost as bad if the law be in doubt) there exists a situation where the equal protection of the laws is not extended to the importer and the domestic manufacturer alike. On the contrary, a practical license is given to the importer to do that which the citizen is forbidden to do.

The foreign manufacturer or importer seldom has any inducement to act in restraint of trade as we commonly understand it, or to monopolize competing plants in this country; quite the reverse. His object is to build his monopoly by destroying a domestic industry, and one of his most potent weapons in doing this, if he be well enough intrenched, is to drop prices in this country below the prices which yield him profits abroad for a long enough period to drive out American competitors; when, having the market to himself, he may raise them again.

The penalties to be invoked against the foreign manufacturer and importer as deterrents are utterly inadequate to deter them from trying it on as before. The most that they can suffer from their practices is, as we have seen, a Commission's order to desist, and perhaps in some cases a suit, difficult to prove, for triple damages.

What is needed is that these people should have before their eyes the same deterrents of fine, imprisonment, forfeiture of goods, triple damages, possible injunction and dissolution, as have rendered American business men careful neither to restrain trade nor monopolize nor indulge in unfair practices. The practices here condemned in reality amount to much more than mere unfair methods of competition; they verge on an illegal attempt at monopolizing. It is of the essence of monopolizing to exclude. The legislation of 1914 does not subject unfair methods in general to the criminal features of the anti-trust laws, and this is doubtless wise. But this particular offense is in its nature monopolistic and criminal, and it is the most effective form by which the foreigner can evade our anti-trust laws and illegally injure or destroy American industry. What is needed is an amendment of the anti-trust sections of the Wilson Tariff act carrying into it the prohibitions against monopolizing of the Sherman Act, even when practiced by one person alone, and expressly defining the practice here condemned as an act of monopolizing. The pains and penalties of the Sherman and Wilson Acts would then follow on these practices as a matter of course.

At the present time, when there can be no longer any thought of procuring additional protection of new industries through the tariff, it will be rash to hope that American capital and enterprise should further embark in any of those industries, new or unknown here, which are firmly intrenched abroad, and where, as soon as the war is over, the foreigner can return to the work of attack and destruction by the methods above mentioned.

This plan, which aims to place Americans and foreigners on the same footing here, could, it seems to me, be easily and quickly enacted by the present Congress. It would put American manufacturers, including American chemists, in a position to act without having all the chances against them. Are they not entitled to at least this much?

I do not believe in hothouse development of industries for which we are not adapted; but save us from the cold-storage conditions resulting from perfect organization being arrayed against us so that our real opportunities, which we are in every way qualified to enjoy, are frozen to death. The little aniline oil experiment alluded to above has come to life again, and in its small way has proved during these war times to be a godsend to our manufacturers. It is gratifying to note that it is even growing in a manner which it is hoped will be permanent. It

seems too bad that it should require a dreadful war to make such a little start possible; it should have been accomplished as soon as our by-product coke ovens and fuming sulfuric acid production made it possible.

To sum up, the effects of the war on the chemical industry already established in this country are measured in general by their effects on the industries consuming chemical products. It has, however, been brought very close to us that certain industries not thoroughly established here but highly organized abroad are of tremendous importance to us. We have seen that this branch of chemical industry has been the result of marvelous ingenuity, patience, research and coöperation during the more than half century since Perkin produced the first coal-tar dye in England. One of the lessons to us which it seems to me lies near the surface and is probably one of the most important lessons this people must thoroughly learn is that of coöperation, which has had more to do with the making of the great coal-tar chemical industry than any other one influence. We as a nation have passed our childhood and youth; we have made gigantic progress at tremendous cost of materials and possibly of moral fiber; we have come to the parting of the ways. If we continue too long as we have been going we shall deserve disaster if we do not actually experience it. We know on the highest authority that "a house divided against itself must fall." The laws of the resultant of forces familiar to us all show us what would happen if we all pulled in different directions. I feel strongly that our future success as a nation lies in universal coöperation—the Government and its departments with the manufacturer, the manufacturer with the workman, and all together for the country and for the world; and this coöperation must not be based solely on self-interest, but more particularly on those moral qualities which lie at the foundation of universal brotherhood. It must not be the survival of the fittest, but the survival of all, and the very best that is in them brought out of all. When we have learned and adopted this lesson of coöperation for the good of all, we have started on the road to a national greatness, both material and moral, which I modestly feel that the possessions of this people qualify it richly to enjoy.

25 Broad Street, New York

## PAINTING DEFECTS: THEIR CAUSES AND PREVENTION[1]

By Gustave W. Thompson

When a defect in painting occurs there are two different attitudes in either of which a person may place his mind. One is to assume that the defect is inherent in the paint used, and the other is to assume that the defect is due to an improper use of the paint. This difference in attitude of mind is not imaginary; it is so real that it seems very desirable that this difference should be explained and amplified.

The principal cost of any painting job is labor, and yet when in the attitude of mind first mentioned, if a paint goes wrong one will condemn the materials used, whereas in the other case he will be inclined to hold that the most costly factor is the one that is probably responsible. It is easier to blame paint materials than it is to blame workmanship. Materials are tangible; workmanship is intangible. Materials can be examined to some extent even long after they have been applied, but there are few means of recording satisfactorily what the workman has done. Every manufacturer of paint feels more or less that if his paint were properly applied it would give perfect satisfaction. Every user of paint is inclined to feel that if he could only get the right materials he would be quite sure to do good work always.

It would appear that perhaps in most cases the manufacturer is inclined to take one of these two attitudes of mind and the consumer the other, but this is not necessarily the case. Some manufacturers are wedded to certain beliefs with regard to materials, which, judging from their advertisements, one would be inclined to think fool-proof, and some few consumers blame their workmen when things go wrong without considering that the materials used may be at fault.

Without attempting to judge the relative value of either attitude of mind, as so much has been written connecting painting defects with materials used, the writer proposes in this paper to take the opposite attitude and to treat of paint defects, their causes and prevention, not with the idea of connecting these defects to any appreciable extent with the materials used, although he will have to diverge from this rule to a slight extent, but principally to state the results of a great many years of study of the subject from this standpoint, and to show how paint defects may in many cases be corrected without radical change in the materials used.

In studying a paint defect from the attitude of mind which is adopted in this paper, one cannot, of course, ignore the materials used, but one can seek to find out to what extent such a defect may be the result of the condition of the surface painted, the proportioning of the materials, the application of these materials, the time allowed between coats, etc. From this attitude of mind all of these factors, and others similar thereto, are included in the general term "application." In studying a paint defect along this line one must use his reasoning powers conscientiously and scientifically. To obtain an intelligent conclusion he must study many defects; he should furthermore be able to reproduce experimentally the defects being considered, before he can reach a positive conclusion as to their causes and cure. It must not be assumed that the writer can explain all paint defects. He makes no such pretensions. But in so far as he is able to speak positively in any case, it is because he has been able to reason out the cause of the defect, and in most cases to reproduce the defect experimentally.

A word must be said here in regard to the proper use of painting tests: those of a controversial nature have not appealed to the writer. The real value of painting tests lies in the information they furnish, in the ability they give the student to classify painting results, whether good or bad. The idea that paint materials can be tested out and their merits determined by a few panel painting tests is, in the opinion of the writer, generally unsound; but if such tests are to be conducted, they should be along lines entirely different from those which have heretofore been pursued, with one or two striking exceptions. The painting of panels indoors and then exposing them to the weather, and from such tests endeavoring to reach conclusions, favorable or unfavorable to certain paints, without having previously determined that the method of testing is a fair representation of what actually occurs in practice, is an unsafe method to follow. To illustrate this by a parallel case—no chemist would dare to adopt a method of analysis or test that had not been checked up by analyzing or testing mixtures of known composition.

One of the exceptions to which reference should be made is the North Dakota tests. There Prof. Ladd is not satisfied with painting panels and exposing them to the weather, but he also has had a number of houses painted following ordinary practice. In the case of the North Dakota tests there are actual painting jobs done which serve as a check upon the panel tests conducted under his direction.

Another striking exception is the painting tests on the Havre de Grace bridge, where the paints were applied both to the bridge proper and to the special panels erected along the side of the bridge. In all cases if the panels do not confirm the actual service tests, they must be considered as of only secondary value. They have value—but only for the information they give.

This aspect of the subject has been driven home to the

[1] Presented before the Maintenance of Way Master Painters' Convention, Detroit, November 18, 1914, and also before the 7th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 2–5, 1914.

writer by the study of many thousands of tests which have been conducted under his direction. He has come to the conclusion that it is very difficult to make a panel test of paint materials which will give results corresponding to those obtained with the same materials in actual use. The writer did not believe this at one time and was inclined to take issue with the statement of experienced paint manufacturers, namely, that panel tests were of little value as showing the merits of materials when in actual use. A little consideration will however show the difficulty of preparing panel tests that will be conclusive as to the merits of paint materials. I refer now to paint materials used for exterior painting. The usual method of preparing such tests is to get nice specimens of wood, paint them indoors, place them on racks between the application of each coat, and when they are thought to be thoroughly dry, they are placed out of doors for exposure. The objection to this method is that we never bring a house indoors to paint it unless it be a toy house, and the drying action of the under coats of paint is never the same indoors as it is out of doors. Indoors there is not the same circulation and abundant supply of air that there is out of doors.

FIG. 1—TEST BOARD DRYING CABINET SUPPLIED WITH CLEAN OUT-OF-DOOR AIR

A great quantity of air is needed to dry paint properly for outdoor exposure. Panels painted indoors will not dry so hard as those painted out of doors. Panels that are stacked fairly closely together will not dry so hard as panels spread out and given a great deal of air. We must not think that this applies only to the outer coat, for that will finally dry when it is placed out of doors, but we must remember that for out-of-door work all coatings are exposed to more or less rapid currents of air which dry them to a proper condition for durability.

A number of different methods have suggested themselves to the writer whereby panels painted indoors can be brought to a condition corresponding to outdoor exposure before the actual exposure is made. The writer has thought that perhaps a short heating of the panels after each coat has been applied, at, say, 120° F., might produce results that correspond to outdoor exposure, or that by drying the panels between coats in a cabinet supplied with fresh out-of-door air from a blower, he could obtain results corresponding to outdoor exposure. Fig. 1 illustrates such a cabinet supplied by a blower with clean out-of-door air. But it is probable that both of these are questionable expedients and that the one way to get correct drying is by out-of-door exposure between coats under conditions where both air and light may be abundantly supplied.

But this is not the only point to which attention should be called with reference to panel tests. Most such tests tend to ignore the modification of composition of the various coats, which the experienced painter finds necessary in order to produce the best results. The principal modification would arise, of course, in the proportioning of the oil and thinner, but sometimes materials are added to paint for definite reasons. The practical question then always arises whether it is best to add these materials to the first, the second, or the third coat, and what the quantities to be added shall be. In other words, panel tests to determine the value of paint materials should be conducted so as to obtain the very best results practicable with the materials used. This usually involves too much trouble and requires too much experience to satisfy the common demand for quick results.

With this explanation of the plan of this paper, a number of defects will now be considered in the double hope that some light may be thrown on their causes, and that the method of procedure adopted may help toward the solving of other defects, for the discussion of which the writer has not now the requisite time.

## CHECKING AND ALLIGATORING

"Checking" and "alligatoring" consist in the development of fine interlacing lines on the surface of a paint, that is, lines embracing areas, which, if small, are called checks, and which, if large, have the appearance of alligator skin. It would appear that the phenomena of checking and alligatoring are closely related and are probably due to the same general cause.

Every varnish manufacturer knows the cause of the alligatoring of varnish. All general experience points to the conclusion that it is due to the application of a hard varnish over a comparatively soft under coat. The alligatoring of varnish is particularly noticeable where cheap rosin varnishes have been used for the under coat. If varnish is applied over a grain surface, the ground of which is a yellow ochre paint which will not harden properly, the surface is quite sure to be alligatored. The reason that alligatoring occurs under these conditions becomes quite apparent with a little consideration. Taking the case of two coats of material applied to a smooth surface, the second is applied as soon as the first has dried sufficiently hard. The second coat then becomes dry. Now observe that while the first coat was sufficiently dry to permit the application of the second, it had not reached what may be considered a fit condition of dryness; *i. e.*, if the second coat had not been applied and the first had been exposed to the air, the hardening due to oxidation would have continued indefinitely. By applying a second coat, this oxidation and consequent hardening of the first was stopped, at least to a very large extent, while the second coat on the other hand can keep on oxidizing and hardening indefinitely.

Now we know that nearly all oleo-resinous varnishes contain drying oils, which have the power of absorbing oxygen from the air and giving off certain products of oxidation, and the longer a drying oil is exposed to the air the more it oxidizes and the harder it becomes. We know also that there is a shrinking in volume during this operation of oxidation and hardening. We know that linseed oil, which is present in oleo-resinous varnish, increases in weight through oxidation in the beginning of the oxidizing operation until it has added to its weight up to 18 per cent, but after this maximum increase in weight has taken place there is a loss in weight due to the liberation of volatile compounds, which are carried away in the air, so that after a time a linseed oil film may reach a weight very close to that which it

originally possessed. Now during these changes the specific gravity of the linseed oil has increased, from which we must conclude that there has been a reduction or contraction in volume. All this has been demonstrated by the investigations of Prof. A. H. Sabin.

We can readily see how in the case of one coat of varnish placed over another, under conditions in which the first coat has not had a sufficient chance to thoroughly harden before the second coat is

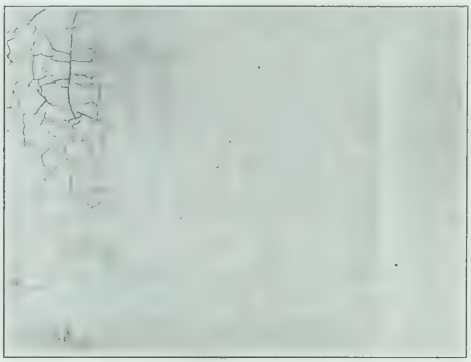


Fig. 2—White Paint over an Asphaltum Paint

applied, the second on drying will contract and decrease in volume, while the first will remain practically unchanged in its volume and in its degree of hardness.

Now in all cases the outer coats of varnish and paint tend greatly to shrink in volume and to become progressively harder and more coherent, thus producing two possible effects. One of these is the rupturing of this outer coat with consequent alligatoring or checking. The other possible effect is that the outer coat becomes thinner without rupturing. Which of these effects occurs depends upon the under coat. If the under coat is soft, the outer coat in oxidizing and shrinking will draw up and slip over it with consequent rupturing. If the under coat is sufficiently hard, the outer coat does not slip over it but simply becomes thinner by shrinkage and no rupturing occurs.

This is the general explanation of the alligatoring of varnish and paint. It is also shown whenever a paint is applied over another that inherently will not dry hard, as in the case of a harder paint applied over an asphaltum one (Fig. 2) or in the case of a harder paint applied over a yellow ochre one (Fig. 3). Very extreme examples of checking or alligatoring occur where a non-volatile mineral oil has been used in an under coat.

This explanation is one that is quite generally accepted, although there may be minor points on which there is disagreement. Now if this is true, in what way does checking differ from alligatoring? From the writer's experience the causes of checking are identical with the causes of alligatoring, and he has experimentally produced a series of paint defects beginning with very fine checks on one side, and ending up with very large alligatoring on the other side (Figs. 4 and 5). If alligatoring takes place, it simply means that the under coat is relatively much softer than the outer coat. If checks occur it means that this difference in the hardness of coats is not so great as in the case of alligatoring, but the difference is in degree, not in kind.

In order to avoid checking and alligatoring, it is best to have the under coats as hard as is practicable, and to have these coats, relatively speaking, much harder than the outer coats. This is the practice in coach and carriage painting, where very little oil is used in the under coats, and as we know, coach and carriage painting is perhaps the best type of painting there is. Now in the case of house painting, suppose we have checking and want to avoid it, how shall we proceed? The answer is inevitable. We must so modify the under coats as to secure a hardness sufficiently greater than that to which the outer coat will attain, and then checking will be avoided. To make the under coats sufficiently hard various methods can be adopted.

The writer would now like to illustrate this matter by referring to some of his experiments. Realizing the limitations already referred to as inherent in panel tests, but still believing that they give information of possible value, he had a number of panels painted with white lead, one of which was ordinary white lead alone and others containing varying percentages of acetate of lead. Of the three photomicrographs (Figs. 6, 7 and 8), the first contains no acetate of lead, the second has 1 per cent, and the third 5 per cent. You will notice that the white lead with no acetate of lead shows very marked checking, while there is practically no checking in the case of the white lead containing 5 per cent acetate of lead. Now I must repeat that I do not consider any of these panels fairly representative of good practice. All were dried indoors, and it is fair to assume that the under coats did not reach that maturity before exposure that they would have reached if the drying had been out-of-doors. This seems to me to be a general defect with panels, the under coats of which have been dried indoors. Nevertheless these tests point in a certain direction and are evidence of the soundness of the view which I have advanced, for here clearly the acetate of lead has acted as a hardening agent on the under coats. It is true that the acetate of lead was used in the outer coat as well as in the under coats, but this does not affect the explanation we give of its action, for the hardening effect was relatively greater on the under coats than on the outer coat. These tests are neither an argument for nor against acetate of lead in white lead—they are simply evidences of the idea advanced.

There is one caution to be made against assuming that in all cases checking is an unmixed evil. I am convinced that in some cases checking is the lesser of two evils, one of which is necessary.

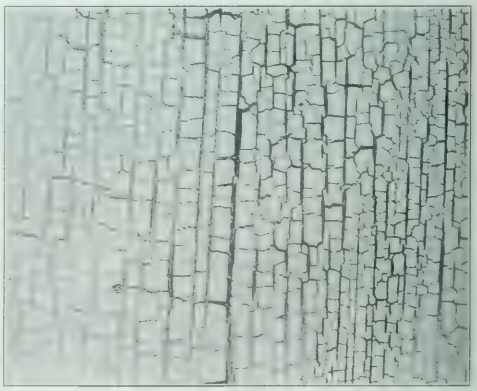


Fig. 3—White Composite Paint over Ochre Priming

You can readily imagine a paint film of so great tensile strength that it will under no circumstances check. Now with the expansion and contraction of the foundation on which such a paint film is applied trouble is apt to ensue, for if the foundation expands or contracts more than the film, the latter is sure to break loose, and the result is scaling. This indeed would be a more serious defect than checking, and the competent painter must use his judgment in some few cases as to whether he would

rather run the risk of a little checking or take the chance of a more serious trouble.

J. Cruikshank Smith, an English writer, in his little book on "Paint and Painting Defects," thinks that the terms checking and alligatoring, which he says are of American origin, are unnecessary and it would be better to describe them as cracking. Cracking, however, as the term is used here, involves parting of a paint film right through to the surface painted. He says

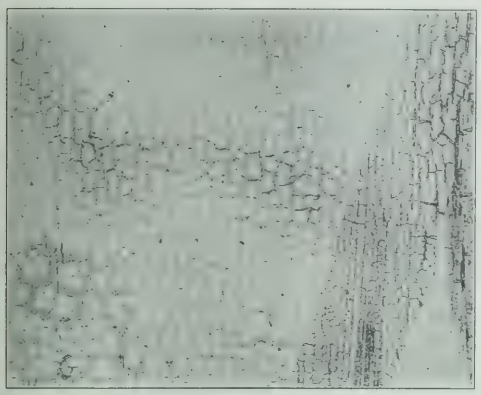


Fig. 4—Composite Paint over Oily White Lead Priming

in his book, "Very often it (cracking) is caused by the final coat being less elastic than the under coat, or again, the last coat may have set too quickly, or may have been applied before the previous coat was quite hard."

All this is in line with what we have said before, if we understand that Mr. Smith is referring to the cracking of the outside layer or layer of paint. In regard to varnish he also says: "This (cracking) is due in the main to causes similar to those which govern the cracking in paints or enamel." Speaking of graining he also says, "As a rule graining cracks on account of the graining color lacking elasticity, or because it has not been modified to suit the ground. If the color is too oily, the application of the graining color may soften the ground, and unequal expansion and contraction, as between the color and the ground, take place. Cracking will also be induced if the varnish applied over the graining color is too hard and non-elastic."

Now, understanding the causes which produce checking and alligatoring, let us see how they can be avoided, going into the matter a little more in detail. Let us direct our attention more particularly to house painting, with which the writer is more familiar. In case of three-coat work, we have first a priming coat—the main purpose of which is to fill the pores of the wood and to produce a proper foundation for subsequent coats. We have over this a body coat, whose function is to supplement the priming coat and to hide the surface painted. We have finally the finishing coat, which supplements the body coat in that it gives hiding qualities to the paint and also gives the finish that is desired. Reversing our line of thought and starting with the finishing coat, we find that the under coats are for the purpose of giving a foundation to the finishing coat. The priming coat is the first foundation layer and the body coat is the second. Considering now merely the question of checking and alligatoring, it is evident from what we have already said that the priming coat and the body coat must together give a firm foundation for the finishing coat. How shall we obtain this firm foundation? It is important to point out here that no materials should be used in the foundation coats which will not harden sufficiently or which can not be made to harden by the addition of other materials. It is hardly digressing much from the policy which the writer has adopted to specify two materials which should not be used in the foundation coats. These are those oils or organic materials which have not in themselves the power of becoming hard, such as all asphaltum, tar or bituminous materials. Furthermore, no mineral oil which is not completely volatile should be used. None of these products hardens sufficiently to give a good foundation coat. Such resinous products as rosin oil, which hardens too slowly to give good results, should not be used.

In all paints a drying oil is used. The drying oil should have in a high degree the power of being oxidized into a solid substance. Linseed oil is the principal material used by painters for this purpose, and it should have this drying quality in the highest degree. The use of linseed oil substitutes which are liable to be deficient in this respect should be carefully avoided. It is important also that those pigments which retard the drying or hardening of priming coats should not be used in excess. This refers particularly to lampblack and yellow ochre. Other pigments of a similar nature will suggest themselves. On the other hand, pigments which assist in the drying and hardening of under coats should be used as far as is practicable.

As we have said, drying oils are essential in paint, but for the prevention of checking and alligatoring no more drying oil should be used in the foundation coats than is necessary for the filling in of the pores of the priming coat and the proper binding of the particles of pigment together in the body coat. By so doing two things are accomplished: one is that the natural hardness of the coating is increased by the increase in proportion of pigment, and the other is that, less oil being used, it takes less time to bring it to a fit condition for the reception of the other coats.

Probably the most important thing to do in the avoidance of checking and alligatoring in the ordinary use of paints is to allow as much time as possible between coats. Prof. Sabin has shown

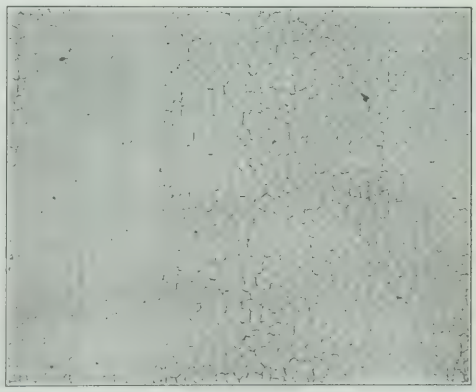


Fig. 5—Cracking and Bulging of Paint Probably Due to Excessive Contraction of the Wood

that the changes which take place in the drying of linseed oil result in the formation of certain volatile constituents, which should be given off before a paint reaches what has been called here a fit state of hardness. Just how long it is necessary to allow a paint to age between coats, it is impossible to say. If the weather is warm and dry, this state may be reached in a comparatively short time. If the weather is moist and cold, it may take a very long time. This suggests a difficulty in ob-

taining the best results in cold weather, when paint dries more slowly. The writer cannot give any time figures here, much as he would like to do so. The important matter, however, is that you should appreciate the points advanced, and with that reasoning in mind resist the tendency to hasten in the application of paint, insisting that the best results can be obtained, particularly with respect to checking and alligatoring, by allowing

FIG. 6 × 8—WHITE LEAD PAINT WITHOUT ADDITION OF ACETATE OF LEAD

ample time between coats for each coat to become thoroughly dry and hard.

CRACKING AND SCALING

It would appear that cracking and scaling are closely related, for in many cases scaling naturally follows cracking. By cracking we refer to the formation of hair-like lines on the surface, which an examination shows extend from the surface practically through the paint layer down to the foundation. In this respect cracking differs from checking or alligatoring, which are superficial, being connected with only the outer coat or coats.

In the case of cracking, the areas included by the cracks are usually relatively large, although not necessarily so. If the painted object is wood, the cracks may be at right angles to or parallel with the grain of the wood. In discussing the question of cracking and scaling in this paper we refer principally to the cracking and scaling of paint which has been applied to wood.

The fact that cracking starts sometimes at right angles to the grain of the wood and sometimes parallel with the grain of the wood indicates that it is probably due to some extent to some action of the wood itself. Wood contracts and expands with cold and heat, just as most substances do. It is doubtful, however, whether this expansion and contraction with heat is a predominating factor as affecting cracking. However, wood is a porous body containing at all times more or less free water or moisture. It has been found experimentally that, in the drying out of wood, the greatest contraction takes place at right angles to the grain. Valuable information on this subject is given in *Bulletin* **10**, U. S. Dept. of Agriculture, Division of Forestry. On page 37 it states:

"Since only an insignificant longitudinal shrinkage takes place (being commonly less than 0.1 inch per hundred), the change in volume during drying is about equal to the sum of the radial and tangential shrinkage, or twice the amount of linear shrinkage indicated in the table.

"Thus, if the linear average shrinkage of soft pine is 3 inches per hundred, the shrinkage in volume is about 6 cubic inches for each 100 cubic inches of fresh wood."

APPROXIMATE SHRINKAGE (IN INCHES) OF A BOARD, OR SET OF BOARDS, 100 INCHES WIDE, DRYING IN THE OPEN AIR

| | |
|---|---|
| (1) All light conifers (soft pine, spruce, cedar, cypress) | 3 |
| (2) Heavy conifers (hard pine, tamarack, yew) honey, locust, box elder, wood of old oaks | 4 |
| (3) Ash, elm, walnut, poplar, maple, beech, sycamore, cherry, black locust | 5 |
| (4) Basswood, birch, chestnut, horse chestnut, blue beech, young locust | 6 |
| (5) Hickory, young oak, especially red oak | Up to 10 |

The reason for this difference in contraction parallel with and across the grain in the drying out of wood is easily understood on a little consideration. The structure of wood is largely fibrous, the fibers running mostly with the grain. Free water or moisture in the wood is probably located between the fibers. This water forces the fibers apart. As the water dries out, the fibers come closer together, producing contraction across the grain. It would appear also that the variation of the amount of water in wood shows very little tendency to affect the length of the fibers, and so produce contraction and expansion parallel with the grain. It is probable that all have noticed the shrinkage of panels which usually takes place so as to expose the wood parallel with the grain, while very little wood is exposed at the ends of the panels. This drying out of wood apparently occurs even when wood has been painted or varnished, the indication being that even under these circumstances paint and varnish films are slightly permeable to moisture and moist air.

I have already referred to the fact that linseed oil on drying shrinks in volume. It would appear, however, that the shrinkage of paint films is not due simply to the shrinkage in volume of linseed oil on drying. Wherever there is a chemical reaction between the pigments of a paint film and linseed oil or any of the other paint constituents, which results in the formation of new chemical compounds, such as soaps, there is still further contraction due to the condensation which takes place with the formation of these compounds. Unfortunately we have no definite figures as to what this condensation or contraction

FIG. 7 × 8—WHITE LEAD PAINT WITH 1% ADDITION OF ACETATE OF LEAD

amounts to. It probably differs with every reacting pigment, so that some pigments will produce a large and others a slight contraction, while in the case of pigments which do not react chemically on the oil, there is probably no contraction due to this cause.

If a paint having this quality of contracting, due both to the oxidation of the oil and to the reaction of the pigment upon the

oil, is applied to a wood which contains moisture, the wood dries out and contracts across the grain, while there is very little contraction with the grain; at the same time the paint contracts both across the grain and with the grain. If the contraction of the paint equals in all respects the contraction of the wood on drying out, there should be little tendency of the paint to crack. Wood, however, as we have shown, contracts mostly

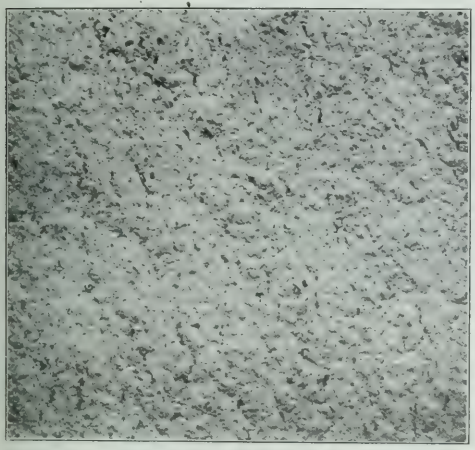


FIG. 8 × 8.—WHITE LEAD PAINT WITH 5% ADDITION OF ACETATE OF LEAD

across the grain. Consequently if the paint contracts across grain less than the wood, there will be a bulging and consequent cracking of the paint with the grain (Figs. 9 and 10). The reverse condition is also possible but not probable, that longitudinal cracks may occur due to the paint contracting more than the wood. On the other hand, the contraction of the paint with the grain may be compensated by a similar contraction of the wood, and cracks may appear, the lines of the cracking showing across the grain (Fig. 11). This is the rational explanation of cracking. It is assumed, of course, when cracking occurs, that the paint has very little elasticity, is very hard, and is high in tensile strength. The size of the spaces enclosed between the cracks is largely dependent upon the tensile strength of the paint film. If the tensile strength is high, the distance between the cracks will be greater than if the tensile strength is low.

Now what is the relation between cracking and scaling? Cracks, as we have referred to them, extend down to the wood. As soon as cracks occur, there is an opportunity for moisture to enter the wood. This moisture, entering by the cracks, travels under the paint film, exerts a pressure against the paint film, the bond between the paint film and the wood is weakened, and scaling results.

Further on in this paper blistering and peeling will be spoken of. It seems to the writer that there is a difference between peeling and scaling. Both are due to moisture forcing the paint film away from the wood. Peeling, however, is due to the presence of moisture under an unbroken paint film in the wood or back of the wood, which forces the paint away from the wood. But in the case of scaling the moisture enters through the cracks and travels under the paint film, causing the scaling.

It is to be noted that as a rule cracking and scaling take place most often when the paint film is thick. It may not occur on a first painting job, but when the work is repainted, cracking and scaling occur. The reason for this is obvious. The thicker the paint film, the stronger it is, *i. e.*, the greater its tensile strength, and it cannot conform as readily to the changes in the shape of the wood. One method of prevention, therefore, is to avoid the accumulation of paint coats upon a surface. If the surface needs repainting, as much of the old paint should be sandpapered off as is necessary, provided, of course, it is too thick, and the new coats of paint applied should be comparatively thin. This refers particularly to paints which are naturally inclined to crack and scale. It is obvious, of course, that those pigments which give hard, strong and contracting coats, should be used only in moderation. Just what moderation is, can be determined only by conditions. It is impossible for the writer to offer more definite advice than this. There are some cases, however, where the painter is in a dilemma. If he wants to prevent cracking and scaling, he can do it only by allowing a certain amount of checking. Reference has already been made to this difficulty. Hard under coats tend to prevent checking, but too hard coats generally favor cracking and scaling. Soft under coats favor checking, but tend to prevent cracking and scaling.

We must suggest also that cracking and scaling can be to some extent avoided by having the wood thoroughly dry and contracted before painting.

I wish I could explain here the scaling of paint on galvanized iron. I regret to say that all attempts at explanation have so far failed. I have found paint scaling on galvanized iron with every precaution taken to prevent it. Galvanized iron has been washed with acid, with alkalies, and with special galvanic primers, such as acetate of copper, etc., without preventing scaling. The scaling on galvanized iron is evidently due to the impossibility of securing a proper bond. It is more apt to occur with hard or thick coatings than it is with more elastic and thin coatings.

### BLISTERING AND PEELING

Blistering and peeling are due to the water in wood forcing its way through the wood to the surface, breaking the bond of the paint and forcing it away from the surface. Blistering is very apt to occur where moist painted wood is subjected to heat, such as the heat of a radiator. Sometimes the heat of the sun

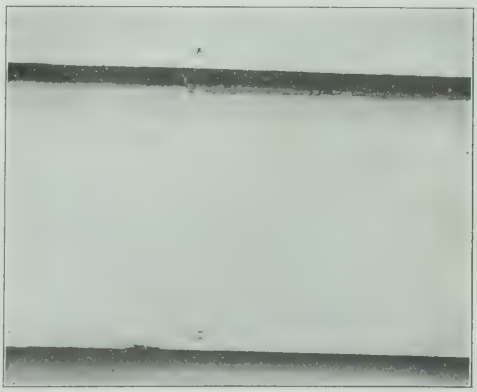


FIG. 9.—WHITE LEAD PAINT OVER OCHRE PRIMING

is sufficient to increase the vapor pressure of the water enough to produce blistering.

Blistering and peeling are more apt to occur if a very impermeable paint is used. Painters sometimes complain that boiled linseed oil favors blistering. If this is true, it can be due only to the fact that boiled linseed oil gives a more impermeable paint. If one paint tends to blister more than another under similar conditions, it is probable that the paint with the greater

tendency to blister is the more impermeable. The one safe method of preventing blistering is to remove the cause, that is, the moisture in or back of the wood. In cold weather wood may appear to be dry, and yet contain a great deal of moisture, which, on a warm day, will force its way to the surface. If one is in doubt as to the condition of wood for painting, the best practice is to allow considerable time after the priming coat

FIG. 10—A BAD CASE OF CRACKING SHOWING THE BULGING AT THE LONGITUDINAL CRACKS

has been put on before applying the body coat. It would appear in general that paint allows moisture to pass out through it to the atmosphere more than it allows moisture to pass the other way. This is probably largely due to the fact that we generally have more dry than moist weather. If a priming coat is applied in this way, it will allow the wood to dry out and to a certain extent will prevent the moisture in the wood from being increased from external causes.

The practice of applying backing paint to window frames and in general on wood apt to become moistened on the inside has for one of its objects the prevention of blistering and peeling.

Blistering on iron and steel is due to a different cause. Here it generally results from the formation of gaseous products under the paint, due perhaps to the corrosion of the iron, which forces the paint from the surface. Sometimes peeling will occur on enameled surfaces which have been painted without proper care being used to roughen the surfaces so as to produce a proper tooth. Sometimes peeling will occur when a paint has such rapid drying qualities that when applied over old work it dries before the oil in it has had a chance to soften up and combine with the old paint surface.

There is another kind of blistering and peeling, to which I refer only incidentally without attempting to explain it. Sometimes it has been found in the case of a recently painted house that after a heavy rain storm, large blisters like those shown in Fig. 12 make their appearance. These blisters are filled with water, the water being as a rule between the coats of paint. The under coats of paint are in sound condition, and it is impossible to conceive of the water having come from the back of the paint. The probabilities are that the water passed through the outer coating of paint by some system of diffusion and collected under it.

### LOSS OF GLOSS AND CHALKING

The chalking of paint is one of those problems most difficult to solve. Perhaps in one sense it should not be referred to at all in this paper. I say this for the reason that the reactions which produce chalking, so far as they have been explained by previous investigators and also by the writer, are purely theoretical. I am speaking of it, however, so that you will know that it has received proper consideration.

Chalking is connected with a loss of gloss which a paint undergoes, that is to say, the antecedent of chalking is loss of gloss. This immediately suggests that loss of gloss and chalking are produced by the same general cause. As to loss of gloss we are pretty sure of its cause. Gloss is due to an excess of oil or binding material, which, lying over the particles of pigment, gives a smooth, even, glass-like surface. The binding material in paints, whether it be linseed oil or varnish, is an organic substance—a substance composed of carbon combined with hydrogen, oxygen, etc. Such organic substances as are used for the binding material in paints are more or less unstable—they are subject to fairly rapid destruction when exposed to the influence of air, moisture, and sunlight. Loss of gloss is due to this destruction, and it would appear that the chalking of paint is but a step further in this destructive action, whereby the binding material is destroyed, and the pigment becomes loosened on the surface. It may be that in some cases this destruction of the binding material is superficially accelerated by the pigment or pigments used. However this may be, the proximate cause of chalking is connected with the destruction of the outside binding material in a coat of paint.

Our description of the phenomena of chalking would not be complete if we did not refer to another type of chalking which occurs in the case of certain pigments which are physically unstable. Such pigments appear to change under the influence of moisture from the state in which they were used into a different state, and in these circumstances are apparently dissolved out of the paint by moisture, and deposited as a film over the outside layer. I refer here particularly to the chalking which takes place in the case of basic sulfate of lead, which is a fire process pigment and seems to be peculiarly susceptible to the influence of moisture. I say nothing in derogation of this pigment and would not mention it at all if it were not necessary to make clear the nature of the chalking which occurs at times in its use. Basic sulfate of lead is one of those pigments which must be kept thoroughly dry or it will deteriorate very rapidly. We all know that sulfate of lead made by wet chemical processes has very little tinting strength. This is due to its crystalline and relatively coarse structure. It would appear that basic sulfate of lead, when treated with water, changes in structure so as to

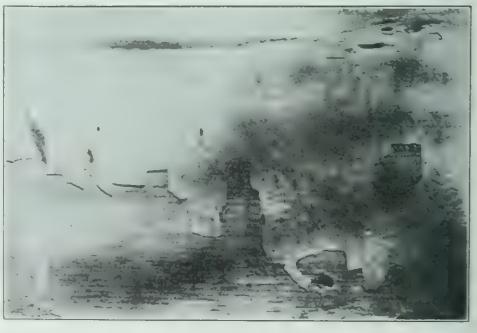


FIG. 11—A BAD CASE OF CRACKING AND CONSEQUENT SCALING THE CRACKS ACROSS THE GRAIN BEING CHARACTERISTIC

approach the characteristics of sulfate of lead prepared by the wet process. Also that basic sulfate of lead when used in paint is soluble to such an extent that it becomes changed physically and is dissolved and deposited in its changed form on the surface of the paint. Such a change may or may not happen along with the decomposition of the oil on the surface, such as takes place in the case of ordinary loss of gloss and chalking. It is very

often found, however, with basic sulfate of lead paints, that if the fine bloom, which shows more strikingly in tinted paints, is removed, the paint is in excellent condition underneath.

Another phase of this question should also be considered. If an elastic paint chalks, it may be that the particles of loosened pigment will be held loosely on the surface, and not be washed

FIG. 12—BLISTERING ON TOP COAT ONLY. THE BLISTERS ARE FULL OF WATER

away by rain to as great an extent as would occur in the case of less elastic paints.

Whatever the cause of chalking may be, it is objectionable principally because of the tendency of the pigment to come off when touched. There is no question but that it is objectionable from this standpoint. There is another point, however, which must not be overlooked. Paint decay is of many kinds, and one of these many kinds is inevitable. The experience of the users of paint points to the conclusion that most painting jobs will not last in good condition longer than three or four years. This being so, a certain amount of chalking, that is, loss in thickness of coating, is the least objectionable form of decay; for if this loss in thickness does not occur, the result on continued repainting will be the production of so thick a coat of paint that scaling is apt to follow. The fact already mentioned, that scaling is more apt to occur with thick layers of paint than with thin, is well verified by experience. Chalking, as it ordinarily occurs, has this further redeeming quality: it nearly always leaves on the surface a roughness, usually called a tooth, which is favorable to repainting.

For the prevention of chalking and loss of gloss, to the extent that this is desirable, we can offer only qualified suggestions. It is evident that what is desired is a vehicle which can be used on the surface of paints that will be less destructible than that ordinarily used. I regret that there is no such material that can be unqualifiedly recommended. I am quite sure that a linseed oil which has been bodied by blowing or real boiling would help in this respect, but here again another danger confronts us. Such an oil, to be satisfactory, should dry sufficiently hard so that it will not be inclined to absorb dirt. The writer remembers using such an oil a number of years ago, with great expectations, but while the oil was less destructible, it remained so soft that dirt readily attached itself to the surface. Sometimes varnish is used in a finishing coat, but so far as I know, this has not prevented loss of gloss or chalking. All that can be said, therefore, is, that if chalking is a defect, it is not an unmitigated evil. Nor is it one that can be readily avoided without other more serious defects arising. You will observe here that I say this with full regard for the plan adopted, that I am not discussing any farther than is necessary for the purpose of this paper, how defects may be corrected by changing the materials used.

### WASHING

The washing of paint is characterized by the surface of the paint giving up certain water-soluble substances. This is noted in the following ways: The surface, when moistened, rubs up like soap: there is a collection of washed down pigment at the footings of columns and similar conspicuous places; there are also noted on the ceilings of porches brown spots consisting of substances which have been dissolved out of the paint by moisture, and when the moisture evaporated, these spots are left, like miniature stalactites or pimples. Apparently washing takes place when a paint contains water-soluble compounds or when water-soluble compounds are formed either through a reaction of the constituents of the air upon the pigment or a reaction between the pigment and the binding material. Usually a surface that shows washing is found to be in excellent condition underneath. Washing very seldom takes place until loss of gloss occurs. Sometimes, as in the case shown in Fig. 13, the dissolved material will run down near to the edge of a clapboard and on evaporating there leave a water mark or stain just above the edge.

Washing is less common in the country than it is in large cities, probably due to the greater quantity of sulfur gases present in the urban atmosphere.

For the prevention of washing, omitting any reference to the avoidance of the use of those pigments most inclined to wash, the only thing that I can recommend is what I have already recommended in the case of chalking. As washing does not occur to any appreciable extent until the gloss of the paint has disappeared, the best method of prevention is to be found in such steps as can be taken to preserve the gloss as long as possible. Washing is apt to give the surface an unsightly and streaked condition, which can usually be quite readily corrected by the application of clean water.

### DISCOLORATION

The discoloration of paint is a very large subject, and can be handled in this paper only to a limited extent. We shall not discuss the changes in color of pigments, which are more or less directly connected with the pigment used, such as the natural tendency of yellow and red paints to darken or certain blue paints to fade. These are mostly due to internal changes in the pigment itself. Our subject divides itself naturally into the following heads: spotting, such as when tints turn white in spots, and the discolorations due to yellowing out of doors; yellowing indoors; dirt; mildew; and sulfur compounds.

SPOTTING—In the spotting of paint, the following characteristics are to be noted. The spots, which may be small or large, are much lighter in color than the remainder of the paint. Such

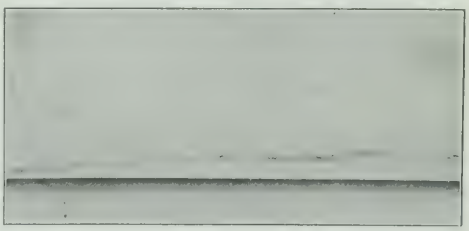


FIG. 13 SHOWING THE WATER MARK DUE TO WASHING NEAR THE LOWER EDGE OF THE BOARD

spots show greater chalking than the body of the paint. Moistened with linseed oil, the spots return to practically the original color of the paint, indicating that there has been no destruction of the tinting material, and indicating also that at these spots there had been some excessive destruction or loss of the oil which was originally present. Spots are very apt to appear along the

edges of cracks in wood. Sometimes they appear over and around putty, indicating the location of nail holes.

The explanation which I would offer as to the most common cause of spotting is that at the points where spotting occurs, the wood was not completely filled by the priming or body coats. Spotting occurs earlier in two-coat work than in three-coat work. It would appear that although a paint may be thoroughly dry, if portions of the surface painted are not fully satisfied by the priming coat, some of the oil in the subsequent coats may be absorbed by these spots. It may be also that in such a case there is a more rapid internal oxidation and destruction of the oil due to the excess of air under and back of the spotted places. Whatever the exact features of the cause may be, the remedy is clear. Spotting is to be avoided by the proper filling of the pores of the wood, and by allowing sufficient time between coats for weaknesses to develop that can be corrected by subsequent coats. Spotting will be avoided to some extent by the competent workman using a stiff brush for the under coats, thereby forcing the paint into the wood.

There is another kind of spotting due to the spattering of lime on wood before it is painted. The lime spots work through the paint and by destroying the oil show on the outer surface.

THE YELLOWING OF PAINT OUT OF DOORS applies mostly to white paint. The term yellowing is a sufficient description of what takes place. There are two known causes of this kind of yellowing: the presence of heavy mineral oil, or of alkalies or alkaline materials. That due to heavy mineral oil appears as follows: a mixture of linseed oil and mineral oil if exposed to the air in thin layers soon becomes clouded, due to the oxidation of the linseed oil and its separation from the mineral oil. The mineral oil remains practically unchanged. If used in all coats of paint on wood, it exerts a solvent action upon the wood painted, bringing to the surface the gums and other soluble organic material present. Mineral oil itself yellows on oxidation.

Linseed oil soap, which is formed by the action of alkalies upon linseed oil, tends to become a very dark orange on exposure to the air. Linseed oil of itself tends to bleach out during oxidation and becomes more nearly white. Hence, if alkalies are present the oil becomes very much darker, and paint, in which the pigment is surrounded by an oil which has undergone such a change, will appear yellow.

The prevention of the yellowing of paint out of doors, in so far as it is caused in these two ways, is by the avoidance of the use of heavy non-volatile mineral oils in paints, and also the avoidance of the presence of alkaline materials such as form soluble soaps with linseed oil, *i. e.*, soda ash, borax, silicate of soda, etc.

YELLOWING INDOORS—The discoloration of paint due to yellowing indoors is a common phenomenon. It has the following characteristics: the yellowing takes place in the dark, and if the object painted can be exposed to the sunlight, the yellowing disappears. In the case of tints, they are changed from the color originally applied. Blue becomes green, and red, if not too deep, an orange, etc. The cause of the yellowing of paint indoors is variously explained, but the one explanation which seems most satisfactory is this: ammonia is more or less present in the atmosphere and turns white paint yellow. Ammonia is an alkali, and this action of ammonia is similar to the action of the fixed alkalies referred to in the yellowing of paint outdoors. Ammonia may be used in manufacturing establishments, where yellowing occurs, as in the case of ice-plants. It may be used for cleaning purposes around the premises painted. It may even be generated from the glue size applied to plaster walls, which have not sufficiently matured. It is well known that glue, which is a nitrogenous body, under some conditions gives off ammonia in the presence of alkalies and alkaline earths. Gloss paints are more apt to yellow than flat paints. Linseed oil yellows more than poppy oil. It would appear that the yellowing of linseed oil, as affected by the pigment used, depends more upon the degree to which the oil is exposed to the action of the atmosphere. The pigment protects the oil more in some cases than in others. The more impermeable paint is less affected by ammonia. A thin coating of varnish over a paint or a little varnish in a final coat will often prevent serious yellowing. The prevention of yellowing therefore is all summed up in these words: have good ventilation, good light, avoid the presence of excessive quantities of ammonia in the atmosphere, and protect the paint as far as practicable by varnish coatings wherever such treatment is necessary.

DIRT—This kind of discoloration of paint, especially white or nearly white paint, is one for which the painter sometimes feels justified in claiming he is not to blame, since dirt comes from outside sources over which he has no control. This attitude is perfectly proper up to a certain point. There still remains the fact, however, that paint will sometimes become dirty more rapidly than exterior conditions would seem to warrant, and to this extent it is a fault of the paint. The dirt, which may accumulate on and stick fast to the paint, comes from smoke, ordinary street dirt, the organic matter from growing plants, such as pollen, and the organic matter from decaying plants. Dirt can be carried great distances by the wind. Discoloration of this kind will occur sometimes in the most inaccessible places. Dirt will collect on roofs, and in the case of storms may be washed down over paint and become attached to it. The examination of paint at very high altitudes greatly removed from smoky chimneys may still show a deposit of smoke and coal dust. The quantity of pollen that is liberated from trees, grasses and many flowering plants is enormous. The fertilization of the seed is dependent upon the wind carrying the pollen and distributing it so that perhaps one particle of pollen in one hundred million is actually serviceable, while the remainder is scattered in all directions. A great deal of this pollen is sticky on its surface. Under the microscope it is shown to possess various forms usually more or less spherical. Decayed pollen massed together appears black, although under the microscope it is observed to be quite translucent and yellow. The conditions favorable to dirt becoming attached to paint are softness and elasticity, conditions which the painter naturally thinks are the best for the paint. Fresh paint is more apt to become discolored by dirt than old paint, simply because fresh paint is more elastic and stickier. After a rain nearly all paint becomes softer than it was before the rain. Under such circumstances, if conditions are favorable, as in the case of the quick drying up of the soil, dirt from roads, etc., may be blown against the paint and remain attached. Some have attributed the increased tendency of paint to become discolored to the increased use of the automobile, which raises clouds of dust on dry days

The obvious method of the prevention of the discoloration of paint is the use of harder coats, obtained either by cutting down the amount of oil in the paint, or by the use of those pigments which tend to harden the paint. The practical painter must choose between these methods. If by adopting the practice of working towards hard coats of paint he prevents discoloration, he may run into the trouble of cracking and scaling.

A curious instance of the discoloration of paint has been brought to our attention in New Orleans. There they are troubled a great deal with mildew to which reference will be made later, but in addition to this they are troubled a great deal with the dirtying of paint due to dust. New Orleans, within the last ten years, has introduced a system of drainage which has resulted in the earth becoming very much drier than it used to be. During the dry season the soil is dry to a greater depth than formerly. Experiments conducted at New Orleans indicate that the quality of the linseed oil used there affects considerably the tendency of paint to become discolored both from mildew and from dirt. It is found, for instance, that La Plata linseed oil, when used in paint in New Orleans, oc-

casions the discoloration of the paint more than North American linseed oil. This is clearly due to the fact that North American oil when used in paint gives a harder coating than does La Plata oil. La Plata oil has a lower iodine absorption, and it would appear fairly conclusive that only the best quality of linseed oil should be used there and in similar places, and furthermore that all linseed oil substitutes made from the semi-drying or non-drying oils should be avoided.

MILDEW—Discoloration of paint on account of mildew is rather uncommon in the North, but is fairly common in the South. Mildew is a fungoid organism propagated by fine spores, which when they develop form a fine network of threads; these threads while black to the eye are more or less transparent under the microscope. It would appear that in some cases mildew exists in the wood itself before painting. In other cases its filaments may penetrate the paint and enter into the wood. The ordinary pigments used do not seem materially to prevent the growth of mildew. It would appear that mildew grows better in elastic paints than it does in hard paints, and that moisture and shade are favorable to its growth. Experiments indicate that mildew is killed by the presence of very small quantities of mercury compounds and that a minute percentage of mercurous chloride added to paint will prevent mildew.

SULFUR COMPOUNDS—Discoloration due to the presence of sulfur compounds occurs with those paints containing lead pigments. It appears as a brownish or grayish metallic continuous film over the surface of the paint, which film is sulfide of lead and may be readily destroyed by peroxide of hydrogen. Sometimes this discoloration is due to the intentional or accidental presence in a paint of small amounts of sulfides of the other metals, particularly sulfide of zinc, which may be contained in lithopone to the extent of 30 per cent. The frequent and common use of lithopone in recent years has led to a number of cases where lithopone has been used accidentally with lead paints with resulting discoloration. It is possible that the presence of lithopone in such cases may come from the use of pails for lead paints, which pails had previously contained lithopone. Sulfide of zinc in lithopone does not always react with lead pigments to produce sulfide of lead. The danger of such a reaction taking place is, however, so great that extreme caution should be used against it. In moist places lithopone is more apt to react on lead compounds than in dry places.

The discoloration of lead compounds due to sulfur compounds in the air is not as common as one would be inclined to believe from what has been said upon the subject. The only chemical compound in the air which will produce sulfide of lead is sulfuretted hydrogen, which is given off from manure and sewage, and is sometimes found around coal mines and oil wells. Discoloration produced from sulfuretted hydrogen in the air is not usually permanent. Very frequently it will appear in a dry season and then will entirely disappear after a good rain storm. This is due to the fact that sulfide of lead is rather unstable and tends to oxidize to sulfate of lead.

There are indeed considerable amounts of sulfur compounds in the air of cities and around factories. That most commonly in the air is, however, sulfurous acid, which does not react upon the lead to produce sulfide of lead. Sulfuric acid is also present. Sulfurous acid reacts on lead to form a white insoluble sulfite of lead, which probably oxidizes under favorable conditions to sulfate of lead, also white. The action of sulfurous acids on lead compounds forming sulfite of lead is paralleled by a similar action upon other pigments to form sulfites, as in the case of the formation of zinc sulfite which readily oxidizes to zinc sulfate, to the formation of which the washing of zinc paints is largely due. Sulfuric acid in the atmosphere forms sulfate of zinc directly.

The presence of sulfur compounds in the air is generally objectionable, and in most cities endeavor is being made to prevent this annoying condition. This is being done by improved sewage systems, high chimneys, and central power plants, as well as by the introduction of hydro-electric power, which avoids the burning of coal. Sulfurous and sulfuric acids are especially active in the corrosion of metals, and those pigments which tend to fix them, that is, form insoluble compounds with them, are in this respect best for the preservation of metals.

There is only one method of preventing the discoloration of paints by the action of sulfur compounds in the air; that is, to prevent the presence of such compounds, for the number of lead pigments which it is necessary for the painter to use is so great that it would seem impossible effectively to prevent discoloration in any other way.

### OTHER DEFECTS

There are other defects, which could be touched upon in this paper, but it is already so long, and the main defects have been so completely treated that the writer hardly feels justified in extending its length.

### CONCLUSION

The main purpose of this paper has been to consider the question of paint defects without reference, except to a minor extent, to the nature of the materials used. The writer has deliberately taken an attitude of mind which he acknowledges is not a perfect attitude. He admits that the materials used must be considered in the study of paint defects. At the same time as there has been so much attention given to the question of the effect of materials upon paint defects, with a neglect of the treatment of the subject followed in this paper, it has been deemed necessary to investigate exclusively the other side of the question, in order to more evenly balance the arguments upon the subject. The tendency to connect paint defects with materials has been too great. This paper will serve to some extent to counteract this tendency.

The practice of connecting paint defects exclusively with materials is a destructive practice. Our plan in this paper has been to present a constructive program. No paint material is perfect, but if it is to be commercially judged in comparison with other paint materials, it should be judged at its best and not at its worst. It is the hope of the writer that some time in the future a new spirit will enter into the discussion of paint materials and that it will be the endeavor of all paint students to find the best way to use paint materials, and that if a paint material is in any way defective, to find out how that defect can best be corrected.

129 YORK STREET, BROOKLYN

## FELDSPAR AS A POSSIBLE SOURCE OF AMERICAN POTASH[1]

By A. S. CUSHMAN AND G. W. COGGESHALL

Two years ago the authors presented a paper before the Eighth International Congress of Applied Chemistry, entitled "The Production of Available Potash from the Natural Silicates." This paper, which was printed in the *Transactions* of this Institute, Vol. V, 1912, not only presented a general discussion of the work that had been done by a great number of investigators in this field, but also described the results of practical mill runs made by the authors on the large scale of operation. This work had been carried to a successful conclusion as far as the purely chemical engineering side of the problem was concerned, but for reasons which seemed important at that time, no presentation or analysis of cost data was included in the first publication.

As a rule, no worker is in general so much hampered by complex commercial situations in his particular field as the chemical engineer, and this is particularly true with respect to potash

[1] Presented before the 7th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 2 to 5, 1914.

problems which rest more or less insecurely upon a network of local, national and international regulations, economics, and special arrangements. The prices of crude and finished potashes have not in the past rested on the firm basis of cost of production and transportation, modified by the just law of supply and demand, but have been subject to unstable arrangements between national governments and international syndicates. The governments of great nations make bad partners for industrial enterprises in these uncertain days, for they themselves seem to be unable to guarantee the validity of their own contractural agreements. Furthermore, the fixing of prices of a necessity of industry and agriculture by international or national syndicates, by which the interest of the ultimate consumer cannot be a prime consideration, is utterly opposed to the present-day tendency in the development of human affairs.

It is one thing to work out a complicated problem in chemical engineering to a successful technical working status on an encouraging basis of costs, but it is quite another thing to assume the responsibility of inducing capital to embark upon an unknown sea of enterprise, especially if this sea is strewn with uncharted rocks and shoals, one, at least, of which may represent the cutting of prices by foreign producers to or below the cost of production for a sufficient period to kill off new-born competition, with the idea of averaging up profits at some future time when the infant industry shall have been effectually strangled. As chemical engineers, however, we may take some comfort for the future from the thought that such premeditated arrangements are becoming unfashionable if not dangerous.

It is the purpose of this second paper, which may be considered an elaboration of our earlier publication, to present the results of some additional investigation, together with a frank discussion of the cost data involved in the possibility of using American feldspars as a practical source of American potashes. Many workers in this field believe it to be a self-evident fact that the potash alone would not pay the cost of extraction, or, in other words, unless the potash yield was merely a by-product recovery in the manufacture of some valuable main product, the attempt to extract it would be foredoomed to failure. After having made a close study of certain phases of this problem, continuing over a period of many years, we wish to state that in our opinion the economic feasibility of turning to the feldspars as a source of potash is, to say the least, open to debate.

Feldspar, which will run quarry-wise 10 per cent in potash ($K_2O$), can be obtained in unlimited quantity favorably situated to our freight and trade routes in this country. The raw material supply, as far as potash ore is concerned, resolves itself, therefore, into a mere question of economical quarrying operations at the usual well-known costs. A comparatively small quarry of such feldspar, containing 1,000,000 cu. ft. of rock or 100 feet in cube, would contain 17,000,000 lbs. of potash, $K_2O$, which, if it could be extracted, would be worth even at ante-bellum prices, $700,000. One ton of such an ore would contain 200 lbs. of potash, worth, if it could all be extracted, about $7. If we assume, however, that only 75 per cent of it would yield to a chemical engineering process, we still have $5 per ton in value to work for. When we remember that in large scale operations in the gold mining industries, quartz that carries no more than $2.00 per ton in valuable constituents has been profitably worked, the problem need not necessarily frighten us away at the outset.

### IMPORTS OF POTASH SALTS

During the fiscal year ending June 30, 1914, there was imported into the United States $15,000,000 worth of potash salts, kainit, manure salts, muriate of potash, and sulfate of potash. In addition to this, considerable quantities of caustic and carbonate of potash, not included in the later available statistics, were also imported. Of the total, $8,000,000 worth was muriate of potash. The fertilizer industry uses, of course, the larger proportion of these potash importations, the percentage in the last few years being about 85 per cent of the total of muriate of potash imported, there being left about $1,000,000 worth of muriate of potash which was used in industrial work. About half of this total was used to make caustic potash and carbonate of potash; these are used principally in the soap industries, although a portion is used as a wrapper tobacco fertilizer and in the manufacture of glass, paper, preparation of colors, in printing, in photography, and in more strictly chemical industries. Some nitrate of potash is manufactured from the chloride. About one-eighth of the muriate is manufactured into chlorate of potash at present, which is largely used in the growing safety-match industry. Potassium bichromate uses about 5 per cent of the muriate and this is used in textile and color industries; also in photography.

Before proceeding with an analysis of cost data involved in the possible use of feldspar as a potash ore, it will be well to consider briefly the present sources of the world's supply. The German mines, located principally in the neighborhood of Stassfurt and Magdeburg in Prussian Saxony, have been for the past seventy years the principal source of the world production of the various potassium salts. Professor O. N. Witt, in an article in the *Chemiker Zeitung* of Oct. 8, 1914, states that borings in Alsace have shown favorable deposits which may prove to be of considerable value. This is interesting news in view of the present doubt as to the future political status of Alsace-Lorraine. The reported discovery of soluble potassium salts in the province of Catalana, Spain, has recently commanded considerable attention and was prominently mentioned in the last annual report of one of our large agricultural chemical companies. According to our latest consular reports under date of Nov. 6, 1914, potash has not been extracted in Spain up to the present time in commercial quantities.[1] If the Spanish prospects should develop so that they would become a basis of a world trade, they would be welcomed for breaking an existing monopoly, but the source of supply would still be over-sea, whereas North American independence in the commodity is highly desirable.

An American source of potassium salts in any considerable or practical quantity, in spite of much expensive government and private exploration, has not yet been discovered. In the Far West the giant kelps of the Pacific coast, some of the brines and bitterns of the saline lakes and wells, and the alunite deposits of Utah and Arizona have been proposed and studied as possible sources of potassium compounds. The fact remains, however, that up to the present time three-quarters of all the potassium salts used in agriculture are consumed east of the Allegheny Mountains, by far the greatest quantity going into the three States of North and South Carolina and Georgia.

The reasons for this segregated demand for potash fertilizers are not at once apparent. The authors have made inquiries and have received the following explanations: Cotton, tobacco, intensive orcharding and truck farming use the largest quantities of artificial fertilizer, while, in addition to this, the educational propaganda of a large southern agricultural chemical company has demonstrated in its more immediate territory the economy of the proper additions of fertilizer to the land. The great effort which is now being made throughout the country to bring up the yield per acre of all our crops, will in all probability largely increase the use of all fertilizing materials not excepting potash.

It is unlikely that even the Panama Canal under the present tolls system would enable western potashes to meet European competition on the Eastern seaboard. The fact that the great feldspar dykes of the Appalachian system are in general located

[1] Consul-General Carl Hurst's Report in *Daily Consular & Trade Reports*, Dept. of Commerce, No. 261, 615.

in close proximity to the places where potassium salts are in the greatest demand makes a special appeal to the chemical engineer. That the growing use for potassium compounds in intensive agriculture and industry will some day make use of the huge quantity locked up in the silicates, seems a safe prophecy. Whether that time has yet arrived is now open to debate.

### AUTHORS' PROCESS

In this paper, the authors will confine themselves to a discussion of their own methods and chemical engineering experience. There is no intention to ignore the fact that other workers have also proposed or to some extent developed methods for extracting potash from feldspar, either with or without the simultaneous production of valuable by-products. With any or all such methods the authors are not in conflict nor debate, the present object being merely to open the subject to discussion along a well-known line. If any other source or method of economically producing American potash is discovered, the authors will follow its development with much interest.

Our previous paper described the working of the process by which the insoluble potash in the feldspar rock was simply converted into the soluble chloride salt, but no separation of this soluble salt from the residual rock was made. The product contained about 4.5 per cent water-soluble potash ($K_2O$) in the form of 7.1 per cent of muriate of potash (KCl), also about 16 per cent of free lime, and the balance was the insoluble mineral material. It was solely a potash-lime fertilizer.

Several hundred tons were produced in regular mill working, and 24-hour-a-day runs were made, so that the feasibility of producing this material continuously and regularly was fully demonstrated.

This fertilizer was distributed free of all charges to some score or more of state experiment stations and large growers in many states for field trials as a straight potash-lime fertilizer to be compared with other potash fertilizers such as wood ashes and various mixtures. The field results were very favorable, as was to be expected from a material of this composition.

As will be shown later, the cost of production of such a potash fertilizer was low but the added expense of freight charges on a material containing so much inert matter was a serious drawback.

Muriate of potash is the chief potash salt imported into this country. It is sold on the basis of "80 per cent muriate" and usually contains from 70 to 80 per cent KCl, or from 44 to 50 per cent $K_2O$. This material, having its values in such a small bulk, will bear the cost of freight shipment easily. It is the cheapest potash salt for use as a raw material for chemical manufacturing, and is also well adapted for mixing into general commercial fertilizers. Any potash salt, however, running not less than 17 per cent $K_2O$ (or 26 per cent KCl) is adapted for use in mixed fertilizers. A salt lower than 17 per cent $K_2O$ could be used only where the final $K_2O$ content in the complete fertilizer was to be less than 5 per cent.

Therefore, for the uses of the fertilizer industry, the economical production of any material containing 26 per cent, or higher, of KCl, would find large use, but for the replacement of all or a portion of the $1,000,000 worth of concentrated muriate salts used yearly in the United States for chemical manufacturing, it is necessary to produce a salt containing at least about 70 per cent KCl.

Our experimental work was continued with the idea of separating and concentrating the soluble potash salts unlocked by this process, and giving a product so concentrated and pure that it may be used either in making fertilizers or be worked up into other potash compounds for more strictly chemical uses.

The salts are easily leached out from the mass as it comes from the furnaces, and by proper methods a solution of about 10 per cent KCl can be obtained, using the wash liquors for leaching new material. The evaporation of large amounts of water is a serious problem in chemical industry and in this particular case it could not be accomplished cheaply by any of the usual methods of evaporation.

The engineers working on this problem, however, have had considerable experience with methods of evaporation by the direct use of hot waste stack gases. A Porion evaporator, using such gases, is an extremely cheap method of evaporation with furnace gases, provided the material in solution is not harmed by the gases themselves. Even cheaper than this is the method of spraying the liquor through the waste hot gases. Experience with this operation had developed such successful results that it was adopted for this particular work. This use of the hot kiln gases, otherwise wasted, has an added advantage in the potash process from the fact that any volatilized KCl is caught at the stack washer.

The chief technical difficulty in the conversion to KCl was due to the high temperature produced by the powdered coal flame. When the charge, moving down the kiln, is brought up to about 1050° C. the reaction is complete and there is then present in the charge free KCl. If the material is then further heated beyond 1150° C., some of the KCl is volatilized and passes as vapor toward the stack. This final overheating of the charge, and the volatilization of KCl, may be prevented by the use of a rotating combustion chamber attached to the lower end of the kiln, the charge passing outside of the extremely hot zone which is inside the combustion chamber. This arrangement prevents all overheating and is so effective that coal itself is dried by this means, in a rotary drier, with heat from burning powdered coal, the hot zone being confined to the combustion chamber rotating with the kiln. Small burners must be used in such cases, however, and in this potash work it is better to overheat than underheat the charge to obtain the full yield of soluble product. In the mill work described in our previous paper, when no rotating combustion chamber was used, about 16 per cent of the KCl was volatilized during its passage through the hot zone of the kiln. This is now all caught in the stack-washer.

### CONCENTRATED POTASSIUM SALTS FROM FELDSPAR

The complete process for the final production from feldspar of potassium chloride salts similar to the concentrated muriates imported from Europe, is outlined below.

A mixture of ground feldspar, containing about 10 per cent of $K_2O$, and burned limestone, is formed into rounded aggregates or "clumps" about $1/4$ inch in diameter, by the device already employed, using a solution of calcium chloride for this purpose. Calcium chloride is the by-product of the ammonia-soda alkali process and is the reactive agent in unlocking the potash from the silica. Mixtures of powdered rock and dry calcium chloride are almost impossible to make, due to the attraction of the chloride for moisture. Moreover, simple mixing of two materials in the form of fine powders does not give an intimate enough contact of the reacting particles to produce good yields in furnacing operations in which neither of the particles is melted, so as to "wet" the other. In this particular case it was found that a certain proportion of burned lime mixed with the powdered feldspar will unite with $CaCl_2$ from a solution sprinkled on the powder, to form an oxychloride compound which cements the whole powder into aggregates, giving such a very intimate union of the particles that when heated the reaction yields are high. These aggregates or "clumps" pass directly into the rotary kiln heated either by oil or powdered coal flame. The clumps fall out of the kiln in the same form in which they entered it, but the potash has been converted from the insoluble form into the water-soluble muriate. These red-hot clumps fall into water in leaching vats, where the potassium chloride goes into solution. Several of these leaching vats

are used so that the solution of the salt, the leaching, washing, etc., is continually performed. The strong solutions are pumped to the evaporators. The weaker wash liquors are used as leaching liquids for a new lot of processed clumps. The strong liquor containing roughly 10 per cent of KCl will be continuously sprayed down through the hot gases passing out of the kilns to the stacks. This operation is well known and has been studied particularly by our engineers.

The bulk of the water in these solutions is thus evaporated and only very concentrated solutions or sludges are allowed to pass out. These very strong hot liquors are finally dried out in a rotary drier placed at the head of the lime-burning kiln, using its hot waste gases. The crusts formed are then ground for the market.

The concentrated solution before complete drying contains a small proportion of sodium chloride, corresponding in amount to the proportion of $Na_2O$ in the original feldspar. On a spar running 10 per cent $K_2O$, the $Na_2O$ content has averaged from 1.5 to 2.0 per cent. This would give from the liquors completely dried at once, without any fractional separation of the NaCl, a product having about the following composition: KCl 70 to 80 per cent, NaCl 14 to 16 per cent, and the balance a very small amount of lime salts and moisture.

To compare this initial product with imported German muriates, we give the following analyses upon which such salts are usually bought in this country:

| Percentages | 70/75 muriate | 80/85 muriate |
|---|---|---|
| KCl | 72.5 | 83.5 |
| $K_2SO_4$ | 1.2 | ... |
| $MgSO_4$ | 0.8 | 0.4 |
| $MgCl_2$ | 0.6 | 0.3 |
| NaCl | 21.2 | 14.5 |
| $CaSO_4$ | 0.2 | ... |
| Insoluble | 0.5 | 0.2 |
| Water | 2.5 | 1.1 |
| | 100.0 | 100.0 |

It is thus seen that without any attempt at fractional separation, muriate of potash may be made from our American feldspars, equal in character to the usual imported muriates, and that they are as well adapted to be used in commercial mixed fertilizers as those imported.

If the hot concentrated liquors are not at once brought to dryness but are given a fractional crystallization treatment, which may be made a continuous operation, whereby most of the NaCl is removed, the KCl crystals then obtained will run pure enough to enable their direct use in the manufacture of chemicals of a high grade of purity. It may be noted that the purchasing analysis of German "90/95 per cent muriates" runs KCl 91.7 per cent and NaCl 7.1 per cent.

## COSTS OF PRODUCTION

However interesting a workable process may be, it must, in order to be successful, produce the final product at a cost less than that of the same material obtained elsewhere. The costs of producing muriate of potash by this process will now be considered somewhat in detail, as we wish to present this subject for the careful consideration of engineers and manufacturing interests in this country.

The plant required is equipped in a general way similarly to a Portland cement mill. There must be rock hoists, trackage, crushers, rolls, rock driers, grinding mills, a rotary lime burner, the "clumpers" and rotary kilns, coal drier and grinder, besides bins, elevators and conveyors, also leaching vats, tanks for strong liquors and for wash water, pumps, flue arrangements at stack for spraying the liquors, driers and pulverizer, also air compressor and general power plant, stairs, ladders, handrails, and buildings to house the plant.

PLANT COSTS AND ANNUAL CHARGES—In order to get the best idea of the various costs, we shall take a concrete example of a plant large enough to handle 300 tons of feldspar per day of 24 hours, this plant being a good-sized commercial undertaking. Such a plant will require three rotary kilns each 100 ft. long and from 7 ft. to 8 ft. in diameter. We may conveniently divide the plant costs into two parts: I—Those for equipment usually present in Portland cement mills. II—Those for special equipment and rearrangements necessary to carry out these potash processes.

I—CEMENT MILL EQUIPMENT

| | |
|---|---|
| Quarry hoists, trackage, cars and tools | $ 4,000 |
| Crushers, rolls, grinding mills | 17,140 |
| Rock driers | 4,600 |
| (3) kilns 7 ft. diam. × 100 ft. (to 125 ft.) long | 24,000 |
| Air compressor and piping | 2,000 |
| Power plant | 20,000 |
| Buildings, stairways, handrails, etc. | 16,000 |
| Miscellaneous equipment 14 per cent | 12,260 |
| Total | $100,000 |

II—SPECIAL EQUIPMENT AND REARRANGEMENTS

| | |
|---|---|
| Belt conveyors | $ 850 |
| Screw conveyors | 1,350 |
| Elevators | 4,300 |
| Feeders | 600 |
| Chutes and gates | 1,140 |
| Bins for dry operations and $CaCl_2$ | 7,000 |
| Lime kiln and burner | 5,000 |
| Oil or coal bins and incidentals | 1,000 |
| Clumpers (3) | 5,000 |
| Leaching, wash tanks and supports | 18,400 |
| Stack alterations and spraying apparatus | 1,800 |
| Liquor drier and stack | 2,800 |
| Stack base | 400 |
| Disposal system (sludge) | 1,000 |
| Pumps and solution piping | 3,500 |
| Line shafting, pulleys and foundations | 700 |
| Miscellaneous foundations | 250 |
| Miscellaneous walkways, etc. | 600 |
| Contingencies | 7,810 |
| | $63,300 |
| Superintendence, etc. | 6,500 |
| TOTAL | $70,000 |

Now, if 5 per cent interest and 7 per cent depreciation is figured on the first item of $100,000, the yearly fixed charge is $12,000. It may be possible to lease a cement mill with this equipment for this amount per year, and, if production was desired rather quickly, such a procedure would recommend itself. If the annual charge on this investment is then taken as $12,000 and there is added to it 5 per cent interest and 10 per cent depreciation on the cost of the special equipment, $10,500 we have as the annual charges to plant investment $22,500, or $64.30 per day.

RAW MATERIAL AND COSTS—We think there is a quite general misunderstanding as to the cost of the feldspar for this use. The only considerable use at present for feldspar is for the production of white china and porcelain ware, and for this purpose it must be free from iron-bearing minerals, such as biotite, garnet, hornblende, tourmaline, etc., so that it will burn white. Therefore, all the feldspar that is put upon the market must be hand-picked and iron-free, and for such material the prices run from $3.00 to $5.00 a ton. For the purpose of producing potash salts from feldspar, it is not at all necessary that the raw feldspar be free from iron. In fact, this process should rightly be called a process for producing potash salts from "feldspathic rock" instead of from "feldspar." Feldspathic rock underlies a large portion of the Appalachian system. Feldspar, free from iron, is a special mineral, occurring in dykes of high purity.

For the purpose of this business, what are now called "feldspar properties" would not necessarily come into consideration at all. The procedure would be to buy by the acre certain lands well located for the purpose and get the feldspathic rock out by open-quarrying operations, the costs of which are low and are quite well known. Limestone is quarried rough for about 20 cents per ton and cement rock is quarried in the Lehigh district for about the same cost. We have figured the cost at 50 cents per ton, and have allowed an equal amount for freight, making the cost of crude feldspar at the mill $1.00 per ton. This low freight charge is made as it would be good policy to have the mill near the feldspar property and we regard this cost per ton as obtainable. However, we later on give the change in the final cost of the product with change in cost of the raw feldspar.

Three hundred tons of feldspar per day at $1.00 would be $300.00 per day or $105,000 per year.

The potash is unlocked from its combination as double silicate by the reaction with calcium chloride under heat, the potash and any soda present uniting with the chlorine, forming alkali chlorides. One part of $K_2O$ requires theoretically 1.18 parts of $CaCl_2$ and one part of $Na_2O$ requires 1.79 parts of $CaCl_2$. A feldspar rock containing 10 per cent $K_2O$ and 2 per cent $Na_2O$ will require 15.4 parts of $CaCl_2$. A charge of 300 tons of such feldspar will, therefore, theoretically require 46.2 tons of actual $CaCl_2$ and in practice some excess of the reactive agent is used. The technical difficulties encountered in making and handling mixtures of feldspar and dry calcium chloride and the means by which these difficulties were overcome, were fully described in our earlier paper. By having a small proportion of free quicklime mixed in with the pulverized feldspar, and by an automatic device by which a strong solution of calcium chloride is continuously sprinkled on a moving layer of the powder, separate aggregates or "clumps" are formed, due to the combination of the free lime with the calcium chloride, with the formation of an oxychloride compound which cements the masses together into an extremely intimate union. The chlorine seems to be in a much more reactive condition in this temporarily formed oxychloride compound than the chlorine in straight calcium chloride, although the higher reaction yields obtained may be due merely to the far more intimate contact of the particles composing the clumps. These clumps are run directly into the rotary kilns.

This automatic method of preparing materials for furnacing operations costs only a few cents per ton and in this and in other furnacing processes it is greatly increasing the reaction yields. It is one of those simple aids to chemical manufacturing procedure which are tending to make continuous operations replace the methods of treating separate batches, and while often increasing the yields, it always decreases the costs.

We shall, therefore, figure the costs, using for every 100 parts of feldspar 20 parts each of lime and calcium chloride, or, for the plant we are considering, 60 tons of each per day. Provision has been made for a rotary limestone-burning kiln. Limestone can be quarried, brought to the mill and crushed to rather small size for under $1.00 per ton. At this figure the raw material cost per ton of lime will be $1.70. The cost for burning will be 63 cents per ton, the items of this cost being shown below in the figures for furnacing the feldspar mix. This gives $2.33 as the cost in the mill for a ton of unground lime and the daily charge will be $140, or $49,000 per year. It may be mentioned here that unusual care in burning the limestone is not required, although good burning is advisable.

Calcium chloride is the by-product of the ammonia-soda alkali process and is produced in great quantities in this country. A large portion of the amount produced finds no ready sale. It may be obtained in solid form containing about 75 per cent $CaCl_2$ and the balance water, or in solution in various strengths. The solutions used in our work are quite strong, between 35 and 40 per cent $CaCl_2$, so that the original solutions shipped in tank cars are suitable for the purpose. The questions of freight charges on the water content of solutions and solid cakes as affecting the final cost at the mill of the actual calcium chloride, has been gone into quite fully, and we feel justified in stating that in our opinion the net cost per ton of calcium chloride at the mill should not exceed $7.33. The 60 tons required per day will then cost $440, and per year $154,000. However, we later on give the change in the final cost of our product with change in cost of the calcium chloride.

MANUFACTURING OPERATIONS AND COSTS—Feldspar crushes and grinds more easily than limestone or cement clinker; it breaks easier, due to its cleavage planes. It has been found that a high-speed mill which will grind 5 tons per hour of crushed limestone so that 65 per cent will pass a 100-mesh screen, will grind 8 tons of crushed feldspar to the same degree of fineness. The operations of crushing, preliminary grinding and fine grinding of the feldspar and the lime so that over 95 per cent of the mixture will pass a 100-mesh screen will cost about 16 cents per ton for power, 14 cents per ton for labor, and 10 cents per ton miscellaneous expenses, making 40 cents per ton total. The labor charge is for three shifts of six men each. This gives the cost for crushing and grinding the feldspar as $120 per day or $42,000 per year. Using the same figure per ton, the crushing of the limestone and grinding of the burned lime is $24 per day or $8400 per year.

The power required for the clumping operation is very small for a pump, elevator, feed roll and conveyor. Three shifts of four men each can handle it. The costs are, per ton clumped, power 1 cent, labor $8^1/_2$ cents, miscellaneous $3^1/_2$ cents, total 13 cents, making a daily charge of $46.80 or $16,380 per year.

The furnacing charges for heating the feldspar clumps are considerably less than those for burning Portland cement, as less heat is required, the maximum temperatures in the kiln being about 1100° C. or 2000° F. In our work with cement kilns it was found necessary to reduce the size of the coal burners, and cut the amount of coal fed in by at least one-third or overheating would result. The coal requirements in burning limestone in rotary kilns show about the same reduction from Portland cement requirements, although a ton of quicklime requires the heat from about 75 lbs. of good coal for the actual decomposition of the limestone from which it is made. We do not know the amount of heat evolved or absorbed in the union of $K_2O$ with the silica and alumina in the formation of feldspar, nor do we know the amount of heat evolved or absorbed when CaO unites with the same substances. The following data, however, are available:

$(K_2 + Cl_2)$ — $(K_2 + O)$ evolves 114,120 gram-calories.
$(Ca + Cl_2)$ — $(Ca + O)$ evolves 38,990 gram-calories.

Using these figures above, in a double decomposition where on the one hand calcium is removed from $CaCl_2$ and unites as CaO with silicates and on the other hand potassium leaves its union as $K_2O$ with silicates and unites with chlorine to form KCl, there is evolved an amount of heat equal to 1440 B. T. U. per pound of $K_2O$. This means that an amount of heat is evolved in the kiln at the reacting temperature, corresponding to 15.5 lbs. of coal for every ton of the charge heated in this process and by that much decreases the amount of fuel necessary to be burned. Our figures are 300 lbs. of coal per ton of burned clumps, but to this we add 20 per cent for the evaporation of the 17 or 18 per cent of water the original clumps contain. This gives a coal consumption of 360 lbs. per ton, or a cost of 45 cents per ton for fuel. Drying and grinding the coal costs 7 cents per ton of furnace product, power for the kilns 5 cents, a labor charge of three shifts of three burner men each comes to $7^1/_2$ cents per ton, and adding $5^1/_2$ cents for miscellaneous expense gives 70 cents per ton furnacing charges on the 420 tons per day produced by this plant. The daily charge is $294.00 and for the year $102,900.

The leaching of the furnace product has been done in a small way, but it has not actually been carried out at present upon a large scale, as no plant has had the necessary equipment. A complete equipment has been designed for a mill of the capacity we are considering. Four leaching tanks per kiln, each with a capacity of 2800 cubic feet; one tank for strong liquor for each kiln, with a capacity of 5600 cubic feet; and one common wash-water tank with a capacity of 19,600 cubic feet are provided, with all foundations, piping, pumps, walkways, etc. Also a rearrangement of the usual stacks so that the liquors are sprayed down through the hot kiln gases and in the same direction in which these gases are traveling at the time, dampers, direct by-passes, and a system for disposing of the residual mineral

sludges to the dump. The power cost per day figures to $10.80, the labor of three shifts of five men each to $39.00, and, adding $10.00 for miscellaneous expenses, the charge to this operation per day would be $59.80 or $20,930 per year. A 10 per cent solution of KCl pumped to the stack evaporators, if concentrated to a 30 per cent solution, will require the evaporation of 10.54 tons of water per hour in the three stacks. If the coal runs 13,000 B. T. U., this means the total heat from 0.91 ton of coal per hour. There will be burned in the kilns 3.15 tons of coal per hour, and it will require only 29 per cent of the heat generated in the kilns to effect this evaporation. This strong hot solution, pumped direct to the final drier between the lime kiln and its stack, will require the evaporation of 3.7 tons of water per hour, requiring the total heat from 0.317 ton of coal. There will be burned in the lime kiln 0.44 ton of coal an hour or an excess of 40 per cent. Should this not be sufficient to effect the complete drying of the crusts of muriate of potash, and if it were necessary to add 50 per cent to the amount of coal burned, the added cost would be $9.50 per day which would increase the total charges per day only 0.64 per cent.

The totals of the above costs are, therefore:

| | Per day | Per year |
|---|---|---|
| Overhead expenses on plant | $ 64.30 | $ 22,500 |
| Raw materials | 880.00 | 308,000 |
| Manufacturing operations | 544.60 | 190,610 |
| TOTAL | $1488.90 | $521,110 |

PRODUCT

In our operation of this process in a Portland cement plant, 83.2 per cent of the insoluble $K_2O$ in the feldspar was converted into KCl. This was done in a short kiln only 55 feet long and better results are possible in longer and more efficient kilns. There is little doubt that 80 per cent can be obtained in the plant under discussion. From a rock containing 10 per cent $K_2O$ there would be recovered, therefore, in the final product 24 tons of actual $K_2O$ in the form of 38.03 tons of KCl. This product should be about 80 per cent strength; therefore, the actual final product will be 47.54 tons per day or 16,639 tons per year, running 80 per cent KCl or a trifle over 50 per cent $K_2O$, a material identical with "80 per cent muriate" imported from Europe.

The cost of this product figures to $31.32 per ton. The following table gives the costs in cents per pound and in terms of fertilizer units.

| Product | Per day | Per year |
|---|---|---|
| (80 per cent KCl = 50.48 per cent $K_2O$) | 47.54 tons | 16,639 tons |
| Actual KCl | 38.03 tons | 13,310 tons |
| Actual $K_2O$ | 24.0 tons | 8,410 tons |
| Cost per ton of product | $31.32 | |
| Cost per pound of KCl: | | |
| Overhead | 0.0845 cents | |
| Raw materials | 1.1570 cents | |
| Manufacturing | 0.7161 cents | |
| TOTAL | 1.9576 cents | |
| Cost per pound of $K_2O$: | | |
| Overhead | 0.1340 cents | |
| Raw materials | 1.8333 cents | |
| Manufacturing | 1.1346 cents | |
| TOTAL | 3.1019 cents | |
| Cost per "Unit" of $K_2O$ | 62.04 cents | |

Each change of 50 cents per ton in the cost of the raw feldspar rock changes the final cost of the $K_2O$ in the product 0.3125 cent. Each change in cost of $1.00 per ton in the cost of calcium chloride changes the final cost of the $K_2O$ in the product 0.125 cent.

If 80 per cent muriate of potash has been heretofore used at a cost in this country of $37.50 per ton, there is thus shown a saving by the above process of over $6.00 per ton or 20 per cent profit on the manufacturing cost. All the materials for the operation are to be had in this country, and the costs as established by the first plant would not be increased in the future by any foreign complications. As to whether the German syndicate will continue after the close of the present war, we can only say that it seems probable, as under no conditions now foreseen will the Stassfurt potash deposits be separated from Prussia nor will Prussia be separated from her potash deposits. A very large production of muriate of potash from American feldspar rock would probably invite price cutting after the war. A reasonably small production, such as outlined in this paper, might supply the requirements of certain industries and still not be a large enough proportion of the whole amount used in this country to warrant a price war. Wise governmental measures might enable even a very large domestic industry to be built up, which would make us independent of foreign materials for this valuable and essential ingredient of our fertilizers. If the crop yields per acre are to be increased in this country, some such independence may be necessary. The permanent assurance that the fertilizers of this country may be supplied from domestic sources and that miscellaneous industries such as the soap, glass, match, color, photographic and strictly chemical industries using $1,000,000 worth of potash a year can be assured of a constant source of supply would go far to stabilize a great many of our manufactories and would, by so much, be an item of true progress, as the raw materials are not at the present time used for any useful purpose whatever. It may be of some interest to record in passing that the present war conditions abroad have caused the market price of muriate of potash to rise. Last week we were quoted this material at about $100 per ton. If a plant of the size we have been describing were put into operation by leasing a cement mill and expending $70,000 on additional equipment, which could be finished in three months' time, and if the muriate of potash were sold at one-half the present quoted prices, or $50 per ton, the profits figure out as $26,300 per month. After three months' operation the plant would have been paid for and at any time afterwards the plant could be scrapped and a good profit still be made on the enterprise.

BY-PRODUCT

We have made no attempt to put a value upon the large amount of by-product rock matter. In the plant we have considered, there would be produced, figured on the dry basis, about 370 tons of this residue per day. It would have a percentage composition about as follows:

| | | | |
|---|---|---|---|
| Silica ($SiO_2$) | 65.8 | Potash ($K_2O$) | 1.9 |
| Alumina ($Al_2O_3$) | 17.4 | Soda ($Na_2O$) | 0.4 |
| Lime (CaO) | 13.5 | | |
| Magnesia (MgO) | 1.0 | TOTAL | 100.0 |

Owing to the volatilization of ferric chloride, the material is almost pure white and might find use in the glass, pottery, porcelain or brick industries. It is similar in chemical composition to some clays except that it has a higher content of lime and a considerable proportion of this lime is already combined with the silica. Some use in glazes might be found. Although high in alumina, certain glass products might be made, using it in mixtures, particularly for plate glass and some bottle glasses. Its freedom from color is a point in its favor and also the assurance of practically constant composition and physical condition. If 50 cents a ton could be obtained for it after being dried, the income would be about $120 per day. This would reduce the net cost of the 80 per cent muriate product to $28.80 per ton, and the cost of the $K_2O$ to 2.85 cents per pound.

CONCLUSION

In concluding this paper, the authors wish to record the fact that they are already familiar with many strong arguments which can be used against the advisability of attempting to manufacture potash in the United States. It is frequently stated that the Stassfurt potashes could be sold in this country for about one-third of the prices which prevailed before the war and still yield profits to the foreign mines. Whether this statement is accurate or not, we have no means of ascertaining, but even if it is nearly true, it clearly proves that the words used

in the introduction to this paper were not too emphatic, in which it is pointed out that special interest rather than the cost of production has controlled prices. If potash has any bearing whatever, through intensive agriculture, upon the production and price of food crops, however indirect this bearing may be assumed to be, the control of the product by any single interest is unquestionably hurtful to the best interests of the people of this country. In the opinion of some more or less well-informed persons, potash is not nearly so important to growing crops as the other principal plant foods, combined nitrogen and phosphates. In other words, there is a tendency in certain quarters to believe that the propaganda in favor of the wide-spread necessity for potash in fertilizers has been overdone and that our agriculturalists could rest contented with potash reserves in the soil for many years to come, provided other conditions are properly looked after. However this may be, it is difficult to persuade either the practical grower or the scientific agriculturist that he does not increase his yields and early bearing, by a wise use of potash in one form or another. Up to the present time, the statistics of our average crop yields per acre are not a source of pride to those of us who study such comparative data. It is the earnest belief of the writers that the American demand for an American source of potash at a fair price will continue to increase in the future. Whether the time has arrived when any progress along this line can be made, still remains in doubt. The foregoing paper has been offered to the Institute with no pretense at settling this important question but merely as a contribution to which we invite the attention and consideration of chemical engineers and others who may be interested.

THE INSTITUTE OF INDUSTRIAL RESEARCH
WASHINGTON

## ASPECTS OF SOME CHEMICAL INDUSTRIES, IN THE UNITED STATES, TODAY[1]

By EDWARD GUDEMAN

The European war has raised a question of very great importance to us, applying specifically to many chemical industries, based on the application of chemistry. Manufacturers and consumers are asking: "Will and can United States chemists prove equal to the emergency created, which makes it impossible, in many cases, to obtain from abroad, many chemical supplies for which the United States in the past has been and is today and will be in the future, dependent on foreign producers?"

One of our Chicago morning papers has put the question directly up to the chemical profession in asking: "Is the American (U. S.) chemist, scientist and inventor so *impotent* that he will see thousands of workmen thrown into idleness, because he *cannot* or *will not* make these needed compounds?"

The italics are my own. This places the whole and full responsibility for a change in the present conditions on the profession I claim as my own, and I accept the challenge and shall try to defend the chemists, as far as I am able and show what in my opinion are the actual reasons and causes of some of these conditions. The inquiry could easily be broadened to include all scientific professions, and their answer would require only the substitution of their own concrete examples for the chemical cases I shall present.

Confining myself to the chemical field makes the answer of such extent that I can give only a very meagre superficial review, and merely indicate the prime and underlying causes that account for many of the present conditions. I am not offering any remedy, but shall point out some changes that may help in developing and protecting lacking chemical industries, having in mind not the present as much as the coming future.

The only manufacturer who is also his own exclusive consumer is the uncivilized savage, whose sole object in life is to protect and sustain his physical body, and perhaps, although not always, that of his own immediate family.

Many, only within the last few weeks, have fully recognized that while they have styled themselves "manufacturers" of this or that, or of this or that "profession" are in the final analysis very important consumers. Many, including the chemists, have, up to the present time, given little thought or consideration, as to how or where their products of consumption actually originated, as long as their supply, quality and quantity could be obtained at satisfactory costs. Today, with a restricted supply and in many cases great advance in costs, there has been a sudden awakening that there are such people as chemists, that this has been recognized in foreign countries, and that we in the United States are absolutely depending on *foreign* chemists and *foreign* chemical industry for our supply of many of certain commodities, all of which we have been importing, such as direct chemicals, medicines, colors (aniline or mineral), alloys, precious and semi-precious metals, etc.

Up to the present time the chemical profession has not been recognized in the United States as it should have been,[1] and it is this sudden awakening to the existence of a chemical profession that has led to the asking of the above-mentioned questions, to which should be added the very necessary one, *why do these chemical industries not exist and flourish in the United States?* It is this complete question that I am trying to answer.

I hold no brief for any of the chemists in the United States, but I say most *emphatically* that the chemists of the United States are *not impotent*, that they *can* and they *will* do more than their full share and I believe that every research, industrial, technical, engineering and manufacturing chemist, and every teacher of chemical science will back me up in this statement. All that is required and necessary is to create in the United States the proper conditions for our chemists to do what they can do and what they are most willing to do.

All must admit that the application of chemistry, or any other science, is only one of the cogs that help drive the wheels of commerce. Commercial chemistry, in its widest or in its most limited sense, is a science built on the dollars and cents, and the actual, direct chemical reaction, or its application or use—the individual result of the mental and physical efforts of the chemist—is not the whole thing; far from it. Every business man, commercial or professional, styled manufacturer or consumer, is of as much if not much more importance than the chemist, as without him, the chemist can do nothing. They are the first consideration as they have and must give to the chemist what he lacks. They, not the chemists, represent engineering problems, labor conditions, market conditions, normal relationships between costs and selling prices, transportation questions, etc.; they stand for quantity and quality, supply and demand, not overlooking legislative enactments and financial resources. Present temporary abnormal war conditions should not be considered in trying to build up a chemical or any other industry.

Has not too much stress been laid on our natural resources and their development, perhaps exhaustion, and some of our so-called wasteful methods? There are two sides to these questions, both of which may be wrong, and the remedy may be in the application of the fourth dimension.

A single smelter, near natural resources of raw material, is daily polluting the atmosphere with enough sulfur compounds to make 2000 tons of sulfuric acid, worth in New York or Chicago, say, $40,000. We chemists know how to recover about $39,999 worth of this *waste*, but we do not do it there, because the sulfuric acid, if produced, would be less than worthless; we could not give it away, and its production would create an additional expense of manufacture and storage, due to the fact that there is no market for that chemical within a reasonable distance of its source of origin.

[1] Address before the 7th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 2 to 5, 1914.

[1] See Gudeman, THIS JOURNAL, 6 (1914), 687.

Natural resources of soda, near the Pacific Ocean, are sufficient to supply the world's demands for years to come, but present costs of transportation and local conditions make them worthless today as a world's commodity. Whether the opening of the Panama Canal route will change this remains to be seen. If distance, *actual mileage*, between source and market were in that part of the United States, as it is east of the Mississippi River and in foreign countries, Montana and California would be able to furnish all the soda and all the sulfuric acid required in the manufacture of all the refined chemicals, coal-tar colors, and medicinal preparations we now import, besides leaving a fair surplus to be used in the soap and fertilizing industries. As cleanliness is next to godliness it would improve us morally and in assisting agriculture would bring us nearer to nature again.

What would the natural soda deposits in British Africa be worth to Great Britain, if the cost of transportation to British ports were about 50 cents per 100 lbs., a fair value of the commodity at the port of entree? The discoverer of these fields told me they were worth to Great Britain hundreds of millions of dollars.

Utilization of natural resources and recovery of some waste products, may be like the tariff, a local issue. Preservation of these natural resources is a much more important consideration and thereon hangs our future welfare.

The chemists of the United States have been, and are today, ready and willing and they have the brains and ability to manufacture here at home every chemical product, raw or refined, without exception, that is now imported, and it is not adverse labor conditions nor a question of tariff, all of which should be considered, that keeps the chemists from so doing.

In many cases, not all, *federal* requirements restrict us so as to actually prohibit and stop us from manufacturing and going into competition with and replacing the imported chemical products.

Patent, trade-mark and copyright acts, with internal revenue acts, stand in the way, firmly braced up by the Sherman Act, so as to block many lines of chemical manufacture. These acts not alone deprive us from the right of manufacture, but from actual use of many commodities, and make us dependent on the good will and ability and policies of foreign nations. You can convince yourselves of this by a study of those United States chemical industries, where this interference, this prevention, is not felt.

Most European and some Asiatic countries, as also Canada, require that under patent, trade-mark or copyright granted, the protected product be actually manufactured or sold for the protection granted, and in some countries that a "reasonable" proportion of the amount used in the country be actually made in that country. Also that actual manufacture be started or license for manufacture be granted, within a fixed time after granting of such exclusive protection.

There is a great difference of opinion between expert authorities, whether such restrictions and limitations are good or bad policies. I hold that under present conditions, and for our future protection, some changes should be made in the requirements of foreign patents granted in the United States, as is made of United States patents granted in these foreign countries. What we grant to others should be granted to us, and what others require of us, we should require of them. This is reciprocity and an application of the Golden Rule.

It is held that rights granted under patents, copyrights and trade-marks are contracts. If so, the breach of contract by one party should and does invalidate the whole contract. The United States certainly cannot be expected to live up to its end of the contract, if the foreign country cannot or will not live up to its part.

It is also held that the rights of patents, copyrights and trade-marks are fixed by the Constitution of the United States. That is correct, but there is nothing in the section applying to these rights that does not allow the United States to issue its rules and regulations in applying this section. The section of the Constitution reads as follows:

Sec. VIII—"To promote the progress of science and useful arts, by securing for limited times, to authors and inventors, the exclusive right to their respective writings and discoveries, etc."

The Constitution of the United States also states, as the very first paragraph of the Constitution:

"Preamble: ....., promote the general welfare, and secure the blessings of liberty to ourselves and our posterity,...."

If the granting of any copyright, trade-mark or patent is not to the welfare of the United States, then the granting of such rights and the protection given under such grant, is contrary to the Constitution.

Can the United States do anything to better existing conditions, and if so, how long need it take to make a change, only temporary if you so wish, to meet conditions of the present foreign war and the near future after the war is over?

A way is pointed out if we consider what Great Britain has done since the beginning of war, and is doing, where similar interests are affected.

On August, 7, 1914, the authority and power of the British Board of Trade was extended beyond the acts of 1905 and 1907, putting thereby absolutely into control and charge of that Board, all matters pertaining to patents, trade-marks and designs, owned or controlled by any of those at war with Great Britain. This official board on that same day appointed a very strong and representative chemical committee, with the following announcement:

"In view of the cessation of imports from Germany and Austria, and the fact that there are many articles hitherto imported from these countries of importance, if not necessity to British manufacturers, information is invited by the Commercial Intelligence Branch of the Board of Trade from importers of such articles as to their precise nature and quality, in order that steps may be taken to ascertain whether similar goods might be produced in this country (G. B.) and if so, where; or if not, from what neutral sources they may be obtained?"

Without waiting for any report from this committee the Board of Trade on that same day, August 7th, amended the Patents, Designs and Trade-mark Acts and on August 21st, issued Statutory Rules and Orders, effective from August 7th, giving to "any person" the right of asking for "avoidance" or "suspension" of any patent, trade-mark or design during the time of war and six months thereafter. On September 7th, those rules were extended so as to apply to patents, trade-marks or designs of those at war with Great Britain, irrespective of where issued, and giving the right to suspend in part or whole any patent, trade-mark or design for the whole time of such protection or registration. In effect this means that Great Britain and also her colonies do not recognize the validity of any patent, copyright or design, in any country that is at war with her and also will place no restriction on any neutral country that may supply any such products.

I hold that the United States should take some action, as the welfare of the country is at a stake; it need not be as drastic as that of Great Britain, but something should be done and be done quickly, either through Executive Order or through action of Congress, confining such action, if you so wish, to foreign patents and protected foreign products. I am not recommending or suggesting the curtailing of any rights under patent, trade-mark or copyright acts, except so far that I hold this as a matter of self-protection and protecting our future, the Constitutional "welfare" of our country, by giving to any person in the United States, under proper restrictions and regulations, the right to use, without claim for payment of royalty and with

protection against damage or infringement suits, such patent or product patent or patented process, as is in actual use in any foreign country, and the owner of which *will not* or *cannot* manufacture himself, or issue license to manufacture in the United States, and thereby compels those in the United States to *rely absolutely* on the *imported article*.

Some authorities have advised that under present existing conditions manufacturers go ahead and ignore these protective acts and take their chances that our federal courts will not sustain any action taken later on by the foreign owners, and uphold them in creating a monopoly of supply and distribution. As it may be unconstitutional for the foreigners to so act, against the welfare of the United States, this is a safe gamble, but I do not recommend it, as the defending of a lawsuit, in which chemical expert testimony may be involved, is very expensive both for winner and loser. Ignoring of foreign patent, trade-mark and copyright privileges may be of temporary benefit, but would not be a very firm basis for the upbuilding of a chemical industry.

In his report as chairman of the Patent Committee of the American Institute of Chemical Engineers, dated June 1, 1914, L. H. Baekeland very truly says:

"It is a pity that, instead of resorting to those haphazard attempts at legislation, this subject should not be entrusted first to a competent commission which could submit a report and recommend such legislation as would render the patent system of the United States adequate to modern requirements of the development of this country. Such a simple procedure, however, seems not to meet the favor of lawyer-politicians, unacquainted with the practical workings of our patent laws."

No doubt it was only a slip of memory for Dr. Baekeland to overlook the "*exclusive importers*," possible retainers of his "lawyer-politicians."

Let me illustrate this point and make use of a product known to all of you—acetylsalicylic acid. I am taking, simply as illustration, a well-known medicinal drug, because no medicines, crude or refined, are today being exported to the United States, the warring nations not having sufficient for their own uses.

Acetylsalicylic acid is a chemical product, commonly known by its protected name, aspirin. Under patent and copyright protection, we would not be allowed to manufacture or sell one grain of aspirin, without permission of the foreign owners of the copyright name of aspirin. A physician knowingly or unknowingly, who prescribes aspirin, calls for a specific product, made by a *specific company*, at perhaps a specific place, and the dispensing druggist has no right under state acts, or under federal act, if interstate commerce is involved, to substitute therefore acetylsalicylic acid, although it is aspirin. It may be that some chemists, druggists, physicians or laymen do not know that acetylsalicylic acid and aspirin are but two names for the same identical substance. This holds good for very many other drug products that are known in the trade by their protected copyrighted names, such as salvarsan, veronal, phenacetin. Some may be afraid to take 5 grains of acetphenedin or oxyethylacetanilide, but have no fear of 5 grains of phenacetin, the difference being only in their names. Substitutions of this kind have been decided by the courts as being illegal. After the patent rights have expired, we can get busy, often with a 17-year handicap of experience against us.

It is against such effects of this kind of protection that many protest: the creating of an absolute monopoly for foreign manufacture and distribution, compelling importation, when the protected foreign owner will neither manufacture nor allow manufacture in our country, nor even issue license to use his protected trade-mark or copyright in our country, and where these protected rights are made use of in other countries.

As is well known, many chemicals, drugs, colors, etc., require the use of grain (ethyl) alcohol in their manufacture or purification. With an internal revenue tax of $2.10 per gallon on such alcohol, we cannot compete with those countries (European, Asiatic, North and South American) that allow tax-free alcohol to be used in the arts.

I know of cases where it pays the United States manufacturer to send his raw material to Canada, to manufacture this into a finished product in Canada, and to re-import to the United States. He thereby gets it cheaper than if manufactured in the United States, even though he pays freight two ways and import duty, simply because in Canada he can use tax-free alcohol in the process of manufacture.

This is a very superficial indication of some of the conditions that should be changed and that quickly, and we should strike while the iron is hot. All should help to release the legislative brakes that are retarding the progress and development of many chemical industries that could and should prosper in this country.

I am fully aware that importers and representatives of foreign houses do not agree with these views, and that any such action will seriously affect their business and their pocketbooks.

Not as a matter of politics must I refer to the Sherman Act as another serious interference in the development of chemical industries, but only to illustrate what can and is done in Germany, which cannot be done in the United States now, without coming quickly into conflict with the Sherman Act; *i. e.*, creating illegal combinations or trusts.

Some of the largest competing chemical industries of Germany, representing combined capital of more than $100,000,000, sold out their interests in the hydro-electro industries of Sweden, Norway and Iceland, manufacturing nitrogen compounds from atmospheric nitrogen. With the support of the German government they formed a new "cartel" (syndicate, combination or trust) to develop in Germany the Haber process of making ammonia direct from the atmospheric nitrogen, as this new process does not depend on cheap water-electric power. What privileges and rights and financial support these companies receive from the government I cannot say, but the fact is that the government is party to this combination. As a result it will not be long after war is ended before Germany will be independent of any foreign country for its supply of all kinds of nitrogen compounds and ready to compete in foreign countries with these compounds. It is as a matter of protection for its agricultural interests that the German government assists and fosters this new industry.

Potash salts are also used in agriculture and the world's supply today is controlled by the German Kali Syndicate, of which the German government is a direct partner, owning some of the mines that are in this trust. When it was found that the coal-tar product saccharin was seriously hampering the beet-sugar industry of Germany, this industry was protected by making the manufacture of saccharin a government monopoly, and prohibiting its use as a sugar substitute—a necessary step as one pound of saccharin has about the sweetening power of 500 lbs. of sugar. But there is no provision limiting the export of saccharin.

How well our beet-sugar industry is protected, need not be mentioned, except that we rely for a very large proportion of our beet-sugar seed on Germany.

Saccharin was first made and patented in the United States, but the German inventor decided to manufacture in Germany, and not until the patent rights expired could the product be made in this country as it is now.

We have tremendous natural vegetable and mineral potash resources. If in order to exploit and develop them quickly, it were suggested that a combination or syndicate or trust or whatever you want to call it, be formed of the firms interested in the manufacture of fertilizers, how long would it be before some legal action would be instituted to unscramble such company as being contrary to or not in accord with the Sherman Act? But it will need the capital at command of such a combina-

tion to develop and introduce the potash industry into our country.

C. S. Bradley and D. R. Lovejoy, two Americans, were the first to commercially make nitrogen compounds from the atmospheric nitrogen, and it was lack of financial backing that drove them into bankruptcy and lost one of the most important industries to the United States, so that today, instead of being the leaders in this industry, we are actually only lookers-on.

The Haber process for the making of ammonia is patented in the United States but whether we shall see the process used here before the patents expire is questionable. If we have to wait until then, about 15 years, we shall again be handicapped with 15 years' experience on the part of foreign workers, not even considering the improvements, modifications and changes that will naturally be made in the operating of this process.

It may be partly due to our great natural resources, and the great ease with which we have been able to dispose of them as such, that we have not developed chemical industries based on them. It was easier and quicker money to sell our raw or crude products instead of changing them into refined and finished products.

The future is very bright and now is the time to begin working it out. It will not be easy for us to get to the head of the procession, where we belong, even if you modify, change or suspend the patent, trade-mark and copyright acts, even if we get tax-free alcohol, and if you would make a dead letter of the Sherman Law, as far as it interferes with prospective manufacture by a combination or trust. It would take a long time, longer than many may anticipate, before we could replace many of the imported chemical products with those "made in the United States." We must realize that these foreign industries are in their highest state of development in Europe, due to the opportunities offered their chemists and experts in the past. These chemical industries are very complex, interlocking at every step, and could not as a whole be moved or transplanted to a new region. The by-product of one process becomes the raw material of another process and in many cases the by-product of one step is the market product exported to us.

This accounts for the cheapness of such products, they being only incidental to some other product. It therefore makes it impossible in many cases to make any specific product as your main product and compete in price with this same product if it is the by-product in some other process. These fully developed concerns in Europe also manufacture the products they use in their processes, which gives them a great advantage over the manufacturer who has to buy such necessary process chemicals. They do not specialize in any one class of chemicals, as is the custom with us as a general rule.

We also differ from them in having spoiled ourselves by measuring everything by tons and carloads, instead of ounces and pounds. It goes against our national grain to work up a carload to obtain an ounce of refined product. We are beginning to recognize this and in our working up of our radium ores we shall get homeopathic output from allopathic doses.

We also lack in this country the application of real, genuine research work and its application to manufacturing industries. We need more and more research and engineering laboratories as integral parts of manufacturing institutions.

You cannot contradict the statement that every manufacturing concern in the United States, which has a well-equipped chemical and engineering research and testing laboratory[1] as to men and apparatus, is on a competing basis with similar concerns in foreign countries, and they are not alone marketing their products in competition, but in many cases are commanding the world's markets. The routes to the North and South poles are marked with the discarded packages that contained products of United States manufacture.

We must get away from the ton and carload methods of giving away our natural crude or raw materials and then importing the refined or finished commodities made therefrom. Our exports of raw or crude chemicals far exceed in money value our total imports of refined chemical products, and we take back in ounces what we sent out in tons.

Real genuine research work and chemical manufacturing experience go together, are absolutely dependent on each other and are the foundation of the development of chemical industries. I referred to the development of the Haber ammonia process; let me illustrate with another case. Prof. Adolph Baeyer, of the University of Munich, Germany, worked for 15 years in his private laboratory before he invented a process for the making of artificial indigo. The Badische Anilin and Soda Fabrik obtained the rights to the Baeyer invention, and it took their chemical and engineering staff another 20 years before they developed this process commercially so as to actually replace nature's product with that made in a chemical factory. Thirty-five years of research and experimental work to manufacture commercially one coal tar or anilin color, and we have thousands of them—and a similar story can be told of others!

My answer to the question "Why do we not manufacture anilin dyes in the United States?" is that *we do*. This is confirmed by the symposium on the American Dye Industry[1] and in the articles of Grosvenor and Frerichs,[2] just published.

The anilin-dye industry is only a small phase of the total chemical industries, in fact, we could say that in many cases dyes are by-products in the manufacture of other chemicals. For figures as to the magnitude of the chemical industries in the United States, we must use the census and other governmental reports. Such reports in many cases enumerate importers, sole agents, distributors (wholesale and retail) as direct manufacturers. Many of these statistical figures are *good* for *nothing*. The nearest I can get to figures for 1913 are[3]

| | |
|---|---|
| Total manufactured products, U. S., 1913 | $13,000,000,000 |
| Chemical and allied products | 1,400,000,000 |
| Strictly chemical products (8.5 per cent), domestic | 120,000,000 |
| Strictly chemical products (6.5 per cent), imported | 90,000,000 |
| Coal-tar dyes, imported (0.7 per cent) | 10,000,000 |

The profits on the $90,000,000 of imported strictly chemical products must be about $30,000,000 for the foreign manufacturers, based on the dividends declared and surpluses set aside by the foreign companies manufacturing them. By the time these imported chemicals reach the hands of the actual consumers, their cost has increased to about $250,000,000.

How the retail prices of chemical products are affected by their manufacture in the United States, generally after patents have expired or license for manufacture is issued, is well shown by Frerichs, who states: ".....Incidentally the community at large was compensated by the *cheapening* of prices for many articles, the *manufacture* of which was *undertaken* in the United States. .....Salicylic acid from $1.25 to 35 c.; Synthetic Oil of Wintergreen from $1.25 to 40 c.; Acetanilid $1.00 against 30 c. (70 c. additional for trade name, copyrighted); and when patents have expired, Acetylsalicylic Acid at 5 c. in place of Aspirin, the same thing, at 43 c. (38 c. additional for patents, protection and copyright)." As Frerichs' figures are of a year ago they were not determined or influenced by the present war conditions.

These figures, and you can supply many others, bear out the statement, that we can manufacture on a competitive basis

[1] United Steel Corporation, Standard Oil Co., Welsbach Co., duPont Powder Co., General Electric Co., Eastman Kodak Co., General Chemical Co., Packing House Co.'s, and many others.

[1] THIS JOURNAL, **6**, 1914, 941.

[2] *Trans. A. I. C. E.*, **1913**.

[3] But in giving them I am in accord with Mark Twain's classification and grading of lies as *First* Lies; *second*—Damn lies; and *third* Statistics. Specifically applied to anilin colors I suggest the change of the letters D to L in the legend that "Some *Dye* to Live and Others Live to *Dye*."

every chemical product that we now import, but we must not be hampered or prevented by adverse legislative acts. Cheap labor is only a minor factor. The $90,000,000 of imported strictly chemical products represent at the highest not over $10,000,000 for actual labor, not over 4 per cent of the actual final selling price of these commodities ($250,000,000).

As soon as all legislative hindrance is done away with and we thereby have a fair opening for manufacture, our schools will do their share and our scientific students will receive the quantity and quality of research instruction to make good in these chemical lines. Many of them are getting it today, although it is valueless as far as its practical application is concerned. It is the *Bread and Butter* consideration that takes many of our students to the scientific schools. I consider it the height of folly, not to designate it as criminal, for our teachers to waste and steal the time of the students, with research instruction, that may be applied on the Moon or Mars or in Foreign Countries, and allow these students to starve, professionally, on that part of the Earth which we designate as the United States. I believe in finding out what the student needs and wants in the United States and giving that to him or her.

Teachers of Chemistry and the Students of Chemistry "Made in the United States" are fully up to and the equals of those who prefix to themselves the legends "Made in Austria, or France, or Germany, or Great Britain, or Italy or Russia, or Turkey" as the case may be.

This is the way the coal-tar color industry has been developed in Germany and the medicinal preparations made in these factories, I designate as by-products of the coal-tar color industry. They are doing the same thing with the nitrogen industry. Artificial rubber, rubber made in the chemical laboratory, is an established fact in Germany. You do not find it in the market today simply because the German government does not want it in the market and is willing to pay a big sum, so I have been told on good authority, to keep it out of the market. If, on account of the present war, Germany should have to give up its African possessions, laboratory rubber will perhaps replace natural rubber, just as laboratory indigo replaced natural indigo. Germany has planted its African possessions with rubber trees, and it is not going to let laboratory rubber interfere with its prospective rubber agricultural interests in its African possessions.

"It is an ill wind that blows no good," and some have read and deciphered the handwriting on the wall. It is gratifying to be able to say that the State of Illinois is going to help along, as the foundation-stone for the new chemical industrial technical and commercial department was laid only the other day. I hope that everyone, whether of Illinois or not, will back President James, so that his plans can be quickly realized.

As to the immediate future, you have it in your hands, to at least apply a relief remedy, as without it future progress will continue to be checked and lay dormant. Modify or change some of our legislative acts that protect the foreign product or process or trade-mark or copyright of every manufacturer or owner, who will not manufacture in the United States nor allow the protected product or protected rights to be used in the United States, and who thereby compels everyone of us to rely on his good-will or his ability or the conditions existing in his country for what may be a necessity to us; or that, through the protection afforded him, allow him to make a convenient *dumping ground* of our country for his surplus or by-product or even for products which he is not allowed to sell in his own country.

The chemists of the United States have the brains and the ability and the gumption to make it not "Made in America" but "Made in the U. S." for everyone of the chemical products we now import. All that the chemists of the United States need and all they ask for, is opportunity, fair play, an open field, not fenced in with adverse legislation. The chemist of the United States will then come to the scratch, toe the mark and cross the finishing line ahead, every time. Their records in the other *open* chemical events prove this.

The chemists of the United States have slept long enough under these heavy legislative blankets. For 50 years they have been compulsory "Rip Van Winkles." Pull off this narcotic legislative cover, and see them jump up, *Wide-Awake*.

The chemists of the United States are not impotent,—far from it. They are very productive, they are willing and ready and *can* and *will* do their full share, if you will only prepare the way for them.

Having tried to answer the opening question, let me ask another in concluding: Why should the United States be made the *dumping ground* for many chemical products, originating and coming to us from foreign countries, fully protected by product or process patents, trade-marks or copyrights, without a single requirement, under these rights and protection granted, to the foreign or home owners, by the United States, to allow anyone in the United States to manufacture or use these protected products, and without a single requirement of the owners to manufacture themselves in the United States or even a requirement of exporting to us, any of their so-called protected products?

SUITE 903–4, POSTAL TELEGRAPH BUILDING
CHICAGO

# OBITUARIES

## CHARLES MARTIN HALL

It is with sincere regret that we record the death of Charles Martin Hall, after a long illness, at Daytona, Florida, on Sunday, December 27, 1914.

Dr. Hall was one of our most successful chemical engineers and inventors. He was born at Thompson, Ohio, December 6, 1863, and graduated in the classical course at Oberlin College, 1885, at the age of twenty-one years and six months. While in college he took special interest in the study of Chemistry, in general, and in the metal aluminum in particular.

Aluminum was known to be the most abundant metal in nature (but it is never found uncombined). It was first isolated by Woehler in 1827, in very small quantities, just sufficient to establish its identity as the metal of alum, clay and other familiar minerals and rocks.

In 1854 Henri St. Clair Deville, of Paris, attempted, with the financial support of Louis Napoleon, to establish the commercial extraction of aluminum. In a certain sense he succeeded, his maximum output reaching 5,000 pounds per annum. But the cost was almost prohibitory. The first price in 1855 was $90 per pound; this was gradually reduced to $12 per pound, the lowest price reached by Deville, whose process consisted in reducing aluminum chloride by sodium.

In 1886 Hamilton Y. Castner, a student in the School of Mines of Columbia University, invented a new and much cheaper process for making sodium, and also improved the process for employing this metal for reducing aluminum chloride. He established works at Oldbury near Birmingham, England, and by 1889 was making 500 pounds per day, and supplying it for $4.00 per pound.

Dr. Hall became interested in the aluminum problem while

in college and made many experiments in the hope of finding a more economical process for its production. Finally his thoughts turned to electrolysis, and about October 1, 1885, he began to seek a suitable anhydrous solvent for alumina, operative at a practicable temperature, which would bring the alumina into a fluid condition in which it would yield to the electric current.

Fluorspar and the fluorides of magnesium, sodium, potassium and aluminum were successively tried, but were found to be too infusible and to dissolve little, if any, alumina.

On February 10, 1886, he tried cryolite, the double fluoride of sodium and aluminum. This fused readily at a very moderate temperature and when he dropped in the white powdered alumina it dissolved and disappeared as does powdered sugar or salt in boiling water. It dissolved to the extent of more than twenty-five per cent and the solution was clear and limpid.

He thus made his first great discovery. He proceeded at once to apply the electric current to this solution. His first experiments using clay crucibles were not successful; but on February 23, 1886, he employed a carbon-lined crucible and was successful in obtaining aluminum. He had achieved success in inventing a process for making aluminum directly from alumina by electrolysis under conditions which promised to revolutionize the industry and furnish the metal at so low a price as to enable it to replace copper, tin, lead, zinc and other metals for an endless variety of purposes.

Dr. Hall's age at this time was two months over 22 years and he had discovered and invented what had escaped Woehler, Rose, Deville and many of the other world-renowned chemists who had busied themselves with aluminum over a period of half a century.

CHARLES MARTIN HALL

On July 9, 1886, Dr. Hall applied for his broad basic patent which was granted April 2, 1889, No. 400,766, with the following claims:

1—As an improvement in the art of manufacturing aluminum, the herein-described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum and a metal more electro-positive than aluminum, and then passing an electric current through the fused mass substantially as set forth.

2—As an improvement in the art of manufacturing aluminum the herein-described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum and sodium and then passing an electric current, by means of a carbonaceous anode, through the fused mass, substantially as set forth.

3—As an improvement in the art of manufacturing aluminum, the herein-described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum, sodium and lithium, and then passing an electric current, by means of a carbonaceous anode, through the fused mass, substantially as set forth.

Dr. Hall also received four additional patents for modifications of his original process. But he did not escape the usual experience of the successful inventor. He was obliged to defend in court the originality of his invention. The suit was brought in the United States Circuit Court of the Northern District of Ohio and after an exhaustive discussion of the prior art the patent was sustained. The opinion was written by Judge William Howard Taft, later President of the United States. He wrote: "Hall was a pioneer and is entitled to the advantages which that fact gives him in the patent laws."

The court declared the patent valid and issued a perpetual injunction against the defendants. For various reasons there was considerable delay in devising suitable means for applying the invention on a manufacturing scale and securing the necessary capital. But at last, in November, 1888, he began work in his factory at New Kensington, near Pittsburgh, producing 50 pounds of metal per day. After that date his progress was wonderful. He soon erected larger works at Niagara Falls as the first consumer of the electricity supplied by the Niagara Falls Power Company. At the present time the company has three establishments at Niagara Falls, one at Massena in New York on the St. Lawrence and one at Shawinigan Falls in Canada. The total consumption of electricity is 140,000 horse power, probably a larger amount than is consumed by any other electrochemical works in the world. The annual output of aluminum is now more than 50,000,000 pounds. The first metal produced at New Kensington was sold at $2 per pound; the price now is about 22 cents per pound. The early dreams of the young undergraduate were certainly realized

Dr. Hall made many other inventions, several of which have been patented. Six of these are for improved methods for preparing pure alumina, one of which is still employed for preparing this material for use in the works. He also patented improved methods for making improved carbon anodes for use in the process.

In 1910 Hall received the degree of Doctor of Laws from Oberlin College, his Alma Mater, and in 1911 he was awarded

the Perkin Gold Medal for distinguished services in Industrial Chemistry, by the Medal Committee representing the Society of Chemical Industry, the American Chemical Society, the American Electrochemical Society and other associated societies.

A full account of Dr. Hall's achievements was published in the March, 1911, issue of THIS JOURNAL, on the occasion of the award of the Perkin Medal. There was also published in *World's Work* for August, 1914, a very interesting illustrated article on "The American Creator of the Aluminum Age."

It was a remarkable coincidence that while young Hall was making his great discovery and invention in Ohio, another young chemist, of the same age, Paul L. V. Hèroult, should have made the same discovery and invention in France. Dr. Hèroult was present at The Chemists' Club on the occasion of the presentation of the Perkin Medal to Dr. Hall; and gave some interesting information with regard to the early history of aluminum. Dr. Hèroult was born in Thury-Harcourt, Normandy, on April 10, 1863, and died May 9, 1914. A short account of his life is given in the June, 1914, issue of THIS JOURNAL.

Dr. Hall was a member of the American Philosophical Society, the American Institute of Mining Engineers, the Franklin Institute, the American Electrochemical Society, and the New York Chamber of Commerce; he was also a trustee of Oberlin College and ex-President of the Niagara Falls Memorial Hospital.

A bequest of $3,000,000 was left by Dr. Hall to Oberlin College. The bequest is in the form of $2,000,000 endowment to be used for any purpose; $500,000 for building an auditorium and $100,000 for its maintenance; $200,000 for campus improvements; all property in Oberlin owned by Dr. Hall; and a valuable art collection.

Dr. Hall was extremely modest, was very youthful in appearance and endeared himself to all who knew him well by his extremely lovable character. His career was remarkable and offers an example to our young college students, who rarely realize what young men may accomplish by serious interest in their opportunities.

C. F. CHANDLER

### SAMUEL BENEDICT CHRISTY

Samuel Benedict Christy, Dean of the College of Mining of the University of California and a pioneer in the development of the cyanide process for the treatment of refractory ores, died on November 30, 1914, at his home in Oakland, California.

Professor Christy was born in San Francisco on August 8, 1853, and received the degree of Bachelor of Philosophy at the University of California in 1874. After his graduation, he studied mining and metallurgy in the same institution, serving as instructor in analytical Chemistry from 1874 to 1879, and as instructor in mining and metallurgy from 1879 to 1885 when he became Professor of Mining and Metallurgy and proceeded to organize and develop one of the leading Schools of Mining in the world.

Engineers whom he has trained hold positions of great importance all over the world. At one time there were more of his graduates in important positions in South Africa than from all the other American universities put together. The Hearst Memorial Mining Building, built by Mrs. Phoebe A. Hearst some years ago as a mining laboratory for the University of California at a cost of $640,000, embodies Professor Christy's ideas as to equipment for mining and metallurgical instruction.

Possessed of a powerful personality and great charm of manner, he was able to gain the confidence of the public at large as well as to impart to his students something of his own enthusiasm and diligence. In addition to his university duties, he carried on numerous laboratory researches of great interest and value to his profession. These included studies of the Monte Diablo Coals, the quicksilver deposits of California, the mines and works at Almaden, Spain, Idria, Austria, and New Almaden, California—all of which are described in his publications. In 1900 he patented an improved and valuable process for the recovery of gold and silver from dilute cyanide solutions. Other publications include a discussion of the practice of chlorination at the Alaska Treadwell mine; a series of very important papers on the metallurgy of gold, silver and mercury; discussions of the training of mining engineers and the relation of American mining schools to the mining industry; and a noteworthy biographical notice of his friend and colleague, Joseph N. LeConte.

In 1902, Professor Christy was the recipient of the honorary degree of Doctor of Science from Columbia University.

Professor Christy was actively connected with the American Institute of Mining Engineers, the California Academy of Sciences, the Society for the Promotion of Engineering Education, the London Institute of Mining and Metallurgy and was an honorary member of the Chemical, Mining and Metallurgical Society of South Africa.

# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

### METALS IN 1914

Among a vast amount of data on the metal market in this country during the last year published in detail in the New York *Evening Post's* Annual Financial Review (December 31, 1914, p. 13), much was of sufficiently permanent interest to warrant being repeated here. To some extent it amplifies C. H. White's article in the last number of THIS JOURNAL, **7** (1915), 62, but it also covers ground that was not touched on there.

COPPER—In January, 1914, following a year of generally declining tendency, copper stood at about $14^1/_4$ cents, and a little rally dating from the beginning of the holiday season was in evidence. No new copper supplies of any magnitude were immediately in sight, and after Inspiration and Chuquicamata should begin to swell the output about the middle of 1915, nothing more of any consequence was foreseen for a long time.

When the war began, a complete closing of foreign outlets except to England, France, and Russia, with dire results to American copper producers, was prophesied. Yet, as things turned out this was an excellent test of the soundness of the readjustment of the previous three months.

The producers did not budge from their position that in offering copper at 11 c. they were taking less than the cost of production and rather than make any further sacrifice they themselves would finance their accumulation indefinitely. The buying movement that began with copper at 11.1 c. at the first of November continued right through that month, the sales aggregating 100,000,000 pounds or more, and at the end of the month the price was $12^1/_2$ c., or just where it closed at the end of July.

LEAD—The price for lead, January 1, 1914, was 4.15 c., New York, which had been named at the end of December, but this was found to check buying, and on January 9th the price was reduced to 4.10 c. This improved things, and the leading interest named 4.15 c. again at the beginning of February, but for the second time there was a chill, and the independent producers, quick to discern that things were out of joint, began to take at cut prices all the business offering, whereupon the American Smelting and Refining Company reduced to 4 c., the bedrock price in former estimation, but what was subsequently to be regarded as something luscious, and indeed was not to be realized again in 1914. The United States has for many years been a large exporter of Mexican lead refined here in bond, but the novelty of 1914 was the exportation of a very large tonnage of domestic lead.

The situation was helped, moreover, by a reappearance of the foreign demand, which again absorbed large tonnages, remote countries like Japan and Russia, cut off from their previous supplies from Australia and Germany, becoming large buyers.

ZINC—Producers make no claim that the war has adversely affected their business. On the contrary, it lifted them out of an extremely awkward predicament. After a very unsatisfactory year in 1913 the zinc smelters found themselves with an unsold stock of 40,000 tons, which was something larger than ever known before in the history of the industry in this country. The price for spelter was about 5.10 c., St. Louis, which was deemed low, and is, in fact, below what is reasonably to be expected as an average.

During the first quarter of 1914 the market hung around 5 @ $5^1/_4$ c., and then the price began to exhibit an unpleasant habit of dipping below 5 c. Production continued large and demand poor, wherefore stocks increased still further. Finally a few of the producers gave up in disgust and closed certain of their plants, but this was not a general movement, and, what was done was too feeble to be a corrective of a bad situation. As the mid-year approached, the common idea in the business was that the stock had increased to 50,000 tons. The price at that time was about $4^7/_8$ c.

The situation had been bad in Europe also, where a stock of about 45,000 tons at the beginning of the year had risen to about 100,000 tons at the middle, in spite of a curtailment of about 18 per cent in production, which the International Convention made effective on May 1st. This huge European stock was held chiefly in Germany, a very important thing, as was subsequently to appear.

On that fateful first of August the first thought in the zinc business was that England, deprived of her German and Belgian supplies, would have to buy spelter in America, especially inasmuch as the great accumulation of the Convention was piled up in Germany. In fact, England did within a week or two begin to buy spelter. England, Russia, Japan, South Africa, and other unusual customers bought spelter here, and within a few days the price jumped to 6.10 c. on export sales, while the same sellers on the same day sold to domestic consumers at $4^7/_8$ c., and were glad to do so.

At this point the export business culminated, purchases having amounted to about 25,000 tons and England having overbought herself, and becoming able to obtain some supplies from Rotterdam, the price here declined almost as rapidly as it had risen, within a few weeks was back at 4.80 c. and pessimism reigned again. But after a while foreigners began to buy again, soberly, steadily, and judiciously, and ultimately this put up the price here to about $5^1/_2$ c., and there was some reason to believe that the market might be held at that level, although right up to the end of the year domestic consumers were poor buyers.

SILVER—In March it was estimated that the available stock in London and in the East was about 8,000,000 ounces less than at the beginning of the year, and early in April it became known that the London syndicate had closed out its holdings. The silver market then naturally began to acquire a little more tone. By the early part of May a price of 27 3-16 d. in London was reached, the Mexican troubles of that time being a contributory bullish influence. About $2,000,000 worth of silver—chiefly from Cobalt—went down in the Empress of Ireland. In June the silver market turned dull and declining upon reduced demand from India and China, and at the mid-year the price was $25^7/_8$ d. In the latter part of July selling by Chinese banks caused a rapid decline to about 24 d.

On August 1st official quotations for silver, both in London and New York, were suspended. On August 8th the official price at London was reëstablished at 26 d., but this was for spot transactions only. An official quotation of 26 d. warranted a New York quotation of 52 c. only, the cost of freight and war insurance added to the usual charges, then amounting to $6^1/_4$ c. per ounce.

GOLD—Statistics will show undoubtedly a decrease in the world's production of gold in 1914. Anyway, we know that the Rand and Australia have made reduced outputs, while the troubled conditions in the United States, Russia and Mexico must have operated in the same way. The prompt suppression of the rebellion in South Africa of course removed the danger of interference with mining there.

In gold mining the greatest scare produced by the war is with respect to the supply of potassium cyanide, which heretofore has come to a large extent from Germany. The fear was relieved, however, by the announcement of the sole American producer that he would be able to take care of the domestic requirements, while the English producers saw to it that there was no shortage in the British colonies. The requirements of Mexico were unprovided for, but were not large, owing to the previous suspension of mining there, and after a while it became possible to get some cyanide from Germany, one cargo of 1,000 tons reaching here. Several parties considered the manufacture of cyanide in this country, but apparently did not think it worth while.

TIN—In January, 1913, the price of tin in New York was about 50 c. per pound, and it had begun to look as if even a higher price might be realized, owing to shortage in the supplies, but contraction in consumption more than offset any shortage, and the general tendency throughout 1913 was declining, the price at the end of that year being about $37^1/_2$ c.

The outbreak of the war caused a tremendous scare about tin supplies, all of which come by sea and were thought likely to be cut off entirely. The price rose for the small quantity of tin actually in stock in New York, 75 c. per pound even being realized. This represented, however, what was merely picayune business—1- to 5-ton lots—and was in nowise representative of a broad commodity price.

In September tin was down to a basis of about $32^1/_2$ c. per pound, and in October it was about $30^1/_4$ c. In November and December it was a few points higher. The position of tin seems to be that the high prices of two years ago stimulated production, while consumption has diminished along with the general contraction of business experienced in the United States in 1913 and 1914.

IRON—In January, 1913, Bessemer pig iron at Pittsburgh averaged $18.15; in December, $15.71. In January, 1914, the average was $14.94; from that time on the monthly averages were steady at about that figure, but in October a declining tendency was manifest and in December the average was probably somewhere about $14^1/_2$ @ $14^5/_8$. The average for 1914 will be more than $2 per ton below the average ($17.09) of 1913.

The following data are from *Iron Age:*

| | 1912 | 1913 | 1914 |
|---|---|---|---|
| January | 2,057,911 | 2,795,331 | 1,885,054 |
| February | 2,100,815 | 2,586,337 | 1,888,670 |
| March | 2,405,318 | 2,763,563 | 2,347,867 |
| April | 2,378,436 | 2,752,761 | 2,269,955 |
| May | 2,512,583 | 2,822,217 | 2,092,686 |
| June | 2,440,745 | 2,628,565 | 1,917,783 |
| July | 2,410,889 | 2,560,646 | 1,957,645 |
| August | 2,512,431 | 2,545,763 | 1,995,261 |
| September | 2,463,839 | 2,505,927 | 1,882,577 |
| October | 2,689,933 | 2,546,261 | 1,783,045 |
| November | 2,630,854 | 2,233,603 | 1,518,316 |
| December | 2,782,737 | 1,983,607 | 1,500,000(a) |

Comparison of the average daily rate of production, in gross tons, is as follows:

| | 1910 | 1911 | 1912 | 1913 | 1914 |
|---|---|---|---|---|---|
| Jan | 84,148 | 56,572 | 66,384 | 90,172 | 60,808 |
| Feb | 85,616 | 64,090 | 72,442 | 92,369 | 67,453 |
| Mar | 84,459 | 70,036 | 77,591 | 89,147 | 75,738 |
| April | 82,792 | 68,836 | 79,181 | 91,759 | 75,665 |
| May | 77,102 | 61,079 | 81,051 | 91,039 | 67,506 |
| June | 75,516 | 59,585 | 81,358 | 87,619 | 63,916 |
| July | 69,305 | 57,841 | 77,738 | 82,601 | 63,150 |
| Aug | 67,963 | 62,150 | 81,046 | 82,121 | 64,363 |
| Sept | 68,476 | 65,903 | 82,128 | 83,531 | 62,753 |
| Oct | 67,520 | 67,811 | 86,772 | 82,133 | 57,518 |
| Nov | 63,659 | 66,648 | 87,695 | 74,453 | 50,611 |
| Dec | 57,349 | 65,912 | 89,766 | 63,987 | 55,000(a) |

(a) Estimated.

## THE RENNERFELT ELECTRIC FURNACE

A new Swedish invention in the field of electric smelting or refining, Mr. Ivar Rennerfelt's furnace, differs from all types which up to the present time are in operation [*Engineering* (London), **98** (1914), 638]. Its practical merits have demonstrated themselves very quickly, and it has met with much attention in Sweden and abroad.

The first Rennerfelt electric furnace was constructed at Hallstahammar, in Sweden, in the year 1912, and it worked

FIG. 1

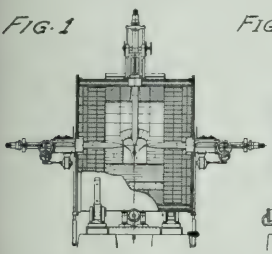
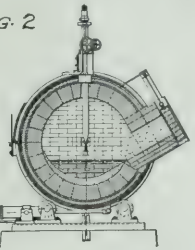


FIG. 2



so satisfactorily that within a year a steel foundry with four electric furnaces was erected at the place (and orders have been received also from the neighboring countries), the furnaces in question varying in size from 300 kg. to 3 tons. The manufactures for which the furnaces already in operation are applied comprise steel castings, iron castings, tool steel, electro-steel from pig-iron and ore, refined steel from liquid charges, etc.

In order to put in a few words the special features of this furnace, it may be described as an economical small furnace for crucible works, steel foundries, copper alloys, and chemical processes requiring a high temperature.

The Rennerfelt furnace is preferably built with a horizontal, cylindrical steel shell, with longitudinal axis, and it turns cradle-fashion, or is tilted round a horizontal-diametrical axle. It is lined with silica, carbon, or magnesite brick, according to the uses to which it is to be put. A charging and casting-door, closely fitting, is placed in one side or in each end of the furnace (Figs. 1–4).

The electric current is transmitted by means of three electrodes, one descending vertically through the top of the roof, and two horizontal, one at each side or end. The positions and arrangement of the electrodes will be seen from the illustrations.

When the furnace is used for melting light scrap, requiring a fair amount of space below the arcs prior to melting, vertically-adjustable electrodes are to be preferred. This is a special feature of the Rennerfelt furnace, and enables the operator to run the furnace with free-burning arcs, independent of the volume of the charge, or with the arcs in contact with the metal, in case he desires to employ the method of heating as used in the different types of arc furnaces previously constructed.

In ordinary working, the electrodes do not come in contact with the slag or steel, the arcs being free burning. This ensures unusually smooth working when melting cold scrap, which always has been a difficult operation, especially in cases where the furnace receives the electric energy from a power plant of limited capacity. As to the nature of the energy, a three-phase current of any voltage or frequency is passed into a transformer arranged for Scott's method of phase transformation, transforming the received energy into a balanced two-phase current (or two-phase current may be directly generated) delivering a single-phase current to each of the horizontal electrodes. A return cable (Fig. 5) connects the common point of the two phases with the central electrode.

The currents entering through the horizontal electrodes neutralize one another, but the action of the returning current into the central electrode generates a field of force which deflects the arc downwards to the bath, thus forming the arcs into an inverted arrowhead, or *fleur-de-lys*. The heat generated in the arcs is here, more than in any other furnace, concentrated down upon the bath, though the electrodes do not touch, or even approach, the slag or the metal. The height of the arcs from the points of the electrodes to the surface of the bath can be adjusted, but it is usually kept at about 6 in. to 12 in.

In operation the charge is rapidly melted and covered by a thin, but unbroken, sheet of slag, which serves as a protection against any oxygen that may be present in the furnace. As a rule, however, the atmosphere is neutral or strongly reducing, being charged with carbon monoxide, for the outside air is not admitted during the melting and refining. When ready the steel is poured into a ladle, and that at a much higher temperature than is obtainable in an open-hearth furnace. It is therefore often necessary to keep the steel in the ladle while it cools down to a temperature at which it can be safely cast without burning the moulds or spoiling the castings. Perfect deoxidation is thus easily obtained, ensuring unusually good castings or ingots free from blowholes or piping.

One steel-melter and two men or boys per shift can work a furnace of several tons capacity, turning out as much as 20 to 30 tons within 24 hours. The lining is threefold: first an insulating lining of asbestos board, then silica or first-quality bricks in rings against the former, and this again forms the bedding for the actual inner lining—acid or basic. This is made of special bricks, which do not require any cutting, and are set in rings of different diameters, so as to form an egg-shaped interior melting-chamber. The electrodes enter into the furnace through circular openings, formed by special bricks. To facilitate relining, the cylindrical shell is divided into an upper and a lower half, the two being bolted together, when lined, and the cost of renewal of lining is stated to be exceedingly low.

The electrodes are held with what may be called a loose but practically gas-tight fit in water-cooled insulated holders of phosphor-bronze or copper, those for the horizontal electrodes preferably being adjustable in the vertical plane. The cables are attached to the electrode-holders, the current being transmitted to the electrodes themselves through sliding contacts or brushes. The size of the electrodes varies from $1^1/_2$ in. to 7 in. for the largest furnace, fitted with several sets coupled in parallel.

Assuming the ingoing current at each side electrode to be I amperes, then the current passing the central electrode will equal $I\sqrt{2}$ amperes, provided that the power on the two-side electrodes is perfectly balanced, as is generally the case. In the same way, if we assume the voltage across the central electrode and each side electrode to be E volts, then the voltage between the side electrodes will equal $E\sqrt{2}$ volts.

With regard to efficiency, a small furnace of 600 kg. at the

FIG. 3

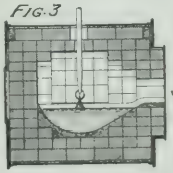


FIG. 4

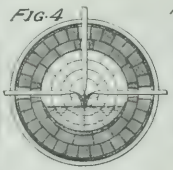
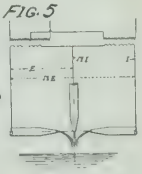


FIG. 5



Ljusne Iron Works, in Sweden, illustrated in Figs. 3 and 4, will melt and refine a full charge of cold scrap with not more than 700-kw. hours per ton. The normal rating of a furnace of this capacity is 125 kw., but 82 kw. to 90 kw. have been shown to be sufficient to complete a 500-kg. heat in five hours, indicating a very satisfactory thermal efficiency even when running with only 75 per cent of full load. White pig-iron has been melted in the same furnace under similar conditions with an average of 405 kw.

hours per ton. With 425 kw. hours per ton, gray pig-iron has been melted and overheated, the melting including 22 kg. basic slag per ton of iron. This consumption of energy indicates a furnace efficiency of about 70 per cent, but the thermal efficiency has been as much as 85 to 90 per cent.

## QUALITY OF SULFATE OF AMMONIA FOR EXPORT

Speaking editorially of the English situation the *J. Gas Lighting* says [128 (1914), 404]:

We cannot afford—either at the present time with nitrate of soda in active competition, nor in future when Germany resumes her operations in the export market—to spoil our position as exporters of sulfate of ammonia by producing an article which does not come up to the standard that is demanded by customers, and which arrives at its destination in a condition, as regards weight and packing, which is anything but conducive to permanence of business relations. An important letter upon the subject from Mr. D. Milne Watson, the Chairman of the Sulfate of Ammonia Association, and a circular which has been distributed among the members, are published in today's issue of the Journal. Both are in the nature of a warning; and the one emphasizes the other. It is hoped that they will have due and immediate effect, because appeal and caution in the past appear to have been in vain. The matter was one to which Mr. Thomas Milne addressed himself at the Sulfate of Ammonia Conference a year ago. He then urged sulfate of ammonia makers not to produce the commodity under a standard of 25 per cent of ammonia, about 2.5 per cent moisture, and not more than 0.5 per cent acid. In Mr. Milne Watson's letter, and in the circulated leaflet, we get the appeal repeated, with the difference that "not more than 3 per cent moisture" is mentioned.

What is found is, and it is a serious disadvantage to the sulfate of ammonia export business, that the bulk of the British production is still made and marketed on a basis of 24 per cent of ammonia, without any mention of moisture and free acid. This condition of things will not do. Nearly all distant consumers have raised their standard from 24 to 25 per cent ammonia; and when they find this standard is not complied with, that there is a loss in weight of 1 to 3 per cent through excessive moisture content, and that the bags in which the sulfate of ammonia is packed, through excess of free acid and moisture, have *en route* declined to maintain their integrity, then they become greatly dissatisfied, and do not need further inducement to turn to sources from which they know their requirements can be fulfilled. The losses fall upon the receiver; and he is indisposed to continue to bear them when there is no reason why he should do so. British producers know how much they depend upon the export market; and it will be suicidal on their part not to recognize what is essential in the matter of quality in order to ensure the market for themselves, and not be driven out of it by continued shortsightedness. Directly the war is over Germany will recommence operations for the development of her export trade. The competition of synthetic ammonia—the production from the nitrogen of the atmosphere—will come into the reckoning again with full force. It will not be surprising, too, to find at the close of the war that Germany will have a decent accumulation of stock with which it will be very pleased to part. The absence of German competition is the opportunity for the British producer to fortify his position abroad; and the best way to do so is to give purchasers the standard material they want, and see that it gets into their hands in good condition and with as little loss of weight as possible. The future of the export market very largely depends upon the action taken in the present. Therefore, the necessity for heeding the warning of Mr. Milne Watson, and complying with the enjoinment contained in both letter and circular, is apparent.

## DANISH ENGINEERS AND THE UNITED STATES

For a considerable number of years Danish engineers, with diplomas from the State Polytechnic College in Copenhagen, have gone to the United States or other parts of the world. According to *Engineering*, 98 (1914), 753, the Danish Society of Engineers has recently looked into this matter, and it has transpired that out of 933 engineers who, during the years 1900–1912 (both included), passed the final examination of the above college, 10 per cent, or, to be accurate, 92 engineers, have gone to North America, and out of these 28 have subsequently returned to Denmark. The largest proportion is among "constructive engineers," of whom about 12 per cent have gone to the United States, while the figure for "factory engineers" is only 4 per cent. All the electrical engineers have remained in America, while two-thirds of the mechanical engineers have returned. Out of six factory engineers, only one has returned; and of 64 constructive engineers, 47 have remained in America.

## CONSUMPTION OF GAS IN ITALY

A recent issue of the *Journal für Gasbeleuchtung* quoted from an Italian paper on acetylene some figures as to the consumption of gas, electricity, petroleum, and calcium carbide in Italy for three years past. The English equivalents of the figures are as follows:

| | Coal Gas | Electricity Board of Trade | Petroleum | Carbide |
|---|---|---|---|---|
| | Cubic feet | units | Tons | Tons |
| 1910–11..... | 9,182,056,000 | 1,460,000 | 83,392 | 23,156 |
| 1911–12..... | 9,358,634,000 | 1,649,000 | 117,337 | 24,913 |
| 1912–13..... | 9,888,368,000 | 1,826,000 | 111,420 | 20,816 |

Though all four classes of illuminants exhibit an increase in the second year over the first, in the last year only coal gas and electricity continue to show an advancing consumption.

Evidently the figures given for coal gas refer only to gas used for lighting and heating, since, according to a table given in W. J. A. Butterfield's lectures on "Chemistry in Gas-Works," the total consumption of gas in Italy in 1910 was 11,985 million cubic feet. But excluding from this total the gas used for industrial purposes, that used for lighting and heating only was in 1910, 9024 million cubic feet.

Peat gas is also used and now that the regions of Mantua and Ferrara have been drained, it has become possible to work the peat bogs below sea-level. A company has accordingly been formed, and works erected, for the production of gas and the recovery of residuals by the Mond process. According to a description in the *Monitore Tecnico*, two bogs, one 1730 and the other 1235 acres in extent, are being worked. The thickness of the bed of peat varies from 1 ft. 8 in. to 3 ft. 3 in. After being dried, the peat is carbonized in six retorts, the capacity of each being 30 metric tons per 24 hours, with a daily production of about a million cubic feet of gas having a heating value of 155 B. T. U. per cu. ft. At the same time 120 quintals of sulfate of ammonia are obtained. There are also adjoining works for the manufacture of the sulfuric acid required for making the sulfate. Large quantities of tar are also produced. The works cover an area of 22 acres. The results are stated to have been satisfactory, from both the technical and the financial point of view.

## PATENTS IN WAR TIME

There have now been heard in England in what have been named the Patents Court quite a number of applications to "avoid or suspend" enemy patents, under the Act which was recently passed for the purpose of regulating this important industrial question. At the outset, naturally, there was doubt as to what would be the attitude adopted in official quarters on particular points; and this, of course, was an uncertainty which could be set at rest only by seeking decision on individual ap-

plications. In connection with the first hearings, the Comptroller-General of Patents gave, as has already been recorded, some indication as to what was likely to be the view taken by those in control [*J. Gas Lighting*, 128 (1914), 406]. After remarking that it would not be fair to deprive a German patentee of his property, he said that, generally speaking, the recommendation the Court would make would probably be that some kind of license should be given; and this license would in all likelihood be subject to a royalty. Now an official notice has been issued for the information of the public, which will be useful to intending applicants, as it sets forth the broad principles on which the Board of Trade will act in dealing with requests for the avoidance or suspension of patents and trade-marks under the "Temporary Rules" of this year. With regard to patents, licenses will, it is stated, as a general practice be granted when the applicants fulfil the conditions laid down in the Act: (1) where there is no manufacture in this country under the patent, and also (2) where what manufacture there may be is carried on by a company or firm on behalf of alien enemies resident abroad, and there is any reason to doubt that the manufacture will continue to be carried on, or where it is in the interests of the country that some other manufacture should be started in the British interests. As a rule, suspension of trade-marks will be granted only: (1) where the trade-mark is the name of a patented article, and a license is granted under the patent protecting it; (2) where it is the only name, or only practicable name, of an article manufactured under an expired patent; or (3) where it is the name, or only practicable name, of an article manufactured in accordance with a known process or a formula which has been published or is well known in trade. Generally speaking, suspension will not be granted in the case of pictorial devices. It is pointed out that, while these principles may be taken as broadly applicable, special cases must, of course, necessarily receive exceptional treatment.

# NOTES AND CORRESPONDENCE

## CONCERNING THE NUTRITIVE VALUE OF VEGETABLE IVORY—PRELIMINARY NOTES

The nut of the vegetable ivory palm (*Phytelephas macrocarpa*) is imported by the United States in large quantities to be used in the manufacture of buttons. Statistics show that the annual consumption is about 10,000 tons and is valued at $1,500,000.

In the process of manufacture there is considerable waste which occurs in the form of chips and sawdust. The latter is frequently finely ground and constitutes the so-called vegetable ivory meal.

At the suggestion of Dr. J. B. Lindsey, a study has been made, incidentally on the chemistry of this product, and more particularly of its digestibility and feeding value, especially for dairy animals. In addition to the ordinary fodder analysis, traces of invert sugar were found and some 2.14 per cent of pentosans. Galactan was not found. The larger part of the vegetable ivory waste is known to consist of mannan which upon hydrolysis yields mannose. Phenylhydrazine yielded the usual buff-colored precipitate, a mixture of mannose- and other phenylhydrazones, with a melting point of 183°. Of the small amount of nitrogen present, about one-third was found to be in the amino form.

A digestion experiment carried out with sheep indicated that these animals were capable of digesting about 87 per cent of dry matter. A feeding experiment was conducted with six cows using a basal ration of bran, cottonseed meal, and hay, and in addition either three pounds of corn meal or three pounds of vegetable ivory meal. The cows did well on both rations and produced within three per cent as much milk on the vegetable ivory ration as on the corn meal ration. The digestion experiment, together with the feeding experiment, indicates that this material, in spite of its tough, horny nature, possesses considerable nutritive value and confirms the feeding experiments carried out in Germany.

It is proposed to continue the investigation of this product and to publish the full results at a somewhat later date.

C. L. Beals

Massachusetts Agricultural Experiment Station
Amherst, January 11, 1915

## ANNUAL MEETING OF THE AMERICAN CHEMICAL SOCIETY—1915

The 1915 Annual Meeting of the American Chemical Society will be held in Seattle, August 31st to September 3rd, inclusive. Following the meeting in Seattle, the Society will adjourn to San Francisco for a social function with the San Francisco Chemists, probably on Monday evening, September 6th. Arrangements will be made for special trains *via* Seattle.

## NITROGEN-PROTEIN TABLE

*Editor of the Journal of Industrial and Engineering Chemistry:*

The accompanying table may be of service to chemists performing a large number of feed analyses, etc.

Column 1 gives cc. of $N/20$ acid used.

Column 2 gives the corresponding amount of nitrogen in centigrams or as per cent on a 1 gram sample.

Columns 3 and 4 give protein in centigrams (or per cent on a 1 gram sample) for the factor heading the column.

| 1 Cc. $N/20$ Acid | 2 N | 3 Protein × 5.7 | 4 Protein × 6.25 | 1 Cc. $N/20$ Acid | 2 N | 3 Protein × 5.7 | 4 Protein × 6.25 |
|---|---|---|---|---|---|---|---|
| 25.0 | 1.7513 | 9.982 | 10 945 | 42.5 | 2.9771 | 16.970 | 18.607 |
| 25.5 | 1.7863 | 10.182 | 11.164 | 43.0 | 3.0122 | 17.169 | 18 826 |
| 26.0 | 1.8213 | 10.381 | 11.383 | 43.5 | 3.0472 | 17.369 | 19.045 |
| 26.5 | 1.8563 | 10.581 | 11.602 | 44.0 | 3.0822 | 17.569 | 19.264 |
| 27.0 | 1.8914 | 10.781 | 11.821 | 44.5 | 3.1172 | 17.768 | 19.483 |
| 27.5 | 1.9264 | 10.980 | 12.398 | 45.0 | 3.1523 | 17.968 | 19.702 |
| 28.0 | 1.9614 | 11.180 | 12.259 | 45.5 | 3.1873 | 18.167 | 19.920 |
| 28.5 | 1.9964 | 11.380 | 12.478 | 46.0 | 3.2223 | 18.367 | 20.139 |
| 29.0 | 2.0315 | 11.579 | 12.697 | 46.5 | 3.2573 | 18.567 | 20.358 |
| 29.5 | 2.0665 | 11.779 | 12.915 | 47.0 | 3.2924 | 18.766 | 20.577 |
| 30.0 | 2.1015 | 11.979 | 13.134 | 47.5 | 3.3274 | 18.966 | 20.796 |
| 30.5 | 2.1365 | 12.178 | 13.353 | 48.0 | 3.3624 | 19.166 | 21.015 |
| 31.0 | 2.1716 | 12.378 | 13.572 | 48.5 | 3.3974 | 19.365 | 21.234 |
| 31.5 | 2.2066 | 12.577 | 13 791 | 49.0 | 3.4325 | 19.565 | 21.453 |
| 32.0 | 2.2416 | 12.777 | 14.010 | 49.5 | 3.4675 | 19.765 | 21.672 |
| 32.5 | 2.2766 | 12.977 | 14.229 | 50.0 | 3.5025 | 19.964 | 21.891 |
| 33.0 | 2.3117 | 13.176 | 14.448 | 50.5 | 3.5375 | 20.164 | 22.110 |
| 33.5 | 2.4367 | 13.376 | 14.667 | 51.0 | 3.5726 | 20.364 | 22.328 |
| 34.0 | 2.3817 | 13.576 | 14.886 | 51.5 | 3.6076 | 20.563 | 22.547 |
| 34.5 | 2.4167 | 13.775 | 15.105 | 52.0 | 3.6426 | 20.763 | 22.766 |
| 35.0 | 2.4518 | 13.975 | 15.323 | 52.5 | 3.6776 | 20.962 | 22.985 |
| 35.5 | 2.4868 | 14.175 | 15.542 | 53.0 | 3.7127 | 21.162 | 23.204 |
| 36.0 | 2.5218 | 14.374 | 15.761 | 53.5 | 3.7477 | 21.362 | 23.423 |
| 36.5 | 2.5568 | 14.574 | 15.980 | 54.0 | 3.7827 | 21.561 | 23.642 |
| 37.0 | 2.5919 | 14.774 | 16.199 | 54.5 | 3.8177 | 21.761 | 23.861 |
| 37.5 | 2.6269 | 14.973 | 16.418 | 55.0 | 3.8528 | 21.961 | 24.080 |
| 38.0 | 2.6619 | 15.173 | 16.637 | 55.5 | 3.8878 | 22.160 | 24.299 |
| 38.5 | 2.6969 | 15.372 | 16.856 | 56.0 | 3.9228 | 22.360 | 24.518 |
| 39.0 | 2.7320 | 15.572 | 17.075 | 56.5 | 3.9578 | 22.560 | 24.736 |
| 39.5 | 2.7670 | 15.772 | 17.294 | 57.0 | 3.9929 | 22.759 | 24.955 |
| 40.0 | 2.8020 | 15.971 | 17.513 | 57.5 | 4.0279 | 22.959 | 25.174 |
| 40.5 | 2.8370 | 16.171 | 17.731 | 58.0 | 4.0629 | 23.159 | 25.393 |
| 41.0 | 2.8721 | 16.371 | 17.950 | 58.5 | 4.0979 | 23.358 | 25.612 |
| 41.5 | 2.9071 | 16.570 | 18.169 | 59.0 | 4.1330 | 23.558 | 25.831 |
| 42.0 | 2.9421 | 16.770 | 18.388 | 59.5 | 4.1680 | 23.757 | 26.050 |
| .... | ..... | ..... | ..... | 60.0 | 4.2030 | 23.957 | 26.269 |

| Tenths Cc. | N |
|---|---|
| | Protein |
| | × 5.7 |
| 0.1 | 0.0070 |
| 0.2 | 0.0140 |
| 0.3 | 0.0210 |
| 0.4 | 0.0280 |
| 0 5 | 0.0350 |
| 0.6 | 0.0420 |
| 0.7 | 0.0490 |
| 0.8 | 0.0560 |
| 0.9 | 0.0630 |
| | Protein |
| | × 5.7 |
| 0.1 | 0.040 |
| 0.2 | 0.080 |
| 0.3 | 0.120 |
| 0.4 | 0 160 |
| 0.5 | 0.200 |
| 0.6 | 0.240 |
| 0.7 | 0.279 |
| 0.8 | 0.319 |
| 0.9 | 0.359 |
| | × 6.25 |
| 0.1 | 0.044 |
| 0.2 | 0.088 |
| 0.3 | 0.131 |
| 0.4 | 0.175 |
| 0.5 | 0.219 |
| 0 6 | 0.263 |
| 0.7 | 0.306 |
| 0.8 | 0 350 |
| 0.9 | 0.394 |

The last column is for interpolating values corresponding to tenths of a cubic centimeter.

R. S. Callaway

Listman Mill Company
LaCrosse, Wis., November 30, 1914

## BENZOL PRODUCTS IN THE UNITED STATES

*Editor of the Journal of Industrial and Engineering Chemistry:*

With reference to numerous inquiries concerning the history and present condition of our company we beg to submit the following information:

The Benzol Products Company was organized in 1910 for the manufacture of aniline oil and other benzol derivatives, but of

the many derivatives that might have been manufactured from benzol it has confined its attention to the production of aniline oil, aniline salt and nitrobenzol. In each of these three instances it has been in competition with Europe only and has produced exclusively from American benzol these three products of a quality equal, if not actually superior, to the European product.

The progress of the company has been seriously retarded through inability to get sufficient crude benzol and by the state of the existing anti-trust laws in the United States which, while regulating American industries, permit the European manufacturer and importer to conduct his business without regard to the same restrictions, and to pursue unfair methods of competition and systematic underselling.

Benzol, a by-product of coke, is the raw material for aniline and aniline is the raw material for a vast number of dyes and the base of many medicinal products. The Benzol Products Co. was inaugurated therefore for the purpose of supplying what might be called the raw materials for the coal-tar dye and chemical industries, with no intention of entering directly into the dye color or medicinal industry.

America imports aniline oil and salt to the value of about $1,000,000 per annum, and it is anticipated that the consumption would increase greatly were the color manufacturer and consumer to be furnished with aniline at a low price and of satisfactory quality.

The lack of crude benzol is not likely to be permanent. This country distils twice as much coal for the purpose of making coke as Germany produces, and an assured demand for benzol will result in the recovery of an ample supply of benzol. It should, therefore, be clearly understood by the consumer of dyes and colors that his insistence upon an American supply of dyestuffs bears on the steel industry because this is the industry which, by substituting by-product coke ovens for beehive ovens, is able to enlarge the supply of so valuable a by-product as benzol.

This company demonstrated its ability to succeed at the prices prevailing prior to 1910, but no sooner had it started than the foreign cartel lowered the price of aniline here to a point much below the European price.

The unfair methods referred to are those which tend to permit European producers to compete through the agency of cartels and combinations in restraint of trade, for the purpose of destroying or preventing the establishment of an industry in the United States.

The legislation of our Government has failed to recognize the international nature of competition and its laws apparently do not apply to a foreign trust in the sense that they do to the American manufacturer, so that the foreign manufacturer or importer, through trust, cartel or convention, has been led to pursue tactics which have made the development of our industry impracticable and profitless.

The war has changed all of this for the moment and the consumer is now willing to pay remunerative prices, since the supply is inadequate to satisfy the demand. To relieve this situation the Benzol Products Company has acquired a tract of land at Marcus Hook, Pa., in order to build a new works, and it hopes within the next six months to be in a position to furnish an important part of the country's needs. It is risking its capital in this way, notwithstanding its previous bitter experience from unfair competition, in the confidence that before the war ends the law will have been amended so as to give the same protection against the unfair practices of the foreign manufacturer as against those of the domestic competitor.

It is our belief that the permanent establishment of this industry will depend absolutely on such change in the law. The development of this industry will also depend on the consuming public's support and coöperation and insistence upon American-made aniline oil and aniline dyes. The establishment of a real aniline dye color industry in this country is an herculean task at best.

BENZOL PRODUCTS COMPANY
*Per* HENRY WIGGLESWORTH, *Vice-President*

25 BROAD STREET, NEW YORK
January 20, 1915

## SEARLES LAKE POTASH—A CORRECTION

*Editor of the Journal of Industrial and Engineering Chemistry:*

Mr. Edward E. Free, of Baltimore, Md., in a letter dated January 18, 1915, calls my attention to an error which I made in my remarks about the Searles Lake potash in an address on "The Effects of the European War on the Agricultural Industries of the United States," at a meeting of the American Chemical Society held recently in Boston. [See THIS JOURNAL, **7** (1915), 59]. Mr. Free writes:

"The original Government estimate of the amount of potash in this deposit was made in March, 1912, by Mr. H. S. Gale of the U. S. Geological Survey and myself. On March 21, 1912, the Geological Survey and the U. S. Bureau of Soils issued identical press bulletins announcing the essential facts of the estimates made by Mr. Gale and myself. I quote from these bulletins: * * * ' the total amount of potassium oxide is estimated at over 4,000,000 short tons. This estimate is believed to be conservative, and the available tonnage may well be expected to exceed 10,000,000 tons, which would supply the country, at the present rate of consumption of potash, for thirty years.' So far as I am aware this estimate has never been publicly questioned by any Government official and, indeed, all information which I have since obtained concerning the property inclines me to the belief that even the estimate of ten million tons is conservative.

"These estimates are on the basis of potassium oxide ($K_2O$). They correspond, therefore, to over six million tons of potassium chloride or about seven million tons of the usual commercial salts of the best grade. Your estimate in the article above cited is over ten times too small."

I am glad to call attention to this correction.

W. H. BOWKER

AMERICAN AGRICULTURAL CHEMICAL CO.
BOSTON, January 20, 1915

## SODIUM ALIZARINSULFONATE AS AN INDICATOR IN AMMONIA TITRATIONS IN NITROGEN DETERMINATIONS

*Editor of the Journal of Industrial and Engineering Chemistry:*

I should like to call the attention of Agricultural and Food Chemists to the advantages of Sodium Alizarinsulfonate as an indicator in the titration of Ammonia in nitrogen estimation. A full discussion of its advantages will be found in Technologic Paper No. 34 of the Bureau of Standards, entitled "Determination of Ammonia in Illuminating Gas," and as this is somewhat out of the line of Food Chemists' work, I feel it is well worth while to call their attention to the use of this indicator. It is easily and quickly prepared, sensitive and economical.

An abstract of the above-mentioned publication appeared in THIS JOURNAL, **6** (1914), 468.

R. S. CALLAWAY

LISTMAN MILL CO.
LA CROSSE, WIS., January 12, 1915

# PERSONAL NOTES

The Perkin Medal was conferred upon Edward Weston, LL.D., D.Sc., for his researches and valuable contributions to the field of applied chemistry at the regular meeting of the New York Section of the Society of Chemical Industry, held in Rumford Hall, Chemists' Building, New York, on January 22nd. The presentation address was made by Prof. Chas. F. Chandler, senior past-president of the Society of Chemical Industry residing in the United States. After the speech of acceptance by Dr. Weston, addresses were made by Dr. L. H. Baekeland and Dr. Carl Hering. A full report of the proceedings and speeches will be published in the March issue of THIS JOURNAL.

Dr. David White, retiring president of the Washington Academy of Sciences, addressed the Academy on "Some Relations in Origin between Coal and Petroleum," on January 14th.

Prof. S. F. Acree, of the Johns Hopkins University, has accepted the position of chief of the Section of Derived Products in the Forest Products Laboratory in Madison, and professor of the chemistry of forest products in the University of Wisconsin.

Dr. Arthur L. Day, director of the Geophysical Laboratory, Washington, D. C., spoke on "The Volcano Kilauea in Action," before the Syracuse Section of the A. C. S., on January 5th.

Dr. E. S. Johnson, of the Solvay Process Company, addressed the Syracuse Section of the A. C. S. on "Aniline and Its Technical Applications," at a special meeting, January 29th.

The name of the Standard Testing Laboratory, Board of Estimate and Apportionment, City of New York, has been changed to the Central Testing Laboratory, Board of Estimate and Apportionment, City of New York. This laboratory is located at 125–127 Worth Street.

Dr. Kurt Gebbard, of Freiburg in Baden, Germany, one of the most brilliant of the younger textile chemists, died in service in October, 1914. Dr. Gebbard was a Lieutenant of Reserves in the 61st Regiment of Field Artillery. Although just past his 30th birthday, he had published numerous articles on the light-fastness of dyed fabrics and on photochemistry. These appeared principally in the *Faerber-Zeitung* and in the *Journal für praktische Chemie.*

The fourth regular meeting of the Maryland Section of the A. C. S. was held in Baltimore on January 16th, with the following program: "The Estimation of Yellow Phosphorus in Pharmaceutical Preparations," by Dr. H. Englehardt, of Sharp and Dohme; "The Action of Fruit Products on Tin Plate and the Preparation of Stannous Glycocollate," by F. F. Fitzgerald, of the National Canners Association Laboratory.

Dr. Henry B. Kümmel, State Geologist of New Jersey, presented a paper entitled, "The Geology of Trenton in Relation to Commercial Development and Engineering Problems," before a meeting of the Engineers' Club of Trenton on January 14th.

The professors of chemistry of the Ohio State University gave a complimentary dinner on December 18th to Mr. John J. Miller, who recently retired from the editorship of *Chemical Abstracts.*

Prof. Cyril G. Hopkins, of the College of Agriculture, University of Illinois, addressed the January meeting of the University of Illinois Section of the A. C. S., on the 18th. His topic was "Problems in the Development of Southern Agriculture."

Dr. Johan Hjort, director of Fisheries of Norway, addressed a joint meeting of the Washington Academy of Sciences and the Biological Society, on January 19th, on "Migrations and Fluctuations of the Marine Animals of Western Europe."

Sir Ernest and Lady Rutherford and Miss Eileen Rutherford spent a week in Montreal on their way home from New Zealand. Sir Ernest addressed the Physical and Chemical Societies of McGill University at a joint meeting on December 23rd, on "The Spectrum of X-rays and Gamma-rays."

The American Institute of Mining Engineers, the American Electrochemical Society and the Mining and Metallurgical Society of America gave a complimentary dinner on Friday, January 15th, at the Hotel Plaza, New York City, to Dr. Frederick Gardner Cottrell, in charge of the San Francisco laboratory of the Bureau of Mines, in recognition of his contributions to research.

Prof. E. A. Ruddiman spoke on "Notes on the Deterioration of Hydrogen Dioxide Waters and the Effect of Acetanilide as a Retarding Catalyst," before the 30th meeting of the Nashville Section of the A. C. S. on January 15th.

Dr. Arthur H. Elliott announces that he has opened an office as consulting engineer and chemist at 30 Church Street, New York City.

Dr. E. P. Wightman, of Washington University, addressed the St. Louis Section of the A. C. S. on January 11th, on "Some Facts Concerning the Chemistry of Photography with Reference to the Photographic Image and Development."

The January meeting of the Cincinnati Section of the A. C. S. was held at the University of Cincinnati on the 13th. "A Study of Aluminium Hydroxide as a Pigment and as a Base for Organic Lakes," the Hostetter Fellowship Prize Essay, was presented by the author, Robt. F. Reed. "A New Indicator of the Azo Type," by Benj. E. Sive, and "The Determination of the Maximum Condensation of Zinc Vapor to Liquid Zinc," by Chas. L. Bloom—honorable mention essays for the same prize, were also given.

Dr. Lee M. Barney, formerly of Elkhart, Ill., but more recently of Miami, Fla., has been awarded damages of $41,500 from the casualty companies on account of loss of sight from a chemical explosion which occurred while he was making experiments in his laboratory.

Dr. C. E. Burke, lately of the University of California, has been appointed instructor in the department of chemistry at the University of Vermont.

The January meeting of the Chicago Section of the A. C. S. was held on the 15th at Hotel Sherman. Mr. W. G. MacNaughton, of the Nekoosa-Edwards Paper Company, Port Edwards, Wis., gave an "Outline of the Manufacture of Sulfite Cellulose."

On February 5th, Lauder W. Jones, of the University of Cincinnati, addressed the Chicago Section of the A. C. S. on "Electro-chemical Dualism, Past and Present."

S. Ross Wreath, member of the Chicago Section of the A. C. S., died November 15th. Mr. Wreath was overcome by fumes of hydrocyanic acid and died in an effort to save the lives of two other men who were overcome under the same conditions. The other two men were resuscitated, but Mr. Wreath, in going to their rescue, was completely overcome. The death occurred in the plant of the Victor Chemical Works, with which company Mr. Wreath had been since 1911.

Prof. Wm. P. Mason, of the Department of Chemistry, Rensselaer Polytechnic Institute, spoke on "Stored Water" before the meeting of the Rochester Section of the A. C. S. on January 18th.

Dr. Robert F. Chambers addressed the Rhode Island Section of the A. C. S. on "Some Chemical Processes in Photography," on January 21st.

The Scientific Specialties Company is a new corporation with

offices and show-rooms in the Pullman Building, No. 17 Madison Avenue, New York. It will be the aim of this company to introduce new specialties in the chemical, metallurgical, physical and bacteriological lines and to handle import orders for colleges, universities, etc. A branch office has been established in Offenbach (Main), Germany. Radium and radium apparatus are among the specialties to be handled.

"A Symposium on Iron and Steel Analysis" was given at the regular meeting of the Pittsburgh Section of the A. C. S. on January 21st. The following papers were presented: "Standard Methods of the U. S. Steel Corporation for the Commercial Sampling and Analysis of Plain Steels," by I. A. Nicholas, Chief Chemist Clairton Works, U. S. Steel Corporation; "The Construction of Laboratory Electric Furnaces," by C. M. Johnson, Chief Chemist Park Works, Crucible Steel Co. of America; "The Determination of Copper in Iron and Steel, and the Recovery of Molybdic Acid," by W. D. Brown, Chief Chemist, Duquesne Steel Works, Carnegie Steel Co.

Mr. T. F. Burton, B.Sc., has been appointed editor of the *Journal of the Society of Chemical Industry*, in succession to Mr. Watson Smith, who has resigned. All communications for his journal should be addressed to Mr. Burton at 63, Melbury Gardens, West Wimbledon, London, S. W.

The January meeting of the New York Section of the American Electrochemical Society was held in joint session with the New York Section of the American Institute of Mining Engineers on January 6th, at the Machinery Club. The subject of the evening, "The Problem of Leaching of Copper Ores," was presented by L. D. Ricketts, followed by a discussion of the details of the various processes by Messrs. Wedge, E. A. C. Smith, Van Arsdale, Bacon, Pope, Antisell, Channing, Canby, Lamb, Dorr and Palmer.

Mr. Otto Mantius presented a paper on "Vacuum Evaporation" before the meeting of the Western New York Section of the A. C. S. at Buffalo University on January 22nd.

The regular monthly meeting of the Southern California Section of the A. C. S. was held at Los Angeles on January 21st. Mr. Walter A. Schmidt, who has recently returned from a six months' business trip through Germany and Central Europe, spoke on "Experiences in the War Zone."

The Connecticut Valley Section of the A. C. S. held its 29th meeting at Middletown on January 23rd. The following papers were given: "The Development of the Dye Industry Abroad," by Dr. M. L. Crossley, and "The Radio Elements and the Periodic Table," by Dr. H. L. Ward. The section also inspected the Wesleyan University buildings and campus and witnessed a demonstration of the liquid air plant and the properties of liquid air.

The Spring Meeting of the American Electrochemical Society will be held at Atlantic City, N. J., April 22, 23 and 24, 1915, with headquarters at the Hotel Chalfonte.

At the meeting of the Cincinnati Section of the A. C. S. on December 9th, Mr. P. Smyth presented a paper on "Chemical and Physical Tests in the Manufacture of Paints," and Mr. C. Bahlmann read an article on "Ice Cream Studies in Cincinnati."

Mr. H. A. Schwartz presented a paper on "Electric Furnaces in the Metallurgy of Iron" before the Indiana Section of the A. C. S. on December 11th.

The December meeting of the University of Illinois Section of the A. C. S. on the 14th was given up to a discussion of "Household Chemistry." The principal speakers were Professors Isabel Bevier and N. E. Goldthwaite, and Dr. Ruth Wheeler, all of the Department of Household Sciences of the University of Illinois.

The New York Section of the American Electrochemical Society met in joint session with the New York Sections of the Society of Chemical Industry and the American Chemical Society at the Chemists' Club on Feb. 5th. The subject for the evening was "The Electrochemical Production of Organic Compounds" and the program as follows: The Commercial Aspects of Organic Chemistry, F. A. Lidbury, Manager Oldbury Electrochemical Co.; The Technical Production of Iodoform and Other Aliphatic Compounds (experiments), Harold Hibbert, Mellon Institute of Industrial Research; The Electrolytic Production of Pure Coal Tar Products (experiments and lantern slides), Geo. Shannon Forbes, Professor of Electrochemistry, Harvard University; General Discussion, led by Dr. L. H. Baekeland.

Mr. George P. Vanier, chief chemist of the Pennsylvania Steel Co., Steelton, Pa., has been awarded a Certificate of Merit by the Franklin Institute, Philadelphia, Pa., for his well-known and widely used potash bulb which was particularly designed for use in the determination, in industrial laboratories, of the total carbon in iron or steel. In such laboratories, time is often a very important factor. Mr. Vanier has also designed zinc tubes and sulfuric acid bulbs for use in connection with the Vanier Combustion Train for the determination of carbon in steel by direct combustion method with the electric furnace.

The Franklin Institute, Philadelphia, Pa., has awarded the John Scott Legacy Medal and Premium to Charles Edward Guillaume, of Serves, France, for his alloy Invar. This alloy contains approximately 63.8 per cent iron and 36.2 per cent nickel; it is characterized by possessing an extremely small coefficient of linear expansion, about 0.0000004 per degree centigrade. Within the limits of atmospheric temperature change, its expansion is very exactly proportional to the temperature. It has a modulus of elasticity of about two-thirds that of steel, and its hardness is greater than that of hard brass. Invar has found a wide application in metrology and horology. In the former, it is particularly useful for secondary standards of length, and in the latter it is employed for pendulum rods, compensating devices for torsion pendulums and balance wheels correcting the secondary error of temperature in chronometers. Dr. Guillaume has done a large amount of research work in connection with iron-nickel alloys, in the course of which he also discovered platinite.

British New Year's honors include two knighthoods conferred on scientific men—Dr. James Johnston Dobbie, F.R.S., principal of the government laboratories, formerly professor of chemistry at the University College of North Wales, and Frank Watson Dyson, F.R.S., astronomer royal since 1910.

Prof. James Harvey Pettit, professor of soil fertility in the college of agriculture and chief of soil fertility in the experiment station of the University of Illinois, died on December 30th at Pasadena, California, where he was spending a leave of absence in the hope of benefitting his health. Dr. Pettit received his bachelor's degree at Cornell in 1900 and his doctor's degree at Göttingen in 1909. Since 1901 he had been connected with the University of Illinois. He was a member of the American Chemical Society and the American Association for the Advancement of Science.

Dr. J. E. Clark spoke on "The Question of a Filtration Plant in Detroit," before the regular monthly meeting of the Detroit Section of the A. C. S. on January 29th.

The Rochester Section of the A. C. S., at its regular meeting on December 21st, discussed the practical value of specifications in purchasing coal. The principal speakers were: Wm. H. Earle, of the Gas Manufacturing Department, Rochester Railway and Light Co.; W. S. Austin, Supervising Engineer for the Kodak Park Works, Eastman Kodak Co.; and Walter H. Howard, Manager Yates Coal Co.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### PUBLIC HEALTH SERVICE

**Bacteriological Standard for Drinking Water.** Public Health Reports, **29**, 2959–66 (November 6, 1914). The standard which was adopted by the Treasury Department for drinking water supplied to the public by common carriers in interstate commerce, is one recommended by a commission appointed to investigate this question for the Government. This article gives the text of the recommendations which have been adopted by the Treasury Department and the full text of the first progress report of the commission which discussed limits of permissible bacteriological contamination. The action of the Department adopting this standard was taken October 21, 1914.

### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Supplement to the Customs Tariff of Japan.**—A supplement to the customs tariff of Japan, which, with the earlier supplement (Tariff Series No. 28A), brings up to date Tariff Series No. 28, published in 1912, has just been issued by the Bureau of Foreign and Domestic Commerce, of the Department of Commerce, as Tariff Series No. 28B. The supplement contains all the changes made in the import tariff and drawback law of Japan since July, 1913. Such changes consist mainly in additions to the drawback schedule, for the purpose of promoting the export trade of Japan, and in slight modification in the schedule of import duties, in order to provide for the classification of certain products formerly dutiable under more general headings of the tariff. Copies of Tariff Series No. 28 are for sale by the Superintendent of Documents, Government Printing Office, at 10 cents each, including the two supplements (28A and 28B), while copies of No. 28B are sold at 5 cents each.

**Commerce Reports.** The "Daily Consular and Trade Reports" which have been popularly known as "Consular Reports" are, beginning with January 1, 1915, to appear under the title of "Commerce Reports." Previously it has been about four days from the receipt of information to the publication of these reports, but arrangements have now been made to issue the daily reports within ten hours. This assures prompt notice to subscribers of the material which reaches the offices of the Bureau. The material for these reports is drawn from the communications of 300 American consuls, 10 commercial attachés, the 8 branch offices of the Bureau of Foreign and Domestic Commerce, and the numerous expert commercial agents in all parts of the world. As has been the case in the past the reports will be mailed for $2.50 per year payable in advance to the Superintendent of Documents. The material taken from these reports for this month's Journal appeared under the old system during December, 1914.

### CONSULAR REPORTS—DECEMBER, 1914

Owing to the shortage of **cereals** in Germany special efforts are being made by the Government to have a large part of the potato crop dried and converted into potato flour, which is cheaper than rye flour. (P. 966.)

The French Government has created a special bureau in the department of commerce to assist in the development of the French **chemical** industries. (P. 975.)

Exportation of **rubber** containing over 15 per cent of impurities from Belgian Congo is forbidden. Plantation rubber will soon be available from the colony. (P. 1050.)

The production of **gum copal** in Belgian Congo is increasing. (P. 1050.)

Conditions in the **nitrate industry** of Chili are very bad, due to falling off in exports. (P. 1078.)

A deposit of gilsonite, useful for **paint, paving, and roofing materials** has been discovered in the Philippines, on the island of Leyte. (P. 1088.)

The use of fermented cocoanut water (now wasted in copra mills) is recommended in the coagulation of the **rubber** latex in Ceylon instead of crude acetic acid. (P. 1120.)

The crushing and extracting of **palm kernels and copra** (dried cocoanut) from the Philippines is soon to be carried on in Hull, England. (P. 1147.)

The British Government has taken steps to coöperate with manufacturers, in developing the **dyestuff industry** in Great Britain. (P. 1150.)

The opportunities for markets for American **coal** in South America, Mexico, Central America and the West Indies are discussed. (Pp. 1201 and 1217.)

**A graphite** deposit has been discovered in British Honduras. (P. 1260.)

Two valuable **fiber plants** in British Honduras, are "pita floja" (*ananas macrodontes*) and "majagna" (*Paritium tiliaceum*). Efforts are being made to introduce these fibers into trade. (P. 1274.)

Chemical problems in Germany that have arisen during the war include **substitutes for gasoline,** for which benzol and alcohol are being used; **rubber substitutes,** for which regenerated rubber and synthetic rubber are proposed; forms of **combined nitrogen** to replace the interrupted supply of Chili saltpeter, all of which available is required for military purposes; and supplies of **jute** for bags and **rosin** for paper. (P. 1276.)

The calumpang nut (Sterculia foetidas) contains 50 per cent of a useful **oil.** (P. 1287.)

The colume-palm nut, found extensively in British Honduras, is being urged as a source of **edible oil.** (P. 1323.)

Methods have been discovered at Huddersfield, England, by which the **"sulfur dyes"** previously used only for dyeing cotton, can be used for wool and other fabrics. (P. 1328.)

Efforts are being made to develop the following new industries in India: **Aniline dyes, glass, matches, heavy chemicals, alcohol, oil, flour, sugar, paper, and starch.** (P. 1331.)

American manufacturers are urged to develop the extraction of **copra** (dried cocoanut), in view of the shutting off of the European markets, for Philippine copra. **Edible and soapstock oil can** be obtained. (P. 1334.)

The current **prices of the principal chemicals** in Japan are given. (P. 1341.) (Reported October 29, 1914.)

The **dairy industry** of Ontario is described in detail. (P. 1345.)

The **dairy industry** of the Philippines is dependent principally on goats and caraboas, and large amounts of milk are imported. (P. 1350.)

The **chicle** industry of British Honduras is increasing. (P. 1372.)

Three plants for converting dog fish into **fertilizer** and **oil** have been erected in Nova Scotia. (P. 1373.)

Japan has placed an embargo on almost all **dyes and chemicals.** (P. 1383.)

Production of **iodides** in Japan is to be increased; and the

manufacture of **carbolic acid** and **candles** is being urged. (P. 1391.)

**Oil** indications are said to be favorable in Papua, New Guinea. (P. 1399.)

A company has been organized in Sheffield, England, for the production of **tungsten** for use in high speed steels. (P. 1400.)

RECENT DEMANDS FOR AMERICAN GOODS OWING TO THE WAR. (PP.)

CUBA—969
China
Earthenware
Porcelain
Enamel ware

GREECE—978
Butter fats
Sheet iron
Coal
Paper
Drugs
Tin plate
Iron
Copper
Lead
Rubber goods
Bottles
Linseed oil
Soda

CANADA—989 and 1081
Cottonseed meal (for cattle food)
Glass
Drugs
Dyes
Chemicals

MADAGASCAR—1027
Petroleum
Soap
Paper
Flour

TRIPOLI, AFRICA—1009
Sugar
Kerosene
Cottonseed oil
Lubricating oils
Metals
Beer

AUSTRALIA—1073 and 1106
Sodium acetate
Beer
Resin
Asbestos
Cement
Paper
Tartaric acid
Enameled ware
Dyestuffs

URUGUAY—1132
Drugs
Pharmaceutical preparations

MOROCCO—1138
Sugar
Cottonseed oil
Soap

CHINA—1358
Window glass
Glassware

SPAIN—1325
Electrical equipment

GERMANY—1178
Phosphate rock

COCHIN CHINA—1170
Canned milk
Mineral water
Beer
Drugs
Acids
Iron and steel

VLADIVOSTOK—1225
Salt
Paints
Varnishes
Paper
Lubricating oils
Chemicals
Soda
Potash
Paraffin
Drugs

ROME—1270
Lubricants
Coal
Benzine
Essences
Sugar
Chemicals
Dyes
Paper
Wood pulp
Iron
Hides

STATISTICS, ETC., REGARDING EXPORTS DURING 1912 AND 1913 TO THE UNITED STATES. (PP.)

DURBAN, SO. AFRICA—963
Hides
Whale oil
Wool grease

JAVA—999
Copra
Gum damar
Hemp
Fibers
Peanuts
Hides
Kapok
Citronella oil
Rubber
Sugar

HONGKONG—1019
Cassia
Cassia oil
Peanut oil
Tin

AUSTRALIA—1112, 1114, and 1234
Hides
Condensed milk
Eucalyptus oil
Zinc dust
Osmiridium
Coal
Tallow
Copper

BURMA—1155
Cutch (dye)
Lac (seed)
Lac (shell)
Gasoline
Copper ore
Paraffin
Hides

SIAM—1306
Gamboge
White pepper
Stick lac
Sapphires

MADAGASCAR—1035
Mangrove bark
Raffia fiber

## BUREAU OF STANDARDS

**Equilibrium in the System: Lead Acetate, Lead Oxide, and Water, at 25°.** RICHARD F. JACKSON. Scientific Paper 232. 16 pp. The investigation reported in this paper was intended to add to our knowledge of the basic acetates which are commonly used as clarifying agents, particularly in sugar analysis. A complete isothermal equilibrium diagram is given.

**Electrical Resistance and Critical Ranges of Pure Iron.** G. K. BURGESS AND I. N. KELLBERG. Scientific Paper 236. 15 pp. This investigation was carried out in order to make as exact a determination of the resistance-temperature relation of pure iron as possible, paying particular attention to the form of the curves over the $A_2$ and $A_3$ critical ranges. The importance of the application of this to an elucidation of the question of the allotropy of iron is indicated.

**Absorption, Reflection, and Dispersion Constants of Quartz.** W. W. COBLENTZ. Scientific Paper 237. 12 pp. The scope of this paper is indicated by the summary given by the author as follows:

"This paper gives quantitative data on the absorption, reflection, and dispersion of quartz, extending from the ultraviolet to $3\mu$ in the infra-red. The data may be used in determining spectral energy curves. Quartz is practically transparent from the ultra-violet to $1.8\mu$. It begins to absorb strongly beyond $1.8\mu$, and tabulated data are given for eliminating the effect of this absorption in a quartz prism. The results show that (within the errors of observation) in unpolarized light, the transmission is not affected by the direction in which the radiations pass through the material with respect to the optic axis."

## BUREAU OF MINES

**Metal-Mine Accidents in the United States during the Calendar Year 1913.** Compiled by A. H. FAY. Technical Paper 94. A statistical summary.

**Notes on the Sampling and Analysis of Coal.** ARNO C. FIELDNER. Technical Paper 76. 61 pp. Paper 10 cents. The discussion given in this paper is intended to supplement that which has been published previously by the Geological Survey and the Bureau of Mines. It includes a discussion of the collection of samples at the mine and gives data to indicate the accuracy of the mine sampling methods which have been used. The relation of mine samples to the commercial shipment is discussed. Sampling of coal deliveries is not discussed, since this has been described in a recent report of the Bureau of Mines by G. S. Pope. Detailed description is given of methods of analysis, including preparation of a laboratory sample; and the interpretation and accuracy of analytical results is discussed. The larger part of the paper is devoted to the discussion of the significance of test data, this being justified by "the wide interest in the sampling and analysis of coal, the progress made in laboratory methods, and the bearing of results obtained on various problems connected with the efficient utilization of coal under the steam boiler or in the gas producer."

**The Electric Furnace in Metallurgical Work.** DORSEY A. LYON, ROBERT M. KEENEY AND JOSEPH F. COLLEN. Bulletin 77. 216 pp. Paper 25 cents. This bulletin is made up of three parts as follows: (1) Design, construction, and operation of electric furnaces; (2) the smelting of metal in the electric furnace; (3) the manufacture of ferro alloys in the electric furnace. The object of the first part is stated as follows:

"The object has been not to present a technical discussion of the electric furnace, but to acquaint the layman, so to speak, with some of the most important essentials in connection with the use and construction of the electric furnace as used in metallurgical work, and to assist those who are unfamiliar with the subject to a better understanding of the process described in Parts 2 and 3 of this bulletin and in Bulletin 67 on 'Electric Furnaces for Making Iron and Steel.'" To accomplish this purpose the various types of furnaces are described and illustrated and each of the details of construction and operation discussed; data are given which permit a clear understanding of the principals of design and construction.

The second part of this bulletin presents "a statement of the extent to which the electric furnace has been applied to metallurgy of metals when the product is in the form of the metal and not of a ferro alloy." The various processes in use for the preparation and treatment of the following metals and ores are taken into consideration in this part: Aluminum, iron, copper, lead ores and complex sulfide ores, gold and silver ores, zinc, and tin.

The third part of this report includes "an account of the development of the manufacture of ferro alloys in the electric furnace, descriptions of some types of electric furnaces used in ferro alloy production, descriptions of several European plants that have been visited by the writer, and information regarding the manufacture and uses of agent ferro alloys."

A glossary of the common terms and a table showing the relation of the various units and other simple data are included, and an extended bibliography of books, published papers, and articles is given for a number of the subjects which are discussed in the report itself.

## NATIONAL MUSEUM

**Notes on Wolframite, Beraunite, and Axinite.** EDGAR T. WHERRY. Separate No. 2060 from the Proceedings of the United States National Museum, 47, 501–11.

### GEOLOGICAL SURVEY

**The Water Resources of Butte, Montana.** O. E. MEINZER. Water Supply Paper 345-G, a separate from Contributions to the Hydrology of the United States, 1914. 45 pp. The information and analyses given in this report are primarily of interest in connection with this locality.

**Quality of the Surface Waters of Washington.** WALTON VAN WINKLE. Water Supply Paper 339. 105 pp. This report is of much wider interest in its application than to Washington State only, since it includes a few discussions of the constituents, uses, purification, methods of analysis, and interpretation of the results of analysis of natural waters. This discussion gives in a clear concise way information which may be utilized by one not experienced in this phase of chemical work. From an industrial chemical standpoint the qualities desirable for various industrial processes and the effectiveness of various methods of purification are of special interest. Many analyses are given of the water collected in the particular investigation for Washington.

**The Production of Antimony.** FRANK L. HESS. Separate from the Mineral Resources of the United States, calendar year 1913. Part I, pp. 279–81. "No antimony ores were mined during the year so far as was reported to the United States Geological Survey. Prices were too low. As has been pointed out in the Survey's reports, at the usual prices antimony ores can not be worked profitably under the high labor costs prevailing in the mining regions of the United States unless the deposits are very large and advantageously situated. No deposits of antimony ores have been found in the United States which fulfil these conditions, and as a result practically all the antimony metal used here is imported from European and Japanese smelters, mostly from England. The ores for these smelters come largely from China, Mexico, France, and Austria."

The following tabulation shows the imports for 1913.

| | Lbs. | Value |
|---|---|---|
| Metal and regulus | 12,479,727 | $798,581 |
| Crude antimony and ore | 4,021,486 | 137,780 |
| Oxide and salts of antimony | 1,968,475 | 117,169 |
| Total value | | $1,053,530 |

The consumption during the same year is indicated by the following tabulation:

| | Short Tons | Value |
|---|---|---|
| Antimony contained in antimonial lead from all sources, including by-product antimony | 2,540 | $430,491 |
| Recovered from wastes, scrap, etc. (including a little ore), nearly all as alloy | 2,775 | 462,115 |
| Imports: | | |
| Metal and regulus | 6,240 | 798,581 |
| Crude antimony and ore (probable antimony content) | 1,200 | 137,780 |
| Approximate consumption of metallic antimony | 12,755 | $1,828,967 |

**Arsenic.** FRANK L. HESS. Separate from Mineral Resources of the United States, calendar year 1913. Part I, pp. 283–4. "The output of arsenic in the United States during 1913 was all in the form of white arsenic or arsenious oxide commonly known as "arsenic," and amounted to about 2,513 short tons, valued at $159,236, against 3,141 tons, valued at $190,757, in 1912, a decrease of 628 tons in quantity and of $31,521 in value."

"White arsenic was produced in this country only from smelter flue or gas-house dusts and by the same three firms which produced it in 1912."

"There is so little direct profit in the manufacture of white arsenic, owing mostly to the long distances it must be shipped to market, that the smelting companies make it largely because they must prevent its escape into the atmosphere. If the demand and prices justified a larger output the production could be greatly increased."

The imports during 1913 amounted to 4,701 short tons of "arsenic or arsenious acid" and "arsenic and arsenic sulfide or orpiment," valued at $410,000 and approximately 100,000 pounds of Paris green and London purple.

**Bismuth.** FRANK L. HESS. Separate from Mineral Resources of the United States, calendar year 1913. Part I, pp. 285–8. "The production of bismuth during the year is thought to have been at least 157,300 pounds, valued at $273,650."

"During 1913, according to figures obtained from the Division of Statistics, Bureau of Foreign and Domestic Commerce, 117,747 pounds of metallic bismuth, valued at $213,257, were imported for consumption. This is a decided drop from the imports of 1912 and preceding years, which probably is to be explained by the large increase in the domestic output."

"The prices quoted during 1913 ranged from $1.75 to $2.25 a pound, but during the latter half of the year it was uniformly $1.95 to $2.15 a pound, as given by *The American Metal Market*."

The statement of the production of bismuth in foreign countries indicates that Queensland, Australia, Bolivia, and Peru are the three principal producers, each having a production valued at more than $50,000.

**Selenium.** FRANK L. HESS. Separate from Mineral Resources of the United States, calendar year 1913. Part I, pp. 289. "During 1913 selenium was produced from the anode muds in electrolytic copper refining by the American Smelting and Refining Company, Nichols Copper Co., and Raritan Copper Works. The production amounted to 29,097 pounds, valued at about $46,900." "Prices in large lots ranged from $1.60 to $1.75 a pound."

"The production of selenium is governed wholly by the demand." Other selenium sources are sufficient to meet largely increased demands if these arise.

"The Raritan Copper Works produced a small quantity of tellurium, which was likewise obtained from copper anode muds. The tellurium was shipped to Europe."

**The Production of Iron Ore, Pig Iron, and Steel.** ERNEST F. BUCHARD. Separate from Part I, Mineral Resources, 1913, pp. 291–338. "The quantity of crude iron ore mined in the United States in 1913 amounted to 61,980,437 long tons, as compared with 55,150,147 long tons mined in 1912, an increase of 6,830,290 long tons, or 12.38 per cent." This includes the ore used for fluxing, but not the ore used for paint; the latter amounted to about 17,000 long tons valued at $45,000. "The average price of ore per ton for the whole country in 1913 was $2.19, as compared with $1.88 in 1912." The character of the ore produced is indicated by the following tabulation:

| Kind of Ore | Long Tons | Average price per long ton |
|---|---|---|
| Hematite | 58,018,295 | $2.21 |
| Brown ore | 1,577,019 | 1.83 |
| Magnetite | 2,357,274 | 2.07 |
| Carbonate | 27,849 | 2.06 |
| Total | 61,980,437 | $2.19 |

The summaries indicate an apparent consumption of iron ore amounting to 61,000,000 long tons as used in the production of pig iron, giving approximately 31,000,000 tons of pig iron, a ratio of pig iron to iron ore of 50.52 per cent. It is interesting to note that in 1913 there was imported approximately 2,600,000 long tons of ore and exported somewhat more than 1,000,000 long tons.

The production of pig iron in the United States during 1913 is indicated by grades in the following tabulation:

| | Long Tons |
|---|---|
| Bessemer and low phosphorus | 11,590,113 |
| Basic (mineral fuel) | 12,536,693(a) |
| Forge pig iron | 324,407 |
| Foundry and ferrosilicon | 5,220,343 |
| Malleable | 993,736 |
| Spiegeleisen | 110,338 |
| Ferromanganese | 119,495 |
| White, mottled, direct castings, etc. | 71,027 |
| Total | 30,966,152 |

(a) Includes a small quantity of basic iron made with charcoal.

The imports of pig iron and ferro alloys amounted to 150,000 long tons during 1913 and the exports were 280,000 long tons. The marketed production of ferro alloys was as follows:

| Kind of Alloy | Long Tons | Value |
|---|---|---|
| Ferromanganese and spiegeleisen | 226,475 | $9,272,269 |
| Ferrosilicon and ferrophosphorus | 67,164 | 1,233,465 |
| Other alloys | 2,568 | 2,509,628 |
| Total | 296,207 | $13,015,362 |

The production of steel ingots and castings during this year was as follows in long tons:

| | |
|---|---|
| Bessemer | 9,545,706 |
| Open-hearth | 21,599,931 |
| Crucible and all other | 155,237 |
| Total ingots and castings | 31,300,874 |

The production of steel by electrical processes amounted to over 30,000 tons which is an increase of 65 per cent over the 1912 production by corresponding methods.

**Cobalt.** Frank L. Hess. Separate from Part I, Mineral Resources, 1913, pp. 339–40. No cobalt was produced from domestic ores during 1913. That used in making high speed steel and stellite was imported either as metal from Germany or as oxide from Canada. The imports of oxide, ore, and zaffer during 1913 amounted to over 200,000 pounds, valued at nearly $100,000. No record is kept of the import of metallic cobalt. The nominal price during 1913 was about $1.90 to $2.00 a pound.

**Molybdenum.** Frank L. Hess. Separate from Part I, Mineral Resources, 1913, p. 341. "No commercial production of molybdenum is known to have been made in 1913, and no promising new deposits were reported during the year. The demand, however, suddenly increased, and in the latter part of the fall a French firm offered the following prices:

| Per cent $MoS_2$ | Price per unit in long tons | Per cent $MoS_2$ | Price per unit in long tons |
|---|---|---|---|
| 50 | $5.00 | 80 | $ 8.50 |
| 60 | 6.00 | 90 | 10.00 |
| 70 | 7.00 | 95 | 12.00 |

"Molybdenum and ferromolybdenum, valued at more than $200 a ton, were imported during 1913 to the extent of 7.8 short tons, valued at $15,939, against 3.9 tons, valued at $4,670, in 1912."

**Nickel.** Frank L. Hess. Separate from Part I, Mineral Resources, 1913, pp. 343–5. No nickel ores, as such, were mined in the United States during 1913. Although this country refines more nickel than any other country, the ore practically all comes from Ontario and New Caledonia. It is reduced to matte and shipped here for further reduction to metal.

The imports for 1913 were divided as follows:

| | Quantity (pounds) | Value |
|---|---|---|
| Nickel, alloys, pigs, bars, etc. | 335,054 | $ 134,303 |
| Ore and matte (nickel content) | 47,109,930 | 6,427,639 |
| Nickel oxide | 1,536 | 613 |
| Total | 47,446,520 | $6,562,555 |

The exports of nickel and nickel oxide during the same period amounted to 29,000,000 pounds, valued at about $9,700,000. No nickel matte is known to have been exported during the year.

**Tin.** Frank L. Hess. Separate from Part I, Mineral Resources, 1913, pp. 347–9. "An equivalent of only 84 short tons of tin ore, carrying 60 per cent metallic tin, valued at $36,970, was produced in the United States during 1913, against an equivalent of 147 tons of 60 per cent ore, valued at $124,800, in 1912."

The average monthly price of Straits tin in New York was 44.225 cents per pound. The imports during the year were 53,000 short tons, valued at nearly $47,000,000, this including about 1,000 tons of scrap tin.

**Titanium.** Frank L. Hess. Separate from Part I, Mineral Resources, 1913, p. 351. All of the rutile produced during 1913 was produced by the American Rutile Company of Virginia, amounting to 305 tons carrying approximately 95 per cent titanium dioxide and valued at about $49,000. The deposits which are worked contain considerable ilmenite, this being removed from the concentrates by a magnetic separator. About 250 tons of ilmenite were thus produced during the year.

**Tungsten.** Frank L. Hess. Separate from Part I, Mineral Resources, 1913, pp. 353–61. "The production of tungsten ore in the United States during 1913, as estimated from returns made to the United States Geological Survey, was equivalent to 1,537 short tons of ore carrying 60 per cent of tungsten trioxide ($WO_3$), with a value of $627,118." This report also includes a discussion of market conditions, the tungsten resources of this country, the uses and production both in this country and abroad.

**Radium.** Frank L. Hess. Separate from Part I, Mineral Resources, 1913, pp. 363–4. "The production of carnotite-bearing ores during 1913 was the largest to date, and amounted to about 2,269 short tons of dry ore, which contained about 81,990 pounds of $U_3O_8$, equivalent to 34.8 tons (31,560 kilograms) of metallic uranium. Rutherford[1] has estimated that the quantity of radium in equilibrium with uranium is about 1 grain of radium to 3000 kilograms of uranium, and workers in the Bureau of Mines have estimated that the uranium in carnotite is accompanied by about 90 per cent of the radium required for equilibrium. On the supposition that these figures are approximately correct and that 90 per cent of the radium present is recoverable, then the ores produced contained 8.5 g. of recoverable metallic radium, equivalent to 15.9 g. of hydrous radium bromide ($RaBr_2.2H_2O$) valued, at $120,000 a gram of metallic radium, at $1,020,000."

"Of the carnotite ores produced, 1,125 dry tons, carrying 36,022 pounds of $U_3O_8$ and 3.7 g. of radium, equivalent to 7 g. of hydrous radium bromide, were kept in this country, and 1,134 dry tons, carrying 45,068 pounds of $U_3O_8$ and 4.8 g. of radium, equivalent to 8.9 g. of hydrous bromide, were shipped to Europe."

**Platinum and Allied Metals.** David T. Day. Separate from Part I, Mineral Resources, 1913, pp. 445–57. It is stated that "the platinum industry remains practically stationary with reference to the world's supply and price." The production in 1913 from domestic sources was 1,000 troy ounces of refined platinum, valued at $46,500. The report includes a discussion of the occurrence of platinum and the prevailing prices for crude platinum sand. The 1913 imports of platinum were valued at more than $5,000,000. A brief discussion of the uses of platinum and the allied metals is included.

**Copper in 1913.** B. S. Butler. Separate from Part I, Mineral Resources, 1913, pp. 523–81. The following summary of statistics of the copper industry gives the more important data of interest

| | Lbs. |
|---|---|
| Production of Copper: | |
| Smelter output | 1,224,484,098 |
| Mine production | 1,235,569,727 |
| Refinery Production of New Copper: | |
| Electrolytic | 1,022,497,601 |
| Lake | 155,715,286 |
| Casting and pig | 58,611,026 |
| Total domestic | 1,236,823,913 |
| Total new and old copper | 1,888,000,000 |
| Total domestic and foreign | 1,615,067,782 |
| Total ore produced (short tons) | 36,361,101 |
| Copper ore produced (short tons) | 36,336,682 |
| Average yield of copper (per cent) | 1.67 |
| Imports | 409,560,954 |
| Exports | 926,441,142 |
| Consumption { Total new copper | 812,068,639 |
| Consumption { Total new and old copper | 1,085,000,000 |
| World's production | 2,198,732,130 |
| Value of Production in the United States | $189,795,035 |

The forms in which copper was cast in 1913 were approximately as follows expressed in percentage of total refinery output: wire bars, 58; ingots and ingot bars, 23; cakes, 9; cathodes, 8; other forms, 2.

"It may be assumed that a large proportion of the 58 per cent cast as wire bars was used for electrical purposes and that the 9 per cent cast as cakes was used largely for rolling. The other forms are less easily classified. The 8 per cent cast as cathodes, together with a portion of the ingots, probably entered the brass industry, and a large quantity of copper ingots was used in

[1] Rutherford, Ernest, "Radioactive Substances and Their Radiations," p. 16, 1913.

casting." The average price of copper in New York was 15.52 cents per pound for electrolytic copper.

**Zinc.** C. E. SIEBENTHAL. Separate from Part I, Mineral Resources, 1913, pp. 621–67. This report gives more detailed data of the zinc industry than has previously been reviewed (see THIS JOURNAL for previous 2 months). The most interesting parts of this report are the discussion of the present practice in the metallurgy of zinc and the report on zinc trade conditions throughout the world.

**Cadmium.** C. E. SIEBENTHAL. Separate from Part I, Mineral Resources 1913, pp. 669–71. The production of cadmium is by 2 firms and no authoritative information as to their methods is yet available and no statement can be made of the quantity and value of their output. Some information is given as to the character of foreign practice and production. "Cadmium is imported into the United States as metallic stick cadmium and as the pigment, cadmium sulfide (CdS), known as 'cadmium yellow.' The domestic quotations on cadmium in 1913 ranged from 75 to 85 cents a pound, and the average price for the year, as based on sales, was a little more than 75 cents a pound."

**Lead.** C. E. SIEBENTHAL. Separate from Part I, Mineral Resources 1913, pp. 709–45. The more important data of the lead industry for 1913 are given in the following summary:

SUMMARY OF LEAD STATISTICS, 1913, IN SHORT TONS

| | |
|---|---|
| Total production of refined lead in the U. S. | 462,460 |
| Production of desilverized lead in the U. S. | 330,593 |
| Production of soft lead in the U. S. (including desilverized soft) | 161,300 |
| Production of antimonial lead in the U. S. | 16,665 |
| Production of lead from domestic ores | 411,878 |
| Production of secondary lead in the U. S. | 72,834 |
| Consumption of lead in the U. S. (disregarding stocks) | 414,281 |
| World production (approximate) | 1,270,458 |
| World consumption (approximate) | 1,290,499 |
| U. S. percentage of world consumption | 32.1 |
| U. S. (domestic) percentage of world production | 32.4 |
| World rank of U. S. in production of lead | FIRST |
| World rank of U. S. in consumption of lead | FIRST |

**Metals and Metallic Ores in 1912 and 1913.** J. P. DUNLOP. Separate from Part I, Mineral Resources, 1913, pp. 747–53. This is a general review giving in a condensed form data of metal production which has been reviewed in greater detail from the extended reports.

**Gold and Silver.** H. D. MCCASKEY. Separate from Part I, Mineral Resources, 1913, pp. 845–85. The production of these metals in 1913 amounted to 4,000,000 fine ounces of gold and 67,000,000 fine ounces of silver, valued, respectively, at $89,000,000 and $40,000,000. The sources of these materials are indicated by the following tabulation.

| PRODUCTION BY | Percentage of total output GOLD | SILVER |
|---|---|---|
| Placers | 24.9 | 0.2 |
| Gold and silver mills: | | |
| By amalgamation | 21.5 | 0.6 |
| By cyanidation | 31.2 | 19.7 |
| By chlorination | 0.3 | .... |
| Total milling | 53.0 | 20.3 |
| Smelting(a) | 22.1 | 79.5 |
| Total(b) | 100.0 | 100.0 |

(a) Both crude ore and concentrates.
(b) Philippines and Porto Rico excluded.

**Fuel Briquetting.** EDWARD W. PARKER. Separate from Part II, Mineral Resources, 1913, pp. 11–16. "The total quantity of manufactured fuel in the form of briquettes, eggettes, coalettes, boulets, etc., all considered in this report under the general head of 'briquettes' amounted in 1913 to 181,859 short tons, valued at $1,007,327, as compared with 220,064 tons, valued at $952,261, in 1912.

"In the production of briquettes in 1913, 7 plants used anthracite culm or fines; 1 used semianthracite; 1 semianthracite and bituminous slack mixed in proportions of 3 to 1; 1 used anthracite culm and bituminous slack, principally the former; 5 used bituminous or semibituminous slack; and 2 used carbon residue from gas works making gas from petroleum. Eight plants used coal-tar pitch for binder, 1 used asphaltic pitch, 1 used water gas pitch, and 5 used mixed binders, the composition of which was not divulged. No additional binder is required in the briquetting of the carbon residue from oil-gas works. The two plants designed for the purpose of utilizing coke breeze, one at Point Breeze, Philadelphia, and the other at Detroit, Mich., have not been operated during the last two years, the abrasive action of the coke on the molds and machinery being too destructive for commercial success in these attempts to utilize an unmerchantable product of the coke ovens."

**Manufacture of Coke.** EDWARD W. PARKER. Separate from Part II, Mineral Resources, 1913, pp. 455–520. The production of coke in 1913 exceeded all previous records amounting to 46,000,000 short tons, valued at $129,000,000, an increase of 5 per cent in quantity and 15 per cent in value over the previous year. It is interesting to note that 70 per cent of the increase in quantity of coke produced was brought about by increase in the output of retort coke.

"The evolution in coke making, which is shown to be in progress of accomplishment, by the figures presented in the following pages, is not only in the steady substitution of the retort oven, and its recovery of the valuable contents of the coal other than coke, for the wasteful beehive; it means also the shifting of the coke-making industry from the vicinity of the mines to the centers of manufacture and population, where the gas may be utilized and the other by-product disposed of at a profit."

The following is a summary of conditions at the end of 1913:

| | |
|---|---|
| Establishments | 551 |
| Ovens { Built | 102,650 |
| Ovens { Building | 1,321 |
| Coal used (short tons) | 69,239,190 |
| Yield of coal in coke (per cent) | 66.9 |
| Coke produced (short tons) | 46,299,530 |
| Total value of coke | $128,922,273 |
| Value of coke per ton | $2.78 |

The value of by-products from coke manufactured during 1913 was as follows:

| | QUANTITY | VALUE |
|---|---|---|
| Gas, M cubic feet | 64,553,941 | $5,694,691 |
| Tar, gallons | 115,145,025 | 2,830,158 |
| Ammonia, sulfate or reduced to equivalent in sulfate, pounds | 173,342,349 | 5,324,444 |
| Ammonia liquor, gallons | 4,102,448 | 537,413 |
| Anhydrous ammonia, pounds | (a)28,663,936 | (a)2,135,656 |
| Other by-products | ..... | 403,579 |
| Total value of by-products | | $16,925,941 |
| Coke, short tons | 12,714,700 | 48,637,852 |
| Grand total | | $65,563,793 |

(a) Mainly ammoniacal liquor sold on pound basis of $NH_3$.

**The Production of Coal.** EDWARD W. PARKER. Separate from Part II, Mineral Resources, 1913, pp. 709–928.

The production of coal in 1913 in short tons was as follows:

| | |
|---|---|
| Bituminous | 438,363,292 |
| Anthracite | 91,594,683 |
| Semi-bituminous | 20,256,877 |
| Lignite and sub-bituminous | 11,012,054 |
| Semi-anthracite | 1,665,237 |
| Block | 1,068,812 |
| Splint | 5,820,050 |
| Cannel | 267,120 |
| Total | 570,048,125 |

The total spot value is given as $760,000,000. The report contains a detailed analysis of production for each state.

**Asphalt.** DAVID T. DAY. Separate from Part II, Mineral Resources, 1913, pp. 537–44. "The production of natural asphalt, including all the varieties of natural asphalt, asphaltic sandstone, and limestone, amounted in 1913 to 92,604 short tons, valued at $750,713." The character of the material produced is indicated in the following summary:

| | SHORT TONS | VALUE |
|---|---|---|
| Bituminous rock and maltha | 57,549 | $173,764 |
| Wurtzilite (elaterite), Gilsonite, and Grahamite | 35,055 | 576,949 |
| TOTAL | 92,604 | $750,713 |
| Manufactured or oil asphalt | 436,586 | 4,531,657 |
| TOTAL | 529,190 | $5,282,370 |

The imports during the same period were as follows:

| | | |
|---|---|---|
| Crude | 207,033 | 738,452 |
| Dried or advanced | 14,750 | 133,336 |
| Bituminous limestone | 6,395 | 38,823 |
| TOTAL | 228,178 | 910,611 |

The principal producers of asphalt imported into the United States are the British West Indies and Venezuela.

# BOOK REVIEWS

**Geschichte des Elektroeisens mit besonderer Berücksichtigung der zu seiner Erzeugung bestimmten elektrischen Ofen.** By OSTWALD MEYER. 206 illus. Published by Julius Springer, Berlin, 1914. 187 pp. Price, 8 Marks.

This book deals with the history of the development of the electric furnace as applied to the iron and steel industry, and is the most comprehensive treatise on the subject in book form that the reviewer has seen. It is a valuable reference book as it embraces much of the subject matter which heretofore has appeared only in the different scientific journals and periodicals, and in addition it presents a broad view of the whole subject in the order of its development.

The treatise is divided into four parts. Part I, entitled "History of the Development of Electric Iron and Steel and the Electric Furnaces for the Same," is by far the most important and is so recognized by the author as he devotes over 70 per cent of his space to its treatment; it is subdivided chronologically into six periods starting at the beginning of the 19th century. The first three periods are of historical importance only, aside from what value they may have from a patent standpoint. From a technical standpoint, only from the fourth period on is of interest. This fourth period (1898–1904) is from Stassano's invention to the Report of the Canadian Commission, and embraces the important early work of Girod, Héroult, Stassano, and other pioneers. The fifth period (1904–1909) extends from the Report of the Canadian Commission to the first real success of the Raw Iron Development in Sweden. This is perhaps the most important period of development of the commercial types of furnaces and is adequately treated by the author, the work done in other countries, particularly in America, France, and Italy being presented in accordance with their respective importance. The last period is from 1900 to the present time (1914) and presents the latest developments and inventions as applied to the industry and also a summary of the present status of electric iron and steel smelting and refining.

Part II deals with the economic aspects of the subject, and presents a complete report of the number, size, kind, capacity, current, and location of electric iron and steel furnaces throughout the world. The data are very complete and well arranged.

Part III gives a classification of known electric furnaces for the iron and steel industry and presents a review and summary of the whole subject, special attention being given to induction furnaces. Part IV is a supplement and deals with the Schatzl-Krieger Electric Furnace System and also with the literature on the subject.

The book is well illustrated and is a valuable addition to the knowledge on the subject of electric furnaces as applied to the iron and steel industry.

ALCAN HIRSCH

**The Microscopy of Drinking Water.** By GEORGE CHANDLER WHIPPLE. Third edition, rewritten. John Wiley & Sons, publishers. 8vo. xxi — 409 pages, 73 figures and 6 plates in the text and 19 full page plates in colors. Cloth, $4.00 net.

This work, now in its third edition, is so well known among engineers and chemists whose interests are along the lines of water supply and water examination that a general review would be superfluous. In the present edition the first part of the book has been rewritten. New material has been inserted in almost every chapter, and several new chapters added, the most important being those on the copper treatment, the stripping of reservoir sites, the purification of algae-laden water, and the use of the microscope and photomicrography. The last named chapter was written by Dr. J. W. M. Bunker and acknowledgment is made to Bausch & Lomb Optical Co. for permission to use their book on "Use of the Microscope" in its preparation. The coloring of the plates illustrating the organisms does not seem to be an improvement. Students have complained to the writer that the colors are incorrect and more confusing than helpful. They prefer the uncolored plates of the earlier editions. The introduction of photomicrographs is an especially good feature of this edition.

A. M. BUSWELL

**Van Nostrand's Chemical Annual.** Edited by JOHN C. OLSEN. Third Issue. Revised. D. Van Nostrand Company, 25 Park Place, New York. 669 pages. Price, $2.50.

Dr. Olsen has been assisted in the revision and extension of the material in this well known handbook by a number of special contributors. A. F. Seeker, U. S. Department of Agriculture, prepared the material on Oils, Fats and Waxes, and the Chemical Constants of Essential Oils; M. C. Whipple, of Harvard, the tables of Gravimetric Factors and Logarithms; E. E. Ried, of Colgate & Co., and C. A. F. Kahlbaum, of Berlin, the tables on Physical Constants of Organic Compounds; A Seidell, of U. S. Public Health Department, the table on the Physical Constants of Alkaloids; and R. H. Ashley and C. H. Lips the chapter on Stoichiometry.

All tables have been carefully revised and corrected to date. New tables, such as the solubility of gases in water, the Bureau of Standards alcohol tables, refractometer tables, tables giving the heats of formation of solutions, etc., have been added. The new chapter on Stoichiometry defines the usual physical constants and outlines and illustrates typical problems often encountered in industrial work.

This book contains a large amount of valuable material arranged in a most accessible form. Each revision shows great improvement and approaches more nearly to that urgently needed Chemical Engineers' Handbook corresponding in quality and density of material to the well known handbooks for Mechanical Engineers.

In addition to the text changes noted in the third issue of the Chemical Annual, the publishers have made radical changes in the physical form of the book. A thin strong paper has been adopted so that the entire 669 pages occupy less than seven-eighths of an inch, and the whole is held in a soft flexible red leather binding. All of this greatly improves both the appearance and utility of the book as a working volume.

M. C. WHITAKER

**Practical Handbook for Beet-Sugar Chemists.** Rápid methods of technico-chemical analyses of the products and by-products and of materials used in the manufacture of beet sugar. By WERNER MOELLER-KRAUSE, Sugar Chemist. The Chemical Publishing Co., Easton, Pa. 1914. 132 p. 19 figs. Price, $1.25.

The purpose of the author, as stated in his preface, has been "to condense the selected practical information obtained from standard works and other sources to a small convenient form."

After a brief account of the common sugars, the author gives a short description of the polariscope and an outline of the manufacture of beet sugar. In succeeding chapters methods are described for the analysis of sugar beets, juices, massecuites, molasses, sirups, waste waters, press cake, saccharates, water, limestone, kiln and chimney gas, coal, coke, etc. Methods are given for preparing solutions and reagents, and a final chapter gives a number of the more commonly used tables.

While the material selected for description is upon the whole

well-chosen, it is to be regretted that more care was not given to its accurate presentation. In a number of places the author's meaning must obviously differ from his text as for example on page 4 where it is stated that the glucosates of calcium and barium "are decomposed into sucrose and the carbonate of the respective metal by carbon dioxide." In other places the author has not made his ideas clear, as on p. 7, where it is stated that compensation is secured "by varying the concentration or length of the interposed polarizing light."

The author has adhered throughout his book to the old Mohr normal weight and unit of volume, notwithstanding the fact that these were rejected by the International Commission in 1900 for the present metric standards. The statement on p. 12 that the Mohr cc. "is now the unit of volume generally adopted in this country for all sugar tests" is incorrect. Many of the most important sugar-testing laboratories in the United States employ only the metric cubic centimeter and the 26 g. normal weight. It is time that the obsolete Mohr standard be once for all rejected.

Opinions will also differ regarding the author's preference in certain matters of technique. The statement on page 62 that "the best way is to first dissolve all the sugar in the scoop before it is transferred to the flask" is open to question. A quicker, and for many purposes a far better, method is to wash the sugar from the scoop into the flask through a funnel and to dissolve on a shaking machine.

While it is of course impossible in a small work of 132 pages to present the entire subject of beet sugar analysis with any degree of fulness, the description of methods should have been made a little more complete in a number of instances. The influence of concentration upon the Clerget factor (pp. 58), for example, is too important a matter to leave unnoticed.

The typography of the book is upon the whole excellent, but the illustration of the filter tube on page 67 is upside down.

As a compendium or vade-mecum for the beet-factory chemist, the new work will no doubt meet with a kind reception and as such it is cordially recommended.

C. A. BROWNE

# NEW PUBLICATIONS

By JOHN F. NORTON, Massachusetts Institute of Technology, Boston

**Atoms: Elektrische Spektralanalyse Chemischer Atoms.** By J. STARK. 8vo. 158 pp. Price, $1.25. Leipzig.

**Calculations: Chemical Calculations.** H. W. BAUSOR. 8vo. 144 pp. Price, $0.75. London.

**Drugs: The Detection of Poisons and Powerful Drugs.** By WILHELM AUTENRIETH. Translated by William H. Warren. 4th Ed. 8vo. 320 pp. Price, $2.00. P. Blakiston's Son & Co., Philadelphia.

**Dyestuffs: The Manufacture of Organic Dyestuffs.** By ANDRÉ WAHL. Translated by F. W. Atack. 12mo. 338 pp. Price, $1.60. The Macmillan Co., New York.

**Electrochemistry: Principes et applications de l'Electrochimie.** By O. DONY-HENAULT, H. GALL AND P. A. GUYE. 8vo. Price, $6.50. Paris.

**Food: Cocoa.** By C. J. J. VAN HALL. 8vo. 515 pp. Price, $3.50 The Macmillan Co., New York.

**Gas: Le Gaz.** By R. MASSE. 8vo. 785 pp. Price, $15.00. Bérenger, Paris.

**General Chemistry: Chemistry of Common Things.** By RAYMOND B. BROWNLEE, ROBERT W. FULLER, W. J HANCOCK, JESSE E. WHITSIT. 12mo. 616 pp. Price, $1.50. Allyn and Bacon, Boston.

**Iron: Some Considerations Regarding Cast Iron and Steel Pipes.** By JOHN SHARP. 8vo. 142 pp. Price, $1.50. Longmans, Green & Co., New York.

**Microscopy: Elementary Chemical Microscopy.** By EMILE M. CHAMOT. 8vo. 350 pp. Price, $3.00. John Wiley & Sons, New York.

**Minerals: Les pierres precieuses.** By J. ESCARD. 4to. 372 pp. Price, $6.00. Dunod et Pinat, Paris.

**Organic Chemistry: Introduction to the Study of Organic Chemistry.** By H. T. CLARKE. 8vo. 492 pp. Price, $2.00. London.

**Paper: Paper and its Uses.** By E. A. DAWE. 8vo. 170 pp. Price, $1.25. C. Lockwood, London.

**Potash: Die Abwässer der Kaliindustrie.** By J. H. VOGEL. 8vo. 139 pp. Price, $2.00. Berlin.

**Technology: The Application of Physico-Chemical Theory to Technical Processes and Manufacturing Methods.** By R. KREMANN. Translated by H. E. Potts. 8vo. 227 pp. Price, $2 50. D. Van Nostrand Co., New York.

**Textiles: Jute and Linen Weaving.** By T. WOODHOUSE AND T. MILNE. 2nd Ed. 12mo. 590 pp. Price, $3.00. The Macmillan Co., New York.

**Textiles: Les Apprets textiles.** By A. CHAPLET. 8vo. 357 pp. Price, $2.00. Paris.

**Ventilation: The Theory and Practice of Heating and Ventilation.** By ARTHUR H. BARKER. 8vo. 656 pp. Price, $8.00. D. Van Nostrand Co., New York.

**Water: Water Supplies, their Purification, Filtration and Sterilization.** By SAMUEL RIDEAL AND ERIC K. RIDEAL. 8vo. 250 pp. Price, $2.50. D. Appleton and Co., New York.

## RECENT JOURNAL ARTICLES

**Carbon Dioxide: Ueber die Bestimmung der freien Kohlensäure in Trink- und Nutzwassern.** By L. W. WINKLER. *Zeitschrift für analytische Chemie*, Vol. 53, 1914, No. 12, pp. 746–55.

**Carbon Dioxide: Zur Bestimmung der Kohlensäure in Mineralien und Gesteinen.** By LEON H. BORGSTRÖM. *Zeitschrift fur analytische Chemie*, Vol. 53, 1914, No. 11, pp. 685–7.

**Concrete: Permeability Tests on Gravel Concrete.** By MORTON O. WITTSEY. *Journal of the Western Society of Engineers*, Vol. 19, 1914, No. 9, pp. 813–58.

**Dyes: Ueber die Verbessung der Lichtechtheit von Färbungen.** By KURT GEBHARD. *Färber-Zeitung*, Vol. 25, 1914, No. 21 and 22, pp. 393–7 and 405–10.

**Electric Conductors: Comparisons of Electric Resistivities at High Temperatures.** By CARL HERING. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 1, pp. 23–8.

**Fertilizers: Die Verwendung des Luftatickstoffs für Dungewecke.** By A. KRAISY. *Zeitschrift des Vereins der Deutschen Zucker-Industrie*, 1914, No. 706, pp. 911–26.

**Flour: Notes on Flour: 1. Acidity of Flour; 2. Natural and Artificial Bleaching of Flour; 3. Sulfates and Lime in Flour.** By R. T. THOMSON. *The Analyst*, Vol. 39, 1914, No. 465, pp. 519–29.

**Fuel: A Comparison of the Economy of Powdered Coal, Oil and Water Gas for Heating Furnaces.** By C. F. HERINGTON. *Engineering News*, Vol. 72, 1914, No. 24, pp. 1156–8.

**Garbage Disposal: Emergency Garbage Disposal in Chicago.** By GEORGE B. YOUNG. *Engineering Record*, Vol. 70, 1914, No. 25, pp. 666–7.

**Gas: Allgemeines und Besonderes über Gasreinigung.** By OSKAR NAGEL. *Chemische Apparatur*, Vol. 1, 1914, No. 20, pp. 269–71.

**Heat: Ueber Füllkörper für Reaktionstürme und Wärnespeicher.** By FRIEDRICH LUDWIG. *Chemische Apparatur*, Vol. 1, 1914, No. 20, pp. 271–2.

**Iron: Handling Iron and Cinder at the Blast Furnace.** By J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 1, pp. 43–50.

**Iron: Note on Crystal Twinning and the Martensitic Structure.** By C. H. DESCH. *Chemical News*, Vol. 110, 1914, No. 2873, pp. 299–300.

**Iron: The Corrosion of Iron.** By L. C. WILSON. *The Engineering Magazine*, Vol. 48, 1915, No. 4, pp. 517–23.

**Iron: Weitere Untersuchungen über die massanalytische Eisenbestimmung in salzsauer Lösung.** By L. BRANDT. *Zeitschrift für analytische Chemie*, Vol. 53, 1914, No. 12, pp. 729–45.

**Meat: Coloring Matter of Raw and Cooked Salted Meats.** By RALPH HOAGLAND. *Journal of Agricultural Research*, Vol. 3, 1914, No. 3, pp. 211–25.

**Milk: Studies in the Expansion of Milk and Cream.** By H. W. BEARCE. *Journal of Agricultural Research*, Vol. 3, 1914, No. 3, pp. 251–68.

**Milk: The Freezing Point of Milk.** By J. BROWNLIE HENDERSON, AND L A MESTON. *Chemical News*, Vol. 110, 1914, Nos. 2871–2, pp. 275 and 283–6.

**Milk: Ueber den Eisengenalt der Kuhmilch.** By F. E. NOTTBOHM AND G. DÖRR. *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel*, Vol. 28, 1914, No. 9, pp. 417–24

**Oils: Two Rapid Methods of Estimating Water in Crude Petroleum, Oil-Fuel and Similar Substances.** By HERBERT S. SHREWSBURY. *The Analyst*, Vol. 39, 1914, No. 465, pp. 529–32.

**Oleomargarine: Ueber die Verwendung des gehärteten Trans in der Margarinebutter-Fabrikation.** By J. KLIMONT AND K. MAYER. *Zeitschrift für angewandte Chemie*, Vol. 27, 1914, No. 96, pp. 643–8.

**Patents: An Argument in Favor of a Compulsory License Patent Law.** By J. CAMPBELL DELANO *Textile Colorist*, Vol 36. 1914, No. 432, pp. 365–7.

**Photography: Kolloidchemie und Photographie.** By LÜPPO-CRAMER. *Kolloid-Zeitschrift*, Vol. 15, 1914, No. 4, pp. 164–6.

**Roads: Repairing and Resurfacing Bituminous Pavements.** By SAMUEL H. LEA. *Engineering News*, Vol. 72, 1914, No. 27, pp. 1308–10.

**Sanitation: Sanitation in Brazil.** By EDWARD STUART *American Journal of Public Health*, Vol. 4, 1914, No. 12, pp. 1159–72.

**Sewage: Advances in Sewage Disposal.** By GEORGE W. FULLER. *Engineering Record*, Vol. 71, 1915, No. 1, pp. 10–11.

**Sewage: Preliminary Report on Emscher Tanks and Kindred Sewage-Clarification Processes.** By K. THUMM AND C. REICHLE. *Engineering News*, Vol. 72, 1914, No. 27, pp. 1306–8

**Silicates: Ueber die chemische oder physikalische Natur der Kolloiden wasserhaltigen Tonerdesilikate.** By GEORG WIEGNER *Kolloid-Zeitschrift*, Vol 15, 1914, No. 4, pp 167–9

**Steel: An Electric Muffle Furnace for the Determination of Carbon and Oxygen in Steel and Tungsten Powder.** By CHARLES MORRIS JOHNSON. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 1, pp 17.

**Steel: Mikroskopische Stahluntersuchung.** By. B. STRAUSS. *Zeitschrift für angewandte Chemie*, Vol. 27, 1914, No. 96, pp. 633–44.

**Steel: The Part Played by the Amorphous Phase in the Hardening of Steels.** By J. C. W. HUMFREY. *Chemical News*, Vol. 110, 1914, No. 2871, pp. 271–4.

**Sulfuric Acid: Apparatus for the Concentration of Sulfuric Acid.** By WILLIAM MASON *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 1, pp. 17–18.

**Sulfuric Acid: Die neueren Schwefelsäurekonzentratoren.** By OSKAR KAUSCH. *Chemische Apparatur*, Vol. 1, 1914, No. 20, pp. 272–4.

**Titanium: Has Titanium Any Influence on the Properties of Steel?** By F. A. J. FITZGERALD. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 1, pp. 28–9.

**Tungsten: The Separation of Tungsten from Molybdenum.** By E. E. MARBAKER. *Journal of the American Chemical Society*, Vol. 37, 1915, No. 1, pp. 86–95.

**Water: A Comparison between the Twenty-Degree and the Thirty-seven-Degree Plate Counts for Enumerating Bacteria in Water.** By J. BOSLEY THOMAS AND EDGAR A. SANDMAN. *American Journal of Public Health*, Vol. 4, 1914, No. 12, pp. 1179–81.

**Water: Progress in Water Supply.** By ALLEN HAZEN *Engineering Record*, Vol. 71, 1915, No. 1, pp. 5–6.

**Water: The Influence of Reservoir Bottoms on Stored Water.** By WILSON FITCH SMITH. *Engineering News*, Vol. 72, 1914, No. 27, pp. 1289–92.

**Water: The Sulfate in River Water.** By H. S. SHELTON. *Chemical News*, Vol. 110, 1914, No. 2874, pp. 307–8.

**Water: Ueber den Blei-, Kupferund Zinkgehalt Künstlicher Mineralwässer und die Bestimmung dieser Metalle.** By C. REESS AND J. DROST. *Zeitschrift fur Untersuchung der Nährungs- und Genussmittel*, Vol. 28, 1914, No. 9, pp. 427–49.

**Wines: Herstellung, Lusammensetzung und Beurteilung des Madeiraweines und seiner Ersatzweine.** By A. KICKTON AND R. MURDFIELD. *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel*, Vol. 28, 1914, No. 7, pp. 325–64.

**Wood: Versuch einer Theorie der Trockendestillation von Holz. I.** By PETER KLASON. *Journal fur praktische Chemie*, Vol. 90, 1914, No. 22, pp. 413–47.

# RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

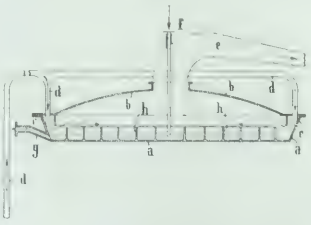
**Bleaching Oils & Fats. C. Baskerville, Oct. 20, 1914. U. S. Pat. 1,114,095.** The oils and fats to be bleached are subjected to the action of a mixture of Fullers' earth and fibrous cellulosic material.

**Revivifying and Preserving Rubber. A. A. Wright, Oct. 27, 1914. U. S. Pat. 1,114,841.** The surface of the rubber is subjected to the action of a solution of camphor gum in alcohol admixed with pulverized pumice.

**Ammonium Phosphate. F. S. Washburn, Oct. 27, 1914. U. S. Pat. 1,115,044.** Ammonium phosphate is produced from crude phosphoric acid and gas house liquor by heating the acid to its boiling point, adding the gas house liquor and causing steam to bubble through the mass.

**Commercially-Pure Nitrates. C. Bosch and W. Wild, Oct. 27, 1914. U. S. Pat. 1,115,164.** Commercially pure nitrates are produced by adding limited quantities of water vapor to gaseous mixtures containing the oxids of nitrogen and the gases thus treated are passed over solid basic substances, such as oxids, hydroxids, and carbonates of the alkaline earth metals at such a temperature that the water set free during the combination of the gaseous nitric acid with the base remains in the state of vapor. The temperature should not be above 300° C.

**Concentrating Nitric Acid. F. Hausmann, Oct. 27, 1914. U. S. Pat. 1,115, 192.** Highly concentrated nitric acids up to mono-hydrate are produced by heating a mixture of sulfuric acid and nitric in one thin layer in a distillation apparatus of the character illustrated. The heated mixture moves horizontally in a continuous stream forward through the apparatus while dry, cold air is passed over the surface of the heated mixture and the fumes of nitric acid and air are conducted away from the remaining sulfuric acid.




**Detinning Process. J. Weber, Oct. 27, 1914. U. S. Pat. 1,115,262.** The tin scrap is placed in a closed vessel and treated with chlorin gas at a temperature above that at which the iron of the scrap is attacked. The gases are circulated within the vessel and means are provided to remove the heat generated by the reaction.

**Separating the Rare Earths, together with Thorium, Cerium and Zirconium, by Electrolysis. L. M. Dennis, Nov. 3, 1914. U. S. Pat. 1,115,513.** The rare earths are fractionally separated by subjecting an aqueous solution of the salts of the rare earths to the action of an electric current at or above the lowest decomposition voltage of the first product desired and fractionally precipitating insoluble compounds of the rare earths from the solution. The steps are repeated as desired while maintaining the cathode surface free from a covering of the electropositive products of the electrolysis.

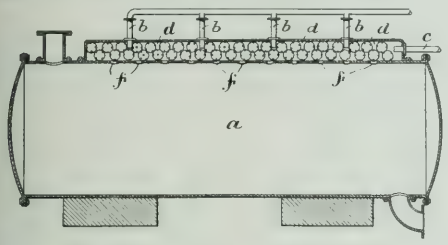
**Continuous or Constant Electric Discharges in Gases. C. F. R. von Kock, Nov. 3, 1914. U. S. Pat. 1,115,625.** The gases to be subjected to the action of the electric arc are first heated electrically or otherwise, in a suitable chamber as 1, to a temperature at which they are electrically conductive and are then brought into contact with the arc, the flow of the gases being longitudinally of the arc.

**Hydrogen. C. Bosch and W. Wild, Nov. 3, 1914. U. S. Pat. 1,115,776.** A gas containing or consisting of carbon monoxid in admixture with steam, is passed over a catalytic agent containing divided iron oxid maintained at a temperature below 650° C.

**Reactive Zeolites. T. R. Duggan, Nov. 3, 1914. U. S. Pat. 1,116,038.** A fused glassy melt comprising alumina, silica, potash and soda with a ratio of soda to potash of approximately

5 : 1, is granulated, extracted with hot water until the glassy character disappears and recrushed to a material of about a 2 mm. mesh.

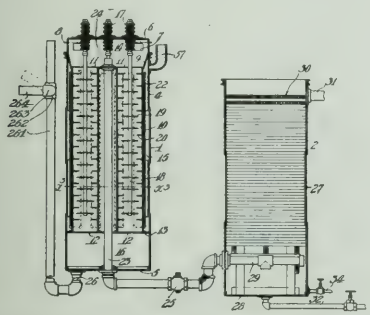
**Tin from Waste Tinned Metal. G. von der Linde, Nov. 3, 1914. U. S. Pat. 1,116,176.** The scrap to be detinned is sub-




jected in a closed chamber, (*a*), to a uniform mixture of air and chlorin produced by diffusion in an adjacent chamber, (*d*).

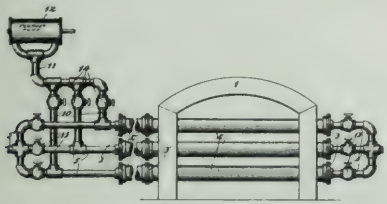
**Fireproofing Materials. W. C. Zeller, Nov. 3, 1914. U. S. Pat. 1,116, 349.** The composition consists of a solution of ammonium sulfate, ammonium phosphate, sodium phosphate and borax.

**Petroleum Emulsions. R. E. Laird and J. H. Raney, Nov. 3, 1914. U. S. Pat. 1,116,299.** Emulsions of petroleum oil and water are subjected to an electric stress for a sufficiently long



time to produce heavy currents through the water particles. The currents are interrupted to allow the coalesced particles to form globules of free water.

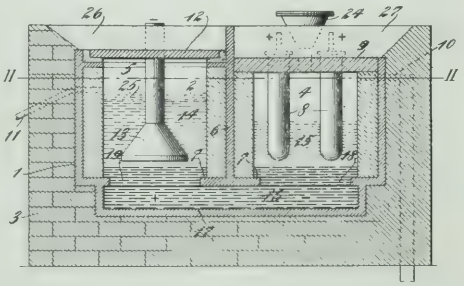
**Cyanogen Compounds. J. E. Bucher, Nov. 10, 1914. U. S. Pat. 1,116,559.** Free nitrogen is brought into contact with an extended surface of molten material, such as sodium cyanid, comprising as one of its constituent elements a metal capable



of combining with nitrogen and carbon and of acting as the base of a stable cyanogen compound under the temperature conditions of the operation. This metal is liberated from the material and, together with nitrogen, combined with the carbon contained in an extended surface of catalytic material having carbon therein to form a cyanogen compound. A large extent of the surface of the catalytic material is maintained free from the bulk of the molten material by distilling off, during the course of the operation, a portion at least of the so formed cyanogen compound.

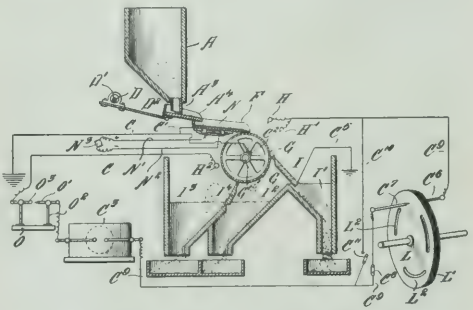
**Oxidizing Lead. C. D. Holley, Nov. 10, 1914. U. S. Pat. 1,116,702.** Finely divided lead is subjected to the simultaneous action of chromate waste liquor containing sodium nitrate and air; the oxidized lead and sodium nitrate are separated afterwards.

**Alkali and Alkaline-Earth Metals. C. E. Acker, Nov. 10, 1914. U. S. Pat. 1,116,865.** Metals belonging to either the alkali or alkaline earth groups are produced by electrolyzing a fluid mass of the desired metal belonging to such groups in a pri-



mary electrolytic cell over a cathode which forms a fusible alloy with the metal and afterward using the alloy as an anode in a secondary electrolytic cell containing an electrolyte comprising a molten cyanid of the light metal, depositing the light metal at the cathode.

**Electrical Separation. H. M. Sutton, W. L. and E. G. Steele, Nov. 10, 1914. U. S. Pat. 1,116,951.** Comminuted materials consisting of conductors and dielectrics are separated by sub-



jecting them to a directly and convectively delivered electrical charge and contacting the material with a source of opposite potential to attract the particles and to retain the dielectric particles while not retaining the conducting particles.

**Manganese Steel from Scrap. H. M. Howe, Nov. 17, 1914. U. S. Pat. 1,117,384.** Manganese steel scrap is melted in a shaft furnace and the relative proportions of manganese in the molten metal adjusted by adding a suitable quantity of ferromanganese. Blown metal of the Bessemer process is then added to the mixture.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JANUARY, 1915

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid | Lb. | 50 | @ | 52 |
| Acetic Acid (28 per cent) | C. | 1.75 | @ | 2.00 |
| Acetone (drums) | Lb. | 17 | @ | 20 |
| Alcohol, denatured (180 proof) | Gal. | 33 | @ | 35 |
| Alcohol, grain (188 proof) | Gal. | 2.58 | @ | 2.60 |
| Alcohol, wood (95 per cent) | Gal. | 45 | @ | 47 |
| Amyl Acetate | Gal. | 2.75 | @ | — |
| Aniline Oil | Lb. | 50 | @ | 60 |
| Benzoic Acid | Lb. | 60 | @ | 70 |
| Benzol (90 per cent) | Gal. | 34 | @ | 35 |
| Camphor (refined in bulk) | Lb. | 41 | @ | — |
| Carbolic Acid (drums) | Lb. | 55 | @ | 60 |
| Carbon Bisulfide | Lb. | 7 | @ | 8 |
| Carbon Tetrachloride (drums) | Lb | 11½ | @ | — |
| Chloroform | Lb. | 30 | @ | 35 |
| Citric Acid (domestic), crystals | Lb. | 55 | @ | 57 |
| Dextrine (corn) (carloads, bags) | C. | | $2.87 | |
| Dextrine (imported potato) | Lb | — | @ | — |
| Ether (U. S. P., 1900) | Lb. | 15 | @ | 20 |
| Formaldehyde | Lb. | 8½ | @ | 9½ |
| Glycerine (dynamite) | Lb. | 21 | @ | 21½ |
| Oxalic Acid | Lb. | 15 | @ | — |
| Pyrogallic Acid (bulk) | Lb. | 1.90 | @ | 2.10 |
| Salicylic Acid | Lb. | 80 | @ | — |
| Starch (cassava) | Lb. | 3¼ | @ | 4 |
| Starch (corn) (carloads, bags) | C. | | $2.09 | |
| Starch (potato) | Lb. | — | @ | — |
| Starch (rice) | Lb. | — | @ | — |
| Starch (sago) | Lb. | — | @ | — |
| Starch (wheat) | Lb. | 5 | @ | 10 |
| Tannic Acid (commercial) | Lb. | 60 | @ | 66 |
| Tartaric Acid, crystals | Lb. | 37 | @ | 38 |

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lead (brown, broken) | Lb. | 7¼ | @ | 7½ |
| Acetate of Lime (gray) | C. | 2.00 | @ | 2.05 |
| Alum (lump) | C. | 2.75 | @ | 3.00 |
| Aluminum Sulfate (high-grade) | C. | 1.30 | @ | 1.60 |
| Ammonium Carbonate, (domestic) | Lb. | 8½ | @ | 9 |
| Ammonium Chloride, (gray) | Lb | 6¼ | @ | 6¾ |
| Aqua Ammonia (drums) 16° | Lb. | 2¼ | @ | 2½ |
| Arsenic (white) | Lb | 4 | @ | 5 |
| Barium Chloride | Ton | 45.00 | @ | 50.00 |
| Barium Nitrate | Lb. | 15 | @ | 16 |
| Barytes (prime white, foreign) | Ton | 19.00 | @ | 25.00 |
| Bleaching Powder (35 per cent) | C. | 1.37½ | @ | 2.00 |
| Blue Vitriol | C. | 4.35 | @ | 4.55 |
| Borax, crystals (bags) | Lb. | 4¼ | @ | 4¾ |
| Boric Acid, crystals (powd.) | Lb. | 8½ | @ | — |
| Brimstone (crude, domestic) | Long Ton | 22.00 | @ | 22.50 |
| Bromine (bulk) | Lb. | 40 | @ | 50 |
| Calcium Chloride (lump) | Ton | 11.70 | @ | 12.00 |
| Chalk (light precipitated) | Lb. | 4½ | @ | 5½ |
| China Clay (imported) | Ton | 14.00 | @ | 16.00 |
| Feldspar | Ton | 8.00 | @ | 14.00 |
| Fuller's Earth (powdered, foreign) | C. | 80 | @ | 90 |
| Green Vitriol (bulk) | C. | 30 | @ | 32 |
| Hydrochloric Acid (18°) | C. | 1.15 | @ | 1.65 |
| Iodine (resublimed) | Lb. | 3.75 | @ | 4.00 |
| Lead Nitrate | Lb. | 8 | @ | 8⅛ |
| Litharge (American) | Lb | 5 | @ | 5¼ |
| Lithium Carbonate | Lb. | 1.00 | @ | 1.10 |
| Magnesium Carbonate | Lb. | 4¼ | @ | 5¼ |
| Magnesite "Calcined" | Ton | 40.00 | @ | 50.00 |
| Nitric Acid (36°) | Lb. | 3⅞ | @ | 4¼ |
| Phosphoric Acid (sp. gr. 1.75) | Lb. | 28 | @ | 28½ |
| Phosphorus | Lb | 35 | @ | 95 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate | Lb | 12 | @ | 14 |
| Potassium Bromide | Lb | 70 | @ | 80 |
| Potassium Carbonate (calcined), 80 @ 85% | C. | 5½ | @ | 6 |
| Potassium Chlorate, crystals | Lb | 18 | @ | 22 |
| Potassium Cyanide (bulk), 98–99% | Lb | 25 | @ | 30 |
| Potassium Hydroxide | Lb. | 8 | @ | 9 |
| Potassium Iodide (bulk) | Lb | 3.15 | @ | 3.25 |
| Potassium Nitrate (crude) | Lb. | — | @ | — |
| Potassium Permanganate (bulk) | Lb. | 16 | to | 21 |
| Quicksilver, Flask (75 lbs.) | | 51.00 | @ | 54.00 |
| Red Lead (American) | Lb. | 5½ | @ | 6 |
| Salt Cake (glass makers') | C. | 55 | @ | 65 |
| Silver Nitrate | Oz | 31½ | @ | 32¾ |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash (48 per cent) | C. | 67½ | @ | 72½ |
| Sodium Acetate | Lb. | 5 | @ | 7 |
| Sodium Bicarbonate (domestic) | C. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate (English) | Lb. | 3½ | @ | 4 |
| Sodium Bichromate | Lb. | 4¾ | @ | 5 |
| Sodium Carbonate (dry) | C. | 60 | @ | 80 |
| Sodium Chlorate | Lb. | 14 | @ | 16 |
| Sodium Hydroxide (60 per cent) | C. | 1.55 | @ | 1.57½ |
| Sodium Hyposulfite | C. | 1.60 | @ | 1.90 |
| Sodium Nitrate (95 per cent, spot) | C. | 1.85 | @ | 1.90 |
| Sodium Silicate (liquid) | C. | 85 | @ | 1.15 |
| Strontium Nitrate | Lb. | 15 | @ | 17 |
| Sulfur, Flowers (sublimed) | C. | 2.20 | @ | 2.60 |
| Sulfur, Roll | C. | 1.85 | @ | 2.15 |
| Sulfuric Acid (60° B) | C. | 85 | @ | 1.00 |
| Talc (American) | Ton | 15.00 | @ | 20.00 |
| Terra Alba (American), No. 1 | C. | 75 | @ | 80 |
| Tin Bichloride (50°) | Lb. | 9¾ | @ | 10 |
| Tin Oxide | Lb. | 38 | @ | 40 |
| White Lead (American, dry) | Lb. | 5 | @ | 5¼ |
| Zinc Carbonate | Lb. | 8¼ | @ | 8¾ |
| Zinc Chloride (granulated) | Lb. | 4½ | @ | 5 |
| Zinc Oxide (American process) | Lb. | 5⅜ | @ | 6⅜ |
| Zinc Sulphate | C. | 2½ | to | 2¾ |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax (pure white) | Lb. | 45 | @ | 57 |
| Black Mineral Oil, 29 gravity | Gal. | 12½ | @ | 13 |
| Castor Oil (No. 3) | Lb. | 8¼ | @ | 9 |
| Ceresin (yellow) | Lb. | 10 | @ | 25 |
| Corn Oil | C. | 5.70 | @ | 5.75 |
| Cottonseed Oil (crude), f. o. b. mill | Gal. | 44 | @ | — |
| Cottonseed Oil (p. s. y.) | Lb. | 6¾ | @ | 6⅞ |
| Cylinder Oil (light, filtered) | Gal. | 20 | @ | 25 |
| Japan Wax | Lb. | 10 | @ | 11 |
| Lard Oil (prime winter) | Gal. | 90 | @ | 92 |
| Linseed Oil (raw) | Gal. | 59 | @ | — |
| Menhaden Oil (crude) | Gal. | 33 | @ | — |
| Naphtha, 68 @ 72° | drums | — | @ | 17 |
| Neatsfoot Oil (20°) | Gal. | 96 | @ | 98 |
| Paraffine (crude, 120 & 122 m. p.) | Lb. | 3⅛ | @ | 3¼ |
| Paraffine Oil (high viscosity) | Gal. | 26 | @ | 27 |
| Rosin ("F" grade) (280 lbs.) | Bbl. | 3.80 | @ | 3.90 |
| Rosin Oil (first run) | Gal. | 25 | @ | — |
| Shellac, T. N | Lb. | 14 | @ | 15 |
| Spermaceti (cake) | Lb. | 27 | to | 28 |
| Sperm Oil (bleached winter), 38° | Gal. | 70 | @ | 71 |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid (double-pressed) | Lb. | 9 | @ | 11 |
| Tallow (acidless) | Gal. | 62 | @ | 63 |
| Tar Oil (distilled) | Gal. | 30 | @ | 31 |
| Turpentine (spirits of) | Gal. | 46½ | @ | 47 |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum (No. 1 ingots) | Lb. | 18½ | @ | 19 |
| Antimony (Hallet's) | Lb. | 14½ | @ | 15½ |
| Bismuth (New York) | Lb. | 2.80 | @ | 2.90 |
| Bronze powder | Lb. | — | @ | — |
| Copper (electrolytic) | C. | 13⅛ | @ | 13¼ |
| Copper (lake) | C. | 13¼ | @ | 13⅜ |
| Lead, N. Y. | C. | | 3.80 | |
| Nickel | Lb. | — | @ | — |
| Platinum (refined) | Oz. | 50.00 | @ | 52.00 |
| Silver | Oz. | 48½ | @ | 50 |
| Tin | C. | 33.75 | @ | 33.87½ |
| Zinc | C. | 5.60 | @ | 5.65 |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | C. | 2.62½ | @ | 2.65 |
| Blood (dried) | Unit | 2.80 | @ | 2.90 |
| Bone, 4½ and 50 (ground, raw) | Ton | 30.00 | @ | — |
| Calcium Cyanamid | Unit of Ammonia | 2.30 | @ | 2.35 |
| Calcium Nitrate (Norwegian) | C. | — | @ | — |
| Castor meal | Unit | — | @ | — |
| Fish Scrap (domestic, dried) | Unit | 3.00 | & | 10 |
| Phosphate, acid (16 per cent bulk) | Ton | 7.00 | @ | — |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble (68 per cent) | Ton | 2.25 | @ | 2.50 |
| Tennessee (70–80 per cent) | Ton | 5.00 | @ | 5.50 |
| Potassium, "muriate," basis 80 per cent | Ton | | nominal | |
| Pyrites (furnace size, imported) | Unit | 13 | @ | — |
| Tankage (high-grade) | Unit | 2.80 | & | 10 |

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# EDITORIALS

## INTERNATIONAL ENGINEERING CONGRESS

The dates for the great International Engineering Congress to be held in San Francisco during the Panama-Pacific Exposition have been definitely announced as September 20-25 by W. F. Durand, Chairman of the Committee of Management. The Congress is to be held under the auspices of the American Society of Civil Engineers, the American Institute of Mining Engineers, the American Society of Mechanical Engineers, the American Institute of Electrical Engineers and the Society of Naval Architects and Marine Engineers. Colonel G. W. Goethals has consented to act as Honorary President and is expected to preside in person over its general sessions.

The papers to be presented before the Congress will cover the general field of engineering. They are intended to treat the various topics in a broad and comprehensive manner and with special reference to the important lines of progress during the past decade, the present most approved practices and the lines of present and future development. It is intended, furthermore, that all such papers shall be accompanied with a reasonably full bibliography of the subject, giving references to the important original papers and sources of information relating to the special topic of the paper. The authors of the papers are distributed over the engineering world, and comprise men eminent in the various branches of the profession.

A special effort will be made to procure discussions, carefully prepared in advance, for presentation with the papers. In addition, opportunity will be afforded for oral discussion at the various sessions of the Congress. It is anticipated that limitations of space may require the ultimate publication of all discussions in condensed or summary form. Discussions will be welcomed in any language at the choice of the writer, and if in other than English will be translated for publication.

The various papers, some 300 or more in number, will be presented before the Congress in 10 or more sections closely approximating the division of subjects by volumes.

The meetings will be held in the new Auditorium building in the Civic Center of San Francisco, in which the Panama-Pacific International Exposition authorities have reserved for the week of the Congress a sufficient number of assembly, section and committee rooms to fully meet all requirements of the Congress.

Subject to necessary modification, the transactions will be published in 10 volumes, 6×9 inches in size, and of about 500 pages each, with one smaller or half volume which will contain the reports of the general or business meetings of the Congress, together with a title and author index and a brief digest of each paper presented.

The schedule of volumes is as follows:

Volume I The Panama Canal (24 topics)
Volume II Waterways (6 topics)
Irrigation (11 topics)
Volume III—Railways (7 topics)
Volume IV Municipal Engineering (8 topics)
Volume V—Materials of Engineering Construction (20 topics)
Volumes VI and VII—Mechanical Engineering (28 topics)
Electrical Engineering (8 topics)
Volume VIII—Mining Engineering (10 topics)
Metallurgy (10 topics)
Volume IX—Naval Architecture and Marine Engineering (19 topics)
Volume X—Miscellaneous
Index and Digest

All engineers and all others who are interested in engineering work, its progress and achievements, are cordially invited to subscribe as members of the Congress.

The general fee for membership in the Congress, open to all engineers or others interested in engineering subjects, is $5.00 U. S. Gold, which will entitle the member to receive the index volume and any single volume of the transactions he may select, together with the right of participation in all general activities and privileges of the Congress.

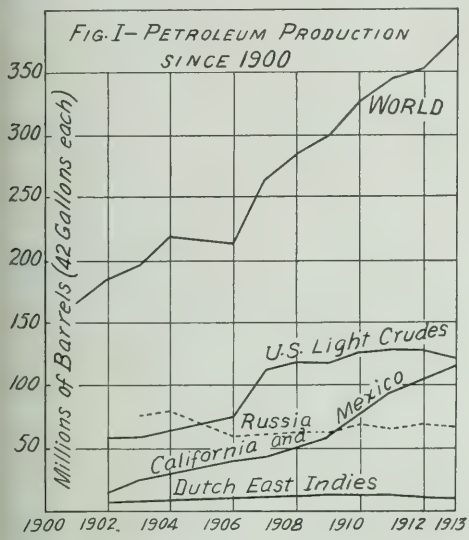
It is expected that there will be arranged a number of excursions to points of engineering and general interest within practicable reach of San Francisco, and every effort will be made to make possible the personal inspection of such engineering works as are especially typical of the Pacific Coast.

## A STATISTICAL REVIEW OF THE QUESTION OF GASOLINE SUPPLY

Some three or four years ago the question of an adequate supply of gasoline threatened to become acute. This situation was brought about by causes the most important of which are familiar to all interested in petroleum. During the brief period of the last three years a large number of patents have appeared, which have for their object the increasing of the yield of gasoline, some of them constituting real advances in petroleum technology and others interesting because of the bizarre transformation which matter, in the form of petroleum, is made to undergo. The situation just prior to the introduction of improved methods of cracking is here briefly reviewed.

Reliable statistics of the production of gasoline are not available, particularly in this country, the largest producer up to the present time. A better index of available gasoline is obtained by reference to the crudes which yield it. The world's production of petroleum since 1900 is graphically shown in Fig. 1. Attention should be called to the fact that the greatest increases in the production of crude have been in fields yielding heavy oil containing little or no gasoline, as is the case with California and Mexican oils. Arnold and Garfias (*Bull. Am. Inst. Min. Eng.*, 1914, p. 394) place the probable maximum annual production of California at about 100,000,000 barrels. Rear Admiral Edwards (*Bull. Am. Inst. Min. Eng.*, 1914, p. 2293) has recently expressed a similar opinion. On

the other hand, some of the fields yielding oil containing relatively large percentages of gasoline have sharply declined, as the Appalachian and Lima-Indiana fields, or have remained practically stationary as has been the case with Russia and the Dutch East Indies. This is indicated in Fig. I. The curve designated as




"U. S. Light Crudes" gives the production in the various fields of the United States with the exception of California and the Gulf, since these latter fields can hardly be considered factors in the production of natural gasoline. While small yields of gasoline are obtainable from some of the Californian, Mexican, and Gulf oils, it is also true that small pools of very heavy oils occur in fields classed in Fig. I as "Light Crudes." It is believed that these factors fairly balance, making the classification used a rational one.

The relative insignificance of foreign sources, such as the Dutch East Indies, is apparent. In this connection it may be of interest to note the production of petroleum in the four principal Baku districts during the last four years.

PRODUCTION OF PETROLEUM IN THE PRINCIPAL BAKU DISTRICTS

| Year | Tons | Price per ton |
|---|---|---|
| October 1909 to October 1910.... | 8,766,000 | $ 4.48 |
| October 1910 to October 1911..... | 7,819,200 | 5.30 |
| October 1911 to October 1912..... | 7,470,000 | 8.74 |
| October 1912 to October 1913..... | 7,192,000 | 11.38 |

The effect on production of increase in the prices paid for light crudes during 1912 and 1913 was very slight indeed, an actual decrease in the total production of light crudes in the United States having occurred, as is shown in Fig. I. (The figures for 1914, including the Cushing pool, are not yet available.)

AVERAGE PRICE OF LIGHT CRUDES PER BARREL IN U. S. FIELDS

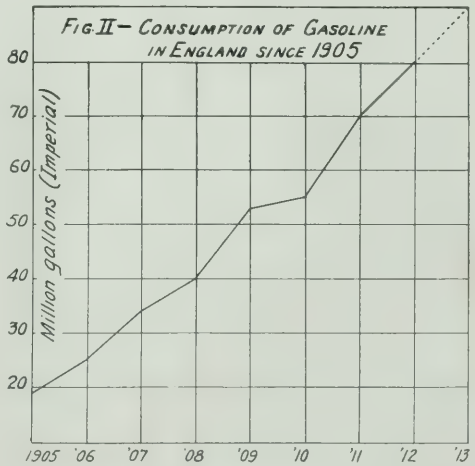
| Year | Penna. | Ill. | Okla. | Texas |
|---|---|---|---|---|
| 1910..... | $1.33 | $0.59 | $0.39 | $0.75 |
| 1911..... | 1.30 | 0.63 | 0.48 | 0.66 |
| 1912..... | 1.64 | 0.85 | 0.67 | 0.75 |
| 1913 August..... | 2.50 | 1.30 | 1.03 | 0.90 |
| 1914 January..... | 2.50 | 1.45 | 1.05 | 0.95 |
| 1914 December..... | 1.50 | 0.89 | 0.55 | 0.55 |

The tremendous increase in the consumption of gasoline has undoubtedly been a big factor in the general increase in prices paid for light crudes. This is indicated by the fact that the oils richest in gasoline showed the greatest advances in price. The gasoline consumption in England, a non-producing country, has been taken as probably indicating most accurately the new conditions confronting the market.

This rapid increase has been due chiefly to the automobile, motor cycle and motor boat. The number of automobiles in England increased from 276,258 in 1911 to 440,000 in 1913. Even more remarkable is the increase in the number of automobiles in use in the United States. In 1910 there were in the United States, as nearly as can be ascertained, from the registration statistics, about 350,000 motor vehicles in use; in 1911 the figure given was 550,000, in 1912 this total had mounted to 990,700, and is estimated at the present time at 1,500,000. (*New York Journal Comm.*, Aug. 8, 1914).

The number of makers of commercial trucks increased from 198 in 1911, to 312 in 1912, and there are now stated to be 85,000 motor vehicles in this class in operation in this country. The rapid increase in the use of motor trucks during the last two years is of the greatest importance, because of the demand for a cheaper grade of gasoline or motor fuel. More accurate data are available giving the number of automobiles *manufactured* in this country since 1903. This is shown graphically in Fig. III.

Evidently the demand for gasoline has been growing at a much greater rate than the production. There are other factors which tend to make higher prices for crude petroleums of practically all classes. The

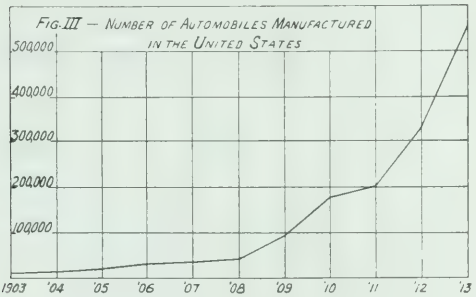



consumption of fuel oil in this country for steaming purposes has doubled since 1906, although its market price has approximately doubled in the same period. [Arnold and Garfias (*Bull. Am. Inst. Min. Eng.*, **1914**, p. 394) call attention to the fact that, considering only the relative heating value and market prices of fuel oil and coal in California, fuel oil should sell for

$0.93 per bbl. The consumption of oil for fuel in this country in 1906 was 15,577,000 bbls. and in 1913 was 33,004,000 bbls.] The production of asphalt from residuum increased 33.7 per cent during the year 1912, the total production amounting to 333,213 tons.

A critical examination of the various ways of meeting a possible shortage of gasoline brings out only more strongly the paramount importance of a plentiful supply of this article.

In general, the gasoline now on the market averages ten degrees Baumé lower gravity than the common market product of only a few years ago. Users of automobiles have found that in most motor vehicles the heavier grades of gasoline are perfectly satisfactory. As expressed by V. B. Lewes in the *Journal of the Royal Society of Arts*, **1913**, p. 706: "for continuous running, with the engine hot, such mixtures of petrol and kerosene give excellent results, showing indeed, an improvement in power over the original spirit." Numerous attempts have been made to devise carbureters to use oil of about 48° Bé., but none has as yet come into wide use. Most of them give difficulty in starting, and the engine does not pick up if allowed to slow down. One type of carbureter




now being advocated is arranged to be started on gasoline and, after the engine is hot, uses kerosene of about 46° Bé. without trouble, but the day of the kerosene motor has not yet arrived, and whether motor fuel heavier than about 55° Bé. will ever give satisfaction in *automobile* engines is very doubtful.

The gravity alone does not necessarily indicate what an oil will do in a gasoline engine. The volatility of an oil and the temperature at which *it will form explosion mixtures* are of greater importance than gravity. As indicated above, the motor fuel now in common use is considerably heavier than that sold a few years ago. It should be remembered that the character of "gasoline" was originally determined by the flash point limits prescribed by law for kerosene and had no reference to the adaptability of the gasoline for internal combustion engines. While considerable work has been done in attempting to utilize kerosene in automobiles apparently no systematic, impartial investigation has ever been made to determine how much of the lighter fractions of kerosene can be included in the various grades of light gasoline for good results with the carbureters and gasoline motors now in common use. The gasoline of the present day may be considered as that fraction boiling under approximately 150° C. It should be pointed out that if the whole distillate boiling below 200° C., which would include approximately a third of the kerosene, could be used as motor fuel, the quantity of the latter available would be doubled. Such motor fuel would have a gravity of approximately 56° Bé.

The manufacturer of casing-head gasoline is increasing the production slightly, but the maximum production from this source is small, probably not more than a million barrels annually. The United States Geological Survey gives the production of natural gas gasoline in this country in 1913 as 571,000 barrels of 42 gallons. Singer, in *Petroleum*, **9** (1913), 453, gives the U. S. production in 1912 as 12,081,000 gallons or about 287,000 barrels. Yet if 1,500,000 automobiles use 10 barrels each per year we arrive at a grand total gasoline consumption of 15,000,000 barrels in this country for automobiles alone. Casing-head gasoline cannot therefore meet more than a small fraction of the requirement. Not all of this will be available for motor purposes, as special uses for it have already been found. The methods which have been suggested for the recovery of similar products are of only very minor importance, such as the condensation of the gases from petroleum stills, which ordinarily escape uncondensed. Groeling (D. R. P., 246,935 of 1909) absorbs the uncondensed vapors by passing them through naphtha. Blau (U. S. Pat. 994,369 of 1911) subjects oil gas to pressure and separates a low boiling gasoline. Wolff (U. S. Pat. 1,000,655 of 1911) liquefies a similar product by the Lindé effect.

The production of shale oil cannot, at present, be considered a factor. Sir Boverton Redwood (*J. Roy. Soc. Arts.*, Dec. 26, 1913) claims that motor fuel from Scotch shale oil contributed last year only 0.75 per cent of England's consumption of motor fuel. The shale oil industry appears to be in a static condition, the production in 1913 having been only 3 per cent greater than in 1904.

Benzol, from coal tar, has found some favor in Europe for motor vehicles, but the largest possible supply is very small compared with the requirements. In 1912 England consumed 80,000,000 gallons of gasoline and produced 8,000,000 gallons of crude benzol (*J. Soc. Chem. Ind.*, **1913**, 514), most of which was exported for use in other industries. The coal coked in by-product ovens in the United States in 1913 was approximately 17,000,000 tons, according to the estimate of H. C. Porter in the U. S. Bureau of Mines Technologic Paper, No. 89. Mr.. Porter estimates the *possible* production of benzol from this source at about 600,000 barrels (of 42 gallons). There were actually produced, in 1913, about 190,000 barrels by passing the gas through heavy oil, and "possibly 24,000 barrels more by tar distillation. Much of this, about one-half, was used in enriching gas for illuminating purposes." The use of by-product ovens is increasing but, on the other hand, oil-gas and oil producer-gas plants are rapidly displacing the coal retort, as the consumption of 13,800,000 barrels of oil in 1909 for gas making in this country show. Data

on the possible production of benzol from oil-gas tar are not available.

Benzol has been recommended as a valuable addition to alcohol for motor purposes. Alcohol, as a motor fuel, has received considerable attention. Although 95 per cent alcohol has little more than half the calorific value of gasoline of 0.710 specific gravity (5833 C. as compared with 10611 C.), it gives a relatively higher efficiency, owing to its greater ease of combustion, smaller proportion of air required for complete combustion, and greater compression with a slightly cooler cycle. It is possible that engines will be perfected which will be better adapted to alcohol than the present gasoline motor. However, industrial denatured alcohol has failed to reach the low prices predicted for it. It is now quoted at 37 cents per gallon, and for the same results in a gasoline motor, would be at least 20 per cent more costly than gasoline at 40 cents per gallon. It is significant that denatured alcohol has not heretofore been used as motor fuel in England even when gasoline sold for 38 to 42 cents per gallon. Ormandy (*Zeitschr. f. angew. Chem.*, **1914**, Ref. 177) has recently published the following results of tests made with different mixtures of alcohol and benzol. [Cf. Moyer, *Power*, **1914**, p. 569].

MOTOR TESTS WITH DIFFERENT MIXTURES OF ALCOHOL AND BENZOL

| PER CENT | | RESULTS COMPARED WITH GASOLINE STANDARD | |
|---|---|---|---|
| Alcohol | Benzol | Power | Fuel consumption |
| 50 | 50 | 1 per cent less | 3 per cent less |
| 66.7 | 33.3 | 8 per cent less | 8.9 per cent greater |
| 75 | 25 | 8.5 per cent less | 24.5 per cent greater |

So far, all attempts to adapt the heavy oil engines of the Diesel type to motor vehicles have failed.

It seems certain, therefore, that gasoline, including the lighter part of kerosene, is for motor vehicles the undisputed necessity of the day, and that there is nothing seriously to compete with it so long as its retail cost does not exceed about 40 cents per gallon, at which figure alcohol may *possibly* become a competitor. Redwood and Lewes regard the eventual employment of alcohol as a motor fuel as inevitable [*Chem. Abs.*, **7** (1913), 3410; Redwood, *J. Roy. Soc. Arts*, Dec. 26, 1913]. Estimating the present production of gasoline in this country as 25,000,000 barrels of 42 gallons each, the amount of corn required to produce the same volume of 96 per cent alcohol by fermentation would be approximately 450,000,000 bushels, an amount certain to affect prices to a marked degree, in view of the fact that we have no corn for export.

Increasing the available supply of gasoline by cracking, particularly by distilling under pressure, has long been known to be a possibility; in fact Dewar and Redwood patented such a process twenty years ago, but with the object of manufacturing illuminating oil, not gasoline.

BENJAMIN T. BROOKS

## WHY NOT A CHEMICAL SHOW?

It has often been said that of all professional work the chemist's is least known to the general public. The bar is known more or less through the press, the clergy through the pulpit, the physician meets all classes in the course of his work, and to the architect and the engineer Sir Christopher Wren's epitaph applies, "*Si monumentum requiris, circumspice*"—if you seek his monument, look about you. The chemist's work is done chiefly in his laboratory out of sight of the public, and it is largely, though vital, only contributory; that is, except in the case of those industries of a purely chemical nature, such as the manufacture of chemicals, the chemist's contribution is often absorbed in a larger whole, as for example in the steel industry, and thus lost to the view of all except those who have an intimate knowledge of the circumstances. These, and not the chemist's native modesty, are probably the chief reasons for the average man's lack of familiarity with the field of applied chemistry.

This is a condition, however, that is continually changing. People in general are much better informed in technical matters now than they were a great many years ago, and this information is continually spreading. The recent crisis in this country brought on by the war has brought home more definitely than ever before the value of the chemist in industry, while at the same time, in spite of the spread of information, it has shown more clearly than ever before, as for example in newspaper discussions of the dye situation, how little appreciation there is of the enormous development chemistry has undergone and the time this development has required.

A time like this, then, would seem particularly propitious for any undertaking that would crystallize out in the minds of the public the knowledge already present in a more or less amorphous shape of what chemistry today means, and at the same time add a large amount of new information of the same kind. Such an undertaking would be of reciprocal benefit to the public and the chemical profession.

The most direct agency of that kind would be an exhibition modeled after the electrical and gas shows and many others of the same kind held in New York annually. It ought to draw the public, for it would not only be a novelty but would contain exhibits fully as spectacular, interesting and instructive as those of other shows. It ought to draw the support of manufacturers of chemicals, chemical products, chemical apparatus and related products, because it would offer unusual advertising facilities. It ought to have behind it the whole profession because it would broaden and stimulate interest in chemistry and appreciation of its value.

It is not possible here to go into the number or kind of exhibits that could be placed on view, but the possibilities are so great that it would probably be more necessary to limit the field than to seek to enlarge it.

Against the scheme may be presented the facts that it would be an experiment, that it would be expensive, and that to carry it out some new organization would probably have to be formed. The only answer to these points would be some general expression of opinion of those interested, particularly those likely to become exhibitors.

MARSTON L. HAMLIN

# ORIGINAL PAPERS

## THE PREPARATION OF GASOLINE AND KEROSENE FROM HEAVIER HYDROCARBONS

By Benjamin T. Brooks, Raymond F. Bacon, Fred W. Padgett and Irvin W Humphrey

Received January 21, 1915

The earlier attempts to convert heavy petroleum hydrocarbons of high boiling points into lighter more volatile products were carried out in most, if not all, cases with the object of increasing the yield of illuminating oil.

The "cracking" of heavy hydrocarbons by heat is to be regarded as simply an instance of the general rule that organic compounds are decomposed by heat. It is well known that the simpler petroleum hydrocarbons are stable at much higher temperatures than those of higher molecular weight. Every refiner knows that certain crudes "crack" more easily than others, which fact is to be accounted for by the presence of hydrocarbons of different constitution. In the case of the simpler hydrocarbons which have been studied, it is known that olefines are in general less stable to heat than saturated hydrocarbons of the same molecular weight, and naphthenes are usually more stable than paraffines. Normal hexane and the more stable methyl cyclopentane are good examples of the latter types. It was to be expected, therefore, that attempts would be made to produce gasoline from heavier hydrocarbons by heat decomposition at temperatures somewhat higher than those employed for the production of kerosene by cracking. A large number of recent patents seek to attain this end. The fatal difficulty with processes of this class, operating at atmospheric pressure, is the large per cent of olefines contained in the resulting gasoline. This figure will vary, when the oil is simply subjected to heat at atmospheric pressure, from 20 to 50 per cent, depending on the temperature at which the oil is cracked. The maximum per cent of olefines demanded by the simple general equation, $RCH_2 - CH_2 - CH_2R_1 \longrightarrow RCH_3 + CH_2 = CH.R_1$, is seldom attained owing to other reactions, such as polymerization of the olefines and the formation of naphthenes. Gasoline made by cracking under atmospheric pressure, the heavier portion of Oklahoma crude, *i. e.*, the part left after distilling off the gasoline and kerosene, in such a way as to condense and return to the still all but gasoline and naphtha, showed a content of olefines of approximately 28 per cent, as indicated by the iodine number and loss to ordinary sulfuric acid. Consequently a number of patents have been issued covering processes which seek to hydrogenate the olefines formed. It has been proposed[1] to hydrogenate the olefines by placing a catalyst, such as platinum or palladium, in the still, but this process is not being operated for obvious reasons. Several proposed processes claim the cracking of heavy hydrocarbons in the presence of steam and iron. The method patented by the New Oil Refining Process Company, Ltd.,[1] requires the passing of petroleum and steam through a retort containing scrap iron at 540° to 650° C. The processes proposed by Adams,[2] Greenstreet,[3] Hyndman,[4] and Turner[5] specify the cracking of heavy oil at higher temperatures (Greenstreet and Hyndman specify a "cherry temperature") in the presence of steam alone. The claim has been made that the water is converted into CO and hydrogen, the latter effecting hydrogenation of the olefines produced. Testelin and Renard[6] vary this by passing the vapors of oil and steam over a red-hot layer of clay or alumina. Vernon Boys[7] passes the oil and steam mixture through heated tubes containing nickel rods. Lamplough[8] cracks in the presence of steam and in contact with nickel in a retort maintained at a dull red heat. Moeller and Woltereck[9] pass oil and steam through tubes containing coke at 600° to 700° C. None of the above processes are being operated on a large scale in this country at the present time.

Another method of subjecting the heavy petroleum hydrocarbons to the higher temperatures required to produce the desired increased yields of gasoline is heating or distilling under pressure. It is known that unsaturated hydrocarbons are condensed to saturated hydrocarbons by the action of heat and pressure. Ipatiew[10] showed that ethylene, probably the most stable of the olefines, could be converted into a mixture of liquid hydrocarbons at 325° C. and 70 atmospheres pressure. At 380° to 400° C. the reaction was sufficiently rapid to cause a fall of 5 atmospheres per minute in the pressure of the closed apparatus. Engler[11] and his collaborators have shown that amylene and hexylene yield saturated compounds of the naphthene type by heating under pressure. It is therefore to be expected that naphthenes will be found in gasoline and kerosene made by pressure distillation of heavier hydrocarbons; indeed, this has been shown by Engler.[12]

In regard to the pressure distillation processes which have been proposed, the older ones sought to increase the yield of kerosene, since gasoline, in the days of such early patents as those of Benton, was of very little value. In the present discussion, only the more important processes are mentioned. In 1869, Peckham[13] claimed to have obtained, by distilling under 20 lbs. pressure, as much as 60 per cent *illuminating oil* of specific gravity 0.810 from a Cali-

[1] U. S. Patent 826,089, July 17, 1906.

[1] French Patent 451,471, December, 1912; Eng. Pat. 28,460, 1911; Eng. Pat. 20,074, 20,075, September 3, 1912; Eng. Pat. 13,675, 1908.

[2] *Petroleum Gazette*, **1910**, July, p. 2.

[3] U. S. Patent 1,110,925; English Patent 16,452, July 13, 1912

[4] French Patent 462,484, September 11, 1913.

[5] French Patent 451,162, 1912.

[6] German Patent 268,176, October 12, 1913.

[7] *Met. Chem. Eng.*, **1914**, p. 180.

[8] English Patent 19,702, August 28, 1912.

[9] Eng. Patent 16,611, July, 1913.

[10] *Ber. d. deut. chem. Ges.*, **44** (1911), 2778

[11] *Ibid.*, **42** (1909), 4610, 4613, 4620; **43** (1910), 388.

[12] Engler, *Ibid.*, **33** (1900), 2015. Nastjukoff, *J. Russ. Phys. Chem. Ges.*, **36** (1904), 881. Kraemr & Spilker, *Ber. d. deut. chem. Ges.*, **33** (1900), 2265.

[13] *Chemical News*, **1869**, p. 183

fornia crude oil yielding 20 per cent kerosene of the same quality when distilled in the usual manner at atmospheric pressure. Thorpe and Young[1] obtained from paraffine, by heating at a "high pressure" and subsequent fractionation, a light oil shown to contain pentane, hexane, heptane, octane and nonane.

A few patented processes,[2] including the recent ones of Testelin and Renard,[3] subject oil to heat and pressure and distil the liquid *after* the pressure is released. Testelin and Renard seek to avoid the deposition of carbon, always obtained when oil or oil vapor is passed through a heated pipe coil, as in some of the earlier processes. This they proposed to do by uniformly heating the pipe coil, containing the *liquid oil*, to a temperature not exceeding 450° C., by submerging the coil in a bath of lead at the desired temperature. A sufficient pressure was maintained on the heated

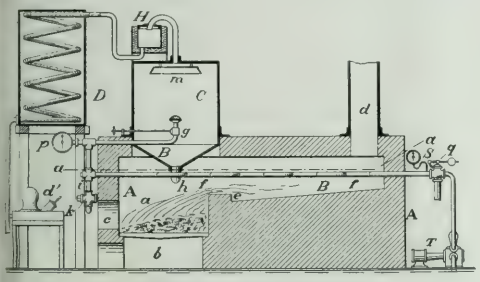


FIG. I—APPARATUS EMPLOYED BY BENTON

oil to keep it in a liquid state. The process patented by Clark[4] describes pumping the oil through heated pipes, collecting the hot oil in a receiving drum where distillation under pressure is permitted. The older patents of Benton[5] also embodied the principle of subsequent distillation after release of the pressure but heated the pipe coils directly by a flame.

As regards actual distillation under pressure, a number of early patents describe the manufacture of *illuminating oils* by the use of low pressures. Thus Young[6] stipulated pressures of 10 to 20 pounds per square inch. Krey[7] recommended two to four atmospheres and claimed to obtain a distillate of a specific gravity of 0.820 (yield not given). Boleg[8] recommended pressures of three to four atmospheres and says that pressures of four to six atmospheres yield more "illuminating oil" but less "lubricating distillate" than the lower pressure. Dewar and Redwood[9] devised an apparatus for distilling petroleum under pressure, which is the general arrangement now employed on a larger scale by a later patentee. Dewar and Redwood, however, did not state *what pressure* gave the results desired nor did they advocate their process as one suitable for manufacturing *gasoline*.

The foregoing brief review outlines the "state of the art" prior to the patent of Bacon and Clark.[1] The latter patent specifies the distillation of heavy petroleum oils between pressures of 100 and 300 pounds. The advantages of the range specified, so far as increased yields of gasoline are concerned, are brought out by the results represented graphically in Fig. III. The yields given are not the maximum obtainable but represent comparative results of a series of experiments obtained by distilling a given quantity of Oklahoma reduced oil at a *uniform rate* from the same apparatus at the different pressures indicated.

The effect of pressure in diminishing the per cent of *olefines* in the gasoline obtained is a noteworthy feature of these results. The same effect is very strikingly shown in the recent results of Whitaker and Rittman[2] on the effect of pressure in the yield of illuminants in oil gas. At 900° C., Whitaker and Rittman obtained from a given quantity of oil 122 liters of illuminants at 0.75 lb. pressure, 50 liters at atmospheric pressure and 15.5 liters at 45 lbs. (absolute) pressure. They were also able to show that at temperatures of 750° to 800° C. the addition of hydrogen to the gas mixture has the effect of partially hydrogenating the olefines and that this reaction takes place more readily as the pressure on the system is increased. Ipatiew[3] has made the interesting observation that, in the distillation of petroleum under pressure, at the higher pressures the evolved gases become continually poorer in hydrogen in spite of the higher temperatures required to maintain the higher pressures. The pressures employed by Ipatiew were 120 to 340 atmospheres. We have found the following:

TABLE I—GASES FROM CRACKING DISTILLATIONS UNDER 100 POUNDS PRESSURE

| Sample No. | (a) From Jennings crude I | II | III | (b) Paraffine I | II | III |
|---|---|---|---|---|---|---|
| Temperature in still | 340° C. | 415° C. | 422° C. | 417° C. | 432° C. | 437° C. |
| $CO_2$ | 1.2 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 |
| CO | 1.2 | 0.5 | 1.3 | 0.0 | 37.0 | 33.5 |
| Illuminants | 15.4 | 15.3 | 13.0 | 25.4 | 0.0 | 0.0 |
| Hydrogen | 0.0 | 4.0 | 4.4 | 0.3 | 0.9 | 3.0 |
| Saturated hydrocarbons | 81.5 | 79.7 | 81.3 | 74.3 | 62.1 | 63.5 |

The analyses in Table I(*a*) were made of the gases evolved during a cracking distillation of a reduced oil prepared by removing from Jennings crude all constituents boiling below 265° C. Sample I was taken as soon as 100 pounds pressure had been reached. Sample II was collected after 40 per cent of the charge had been distilled, and Sample III after 75 per cent had distilled.

The liberation of hydrogen from petroleum hydrocarbons at various temperatures has been studied by Engler[4] and his students. They obtained no hydrogen below 470° at atmospheric pressure from *kerosene* fractions boiling below 280° C. The liberation of hydrogen from different hydrocarbons at a given

[1] *Chem. News*, **1871**, (23), 124; **1872**, (26), 35.
[2] Shuchoff and Gawryloff, *Zeitschr. f. angew. Chem.*, **1893**, p. 231.
[3] Renard, Eng. Patent 3,413, February 10, 1913.
[4] U. S. Patent 1,119,496 Dec. 1, 1914.
[5] U. S. Patent 342,564 and 342,565.
[6] English Patent 3,345, December 27, 1865.
[7] German Patent 37,728 (1886)
[8] *Chem. Rev.*, **9** (1898), 24.
[9] U. S. Patent 419,931, 1890, 426,173, 1891, English Patent 10,277, 1889; 13,016, 1890; 5,971, 1891.

[1] U. S. Patent 1,101,482. Under Int. Conv., May 6, 1912
[2] THIS JOURNAL, **6** (1914), 479.
[3] *Ber. d. deut. chem. Ges.*, **37** (1904), 2969.
[4] Engler and Höfer, *Das Erdöl*, **1**, 574.

temperature depends somewhat on their constitution. Thus, benzol yields appreciable quantities of hydrogen only at temperatures above 500° C.

Our work indicates that *if* hydrogenation of the liquid olefines takes place during distillation under pressure, it occurs simultaneously with their initial formation. A sample of cracked naphtha, having an iodine number of 55.0, was heated to 196° C. with hydrogen for thirty hours under 3,000 lbs. pressure per square inch. The iodine number and refining loss with sulfuric acid were practically unaffected, the iodine number of the final product being 52.9. Results closely parallel to this were obtained by Mr. Edmund Rhodes, in this laboratory, working with liquid fatty oils. The apparatus employed was a steel bomb connected with a solenoid stirrer constructed as described by Stucker and Enduli.[1]

Uebbelohde and Woronin[2] showed that in the presence of nickel, hydrogen was split off from a Baku crude oil at as low a temperature as 180° C. The results of Zelinski[3] with platinum as a catalyst show that

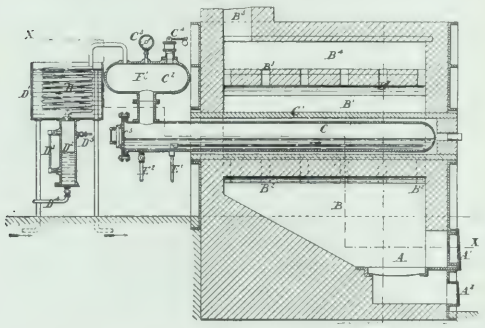


FIG. II—APPARATUS EMPLOYED BY DEWAR AND REDWOOD

dehydrogenation at temperatures above 300° C. in the presence of platinum is to be expected. Ostromisslenski and Bujanadse[4] showed that in the presence of nickel a Russian crude oil gave only coke, 40 per cent, and gas at temperatures between 600–700° C., no tar or liquid being obtained at all. Furthermore, the gas contained 72 to 75 per cent of hydrogen and the remainder consisted of saturated hydrocarbons. These facts are quite significant in view of the proposed cracking processes of Vernon Boys, Lamplough and others, who introduce nickel into the cracking zone. A series of experiments were made in this laboratory at atmospheric pressure and at temperatures of 500–550° C., employing various catalytic substances. Kerosene and solar oil vapors passed through an iron tube containing burned clay, carbon, coarse and finely divided iron, coarse and finely divided copper, heated to the above-named temperature, yielded gasoline fractions, which showed an olefine content of approximately 25 to 30 per cent. When nickel was employed the per cent of olefines in the gasoline product was 48 per cent.

THE EFFECT OF NICKEL in increasing the per cent of olefines, when operating at atmospheric pressure, opens up the question of the effect of foreign substances on the polymerization of olefines and the effect thereon of different physical factors. The percentage of olefines indicated in the above figure does not represent the minimum obtainable even without the addition of a "catalyst."

The claim is made by Burton[1] that by placing the pressure-controlling valve beyond the condenser so as to condense the volatile gasoline vapors produced by distilling heavy petroleum oils under about 75 lbs. pressure, olefines are not produced, whereas, if the pressure-controlling valve is placed between the still and condenser, olefines are found in the condensate to such an extent as to render the latter process of doubtful commercial utility. The authors felt that if olefines could somehow be squeezed together or polymerized by 75 pounds pressure in a condenser containing cold water, this fact would be an interesting contribution to science, but the experiment noted above, in which a cracked petroleum naphtha was heated for thirty hours at 196° C. under 3,000 lbs. pressure per square inch practically without change (iodine number reduced from 55.0 to 52.9), seemed to render such a reaction as Burton describes improbable. We accordingly prepared several gallons of gasoline by distilling Oklahoma "reduced" oil at approximately 80 lbs. pressure, in one case with the valve between the still and the condenser, and in another experiment with the still and condenser in free communication, so as to condense the vapors under pressure, all other conditions remaining the same.

| GASOLINE | I | II |
|---|---|---|
| Per cent refining loss by 5 per cent conc. $H_2SO_4$ | 7.9 | 8.0 |
| Per cent refining loss by 5 per cent "oleum" | 12.2 | 12.0 |
| KEROSENE, boiling point 302–392° F. | | |
| Per cent refining loss by 5 per cent "oleum" | 9.0 | 8.0 |

In I the valve was interposed between still and condenser; and in II the still and condenser were in free communication, control valve being beyond the condenser. These results indicate that the claim made by Burton concerning the effect on the yield of olefines caused by different positions of the pressure-controlling valve are unwarranted.

Dewar and Redwood[2] specified clearly that they condensed the distillate, obtained in their process, under pressure. In U. S. Patent 726,173, they make the statement: "For this purpose we arrange a suitable boiler or retort and a condenser in free communication with one another, without interposing any valve between them; but we provide a regulated outlet for condensed liquid from the condenser." The remarkable effect of the position of the valve on the percentage of olefines in the resulting product was evidently overlooked by Dewar and Redwood. However, in view of the fact that it is not common practice to glean our scientific data from the patent literature, this error on the part of Dewar and Redwood is not such a serious

[1] *Zeitschr. f. Elektroch.*, **1913**, p. 570.
[2] *Petroleum*, Berlin, **1911**, pp. 7, 9.
[3] *Ber. d. deutschen chem. Ges.*, **1912**, pp. 45, 3678
[4] *J. Russ. phys.-chem. Ges.*, **1910**, p. 195.

[1] U. S. Patent 1,049,667. Under Int. Conv., July 3, 1912.
[2] *Loc. cit.*

matter as it might be. Aside from the above noted discovery as claimed by Burton, it is difficult to find any novelty in his patent. The operating pressures specified by Burton are four to five atmospheres. Boleg[1] described distillation under four atmospheres pressure and in 1886 Krey[2] published the results obtained by distilling various crude oils, heavy oils and residues

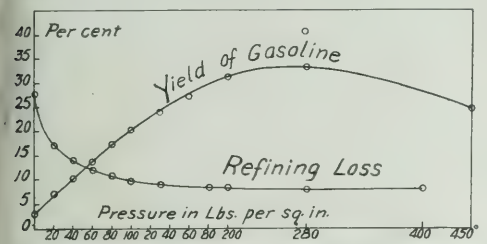



FIG. III—YIELDS AND REFINING LOSSES OF GASOLINE OBTAINED BY DISTILLING OKLAHOMA REDUCED OIL UNDER PRESSURE

Gasoline = Distillate below 150° C.
Refining, by 1/10 volume concentrated $H_2SO_4$

under pressures of three to six atmospheres. Engler[3] confirmed the claims of Krey but, like Dewar and Redwood, Engler and Krey did not discover the *remarkable* effect of the position of the pressure-controlling valve, as referred to above.

It has been pointed out that the results presented in Fig. III do not represent the maximum yields of gasoline or the minimum percentage of olefines obtainable in the gasoline distillates made by distilling under pressure. It is not the purpose of this paper to point out the optimum working conditions of the process. However, in the patent of Bacon, Brooks and Clark[4] it has been shown that the ratio between the volume of the oil heated and the area of the heating surface of the apparatus employed is an important factor. This relation may perhaps be more clearly understood if it is stated that, other conditions remaining the same, cracking does not occur throughout the mass of heated oil, but that the *cracking effect produced in a given quantity, in a given time, will, within certain limits, be approximately proportional to the heated surface in contact with the oil.* It is obvious that distilling slowly will have approximately the same effect as increasing the relative area of heated surface. Another fact brought out in this process is that the deposition of coke on vertical heating surfaces is very much less, one-third to one-fifth of the amount deposited on the upper side of a horizontal surface, such as an ordinary still bottom, in a given length of time.

Under higher pressures, such as 200 lbs. per square inch, oils having boiling points above 300° are almost completely prevented from distilling at the mean temperatures in the still, *i. e.*, 370° to 420° C.

Laing,[5] operating at much lower pressures, attempts to *return* the heavier boiling fractions of the distillate to the still by employing an apparatus such as is shown in Fig. IV.

Although hydrocarbons of the type contained in gasoline are more stable than the heavy hydrocarbons such as are contained in "reduced" oils, it is nevertheless important to remove the gasoline from the "sphere of reaction" as fast as formed. Thus, heating a certain volume of heavy oil under a given pressure for a given period of time and subsequently distilling at atmospheric pressure does not yield nearly as much gasoline as distillation under the same pressure, thus removing the gasoline and kerosene as fast as formed. This was well shown by an experiment in which Oklahoma "reduced" oil was heated under a pressure of 180 lbs. per square inch for two hours and then distilled at atmospheric pressure. There was obtained in this way only 5 per cent of gasoline, while another experiment under the same conditions, except that the gasoline was distilled as fast as formed, yielded 30.4 per cent gasoline. This indicates that the gasoline hydrocarbons themselves slowly decompose in the cracking still. In view of this fact, it is all the more remarkable that the kerosene fractions of the pressure distillate obtained from Oklahoma reduced oil by distilling inder 100 lbs. pressure are optically active.

### OPTICAL ACTIVITY OF KEROSENE HYDROCARBONS MADE BY CRACKING HEAVIER HYDROCARBONS

The kerosene fractions of most crudes show very little, if any, optical activity. The maximum rota-

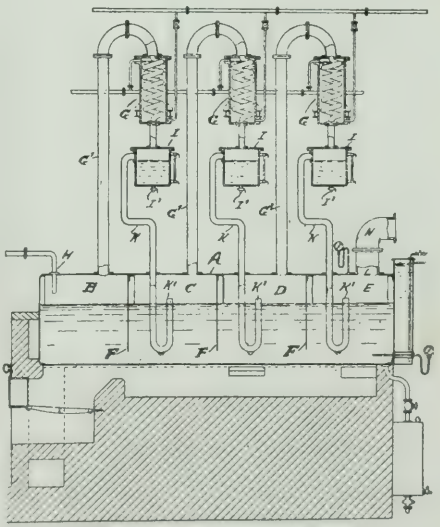



FIG. IV—APPARATUS PATENTED BY LAING

tions are noticed in the fractions boiling from about 230° to 290° C. under 12 to 14 mm. pressure. A Galician oil studied by Engler yielded a fraction boiling from 200° to 250° under atmospheric pressure, which showed a rotation (200 mm. tube) of +0.2° on the saccharimeter scale. The fraction boiling

[1] *Chem. Rev. d. Fett- u. Harz Ind.*, **1898**, pp. 9, 24.
[2] German Patent 37,728 (1886).
[3] *Ber. d. deutschen chem. Ges.*, **30** (1897), 2919.
[4] U. S. Patent Ser. No. 764,982—Allowed Nov. 24, 1914. Under Int. Conv., May 2, 1913. To issue March 9, 1915.
[5] German Patent 260,858. October, 1911; *Chem. Ztg.*, **1913**, p. 375.

from 200° to 250° C., made by cracking Oklahoma reduced oil under 100 lbs. pressure, showed a rotation in a 400 mm. tube of +0.36° on the saccharimeter scale. Other samples showed rotations of approximately the same degree. In view of the high temperatures prevailing in the pressure still, 360°–420° C., the fact that complete racemization has not occurred indicates that these optically active hydrocarbons undergo racemization with greater difficulty than optically active compounds of any other class. The corresponding fraction, boiling from 200–250° C., distilled off the original Oklahoma crude, had a rotation of +0.2° in a 200 mm. tube on the saccharimeter scale. Since the optically active kerosene hydrocarbons made by cracking under pressure are to be regarded as products of the "splitting" of heavier hydrocarbons of higher molecular weight, the fact of their being optically active is even more remarkable. Engler and Bobrzynski[1] showed that a fraction of Galician oil still showed an optical rotation of 0.8° (saccharimeter scale) after heating at 350–360° for four hours. Engler has also shown that optically active oils may be obtained by the destructive distillation of cholesterol.

Engler[1] and Marcusson[2] have suggested that the optical activity of petroleum oils is due to hydrocarbons of the naphthene type. This is confirmed by our observations that a viscous lubricating oil prepared from Jennings crude, after refining several times with "oleum" and finally clarifying with Fuller's earth, showed an optical rotation in a 400 mm. tube of 4.04° arc or 11.6° on the saccharimeter scale. Since this oil was odorless and tasteless, optically active naphthenic acids could not have been a factor.

PRODUCTS OF CRACKING DISTILLATION UNDER PRESSURE

FORMATION OF BENZENE, TOLUENE AND XYLENE—The formation of aromatic hydrocarbons from petroleum oils has heretofore been assumed to be due to complex and little understood changes such as dehydrogenation of naphthenes and the formation of acetylene and the condensation of the latter to benzene and its homologues.

We have found the above-named aromatic hydrocarbons in gasoline made by cracking heavy Oklahoma reduced oil under a pressure of 100 lbs. per square inch. Treatment of the gasoline by liquid sulfur dioxide gave 10.0 per cent of olefines and aromatic hydrocarbons, which mixture was fractionated several times and the fractions whose boiling points corresponded to the boiling points of benzol, toluol and xylol were nitrated in the usual manner, water added, and the crude crystalline mass thus obtained recrystallized several times from alcohol. We obtained in this way *1,3-dinitrobenzol*, melting point 90.0° C., also *2,4-dinitrotoluol* of melting point 70.0° C., and *2,4,6-trinitrometaxylol*, melting at 182.0° C.

Since relatively little gas[3] is evolved when distilling under 100 lbs. pressure and since the gas evolved contains not more than 4.4 per cent hydrogen, it appears highly improbable that the aromatic hydrocarbons in question are produced, either directly or indirectly, by a process of splitting off of hydrogen. *We believe the evidence points to the splitting off of benzol, toluol and xylol from large so-called petroleum hydrocarbons, which contain the phenyl radical.*[4] In order to test this hypothesis further, we have made "gasoline" by heating Oklahoma reduced oil with anhydrous aluminum chloride. In this reaction very little gas is evolved from dry petroleum oils. Should the phenyl radicals exist in the complex petroleum hydrocarbons, one might expect a splitting of the molecule just[5] as is known to occur when toluol is treated with aluminum chloride,

$$C_6H_5 \longleftarrow C_6H_5.CH_3 \longrightarrow C_6H_4\begin{matrix}CH_3\\CH_3\end{matrix}$$

yielding both benzol and xylol.

Twenty liters of Oklahoma reduced oil were slowly heated with 6 per cent anhydrous aluminum chloride until four liters of light distillate were collected. This was treated with liquid sulfur dioxide, 0.40 liter of sulfur dioxide soluble extract being obtained. This was fractionated three times and the proper fractions nitrated in the usual manner. Metadinitrobenzol, 2,4-dinitrotoluol and 2,4,6-trinitro-metaxylol were easily obtained in a state of purity after recrystallizing several times from dilute alcohol.

There are, of course, other conditions in which aromatic hydrocarbons are formed by complex reactions carried out at much higher temperatures attended by the evolution of large quantities of hydrogen and unsaturated hydrocarbons, as in the manufacture of oil gas. These conditions, however, are very different from those prevailing in the above experiments.

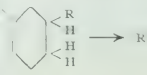
Since practically all of the crude petroleums of the world which have been examined, yield gasolines and kerosenes containing small percentages of aromatic hydrocarbons and in view of the commonly accepted theory of the origin of petroleums from animal and vegetable remains, it is to be expected that hydrocarbons of high molecular weight containing the phenyl radical are to be found in heavy petroleum oils. Such hydrocarbons, containing aromatic radicals, cannot be formed by any simple anaerobic degradation of fats, but probably, like the nitrogen bases, have been derived originally from protein material. We may therefore expect to find relatively large percentages of *aromatic compounds in petroleums that are also rich in nitrogen*. This appears to hold true in the case of the California petroleums, which are high in nitrogen, and, according to unpublished work done in this laboratory, this is also true of certain heavy Mexican oils. On the other hand, it may be pointed out that the

[1] Engler, *Das Erdöl.*, **1**, 218.

[2] *Chem. Ztg.*, **1911**, p. 729.

[3] This will vary with different oils and the evolution of gas becomes much more rapid toward the end of a distillation when much coke is produced

[4] Jones and Wheeler *Jour. Chem. S.*, **1914**, 2562 have shown that hydrocarbons of the aromatic series are produced in the distillation of coal at 350° C. or below the temperatures at which hydrogen is split off. They suggest that aromatic compounds may be formed by reactions such as the following



oils of Borneo, Sumatra and Java are relatively rich in light aromatic compounds, but low in nitrogen. The latter oils, however, are very light and fluid and very different from the heavy pitch-like oils of California and Mexico, and it has been frequently suggested that these light fluid oils have been purified by filtration through porous strata. Such light, supposedly filtered, crudes are low in sulfur as well as

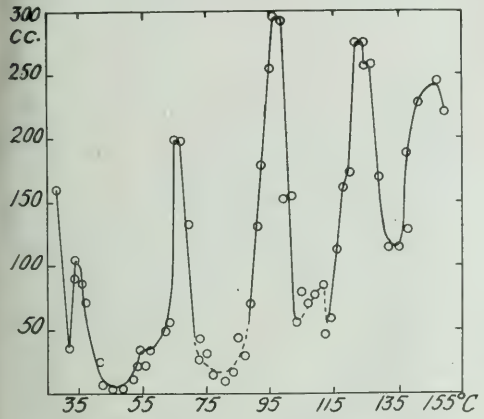



FIG. V—FRACTIONAL DISTILLATION OF GASOLINE MADE BY CRACKING UNDER 100 LBS. PRESSURE

nitrogen. Thus the converse of the above statement does not hold, probably for the reasons just indicated.

Another noteworthy feature of gasoline made by cracking under a pressure of 100 lbs. is that *normal paraffine hydrocarbons* appear to be the predominating constituents. The amount of isopentane exceeds that of normal pentane but the hexane and heptane fractions appear to consist chiefly of the normal paraffines. These facts are brought out by Fig. V, representing the results of seven fractional distillations.

| Per cent | Found | Calculated For $C_5H_{12}$ | Calculated For $C_6H_{12}$ |
|---|---|---|---|
| Carbon | 85.06 | 83.72 | 85.72 |
| Hydrogen | 14.93 | 16.28 | 14.28 |

Only a very small amount of naphthenes appears to be present. Some evidence of the presence of methyl cyclopentane was shown by the above combustion analysis of the fraction boiling from 68° to 70° C.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
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## THE ANALYTICAL DISTILLATION OF PETROLEUM[1]

By W. F. Rittman and E. W. Dean

Received January 4, 1915

In the study of petroleum and petroleum products one of the most important processes of examination is a quantitative distillation. The information obtained by this method is of the utmost value, both from a technical and from a purely scientific point of view. Unfortunately, distillation methods have never been satisfactorily standardized, and frequent complaints are heard that the reports of different chemists often fail to agree with each other and rarely agree with the results obtained in the refinery. One great reason for this seems to lie in the fact that knowledge regarding the fractionation of complex mixtures, like crude oil, is in a rather unorganized condition.

The United States Bureau of Mines has undertaken a study, which, it is hoped, will serve ultimately to secure the desired standardization of conditions of distillation.

Some preliminary experiments were conducted, at the request of the Bureau, by Professors M. C. Whitaker and F. J. Metzger of Columbia University.

TABLE I—PERCENTAGE ANALYSES OF OKLAHOMA CRUDE PETROLEUM BY VARIOUS METHODS(*a*)

| | Engler(*b*) | Ubbelohde(*c*) | Regnault(*d*) | Nawratil(*c*) |
|---|---|---|---|---|
| B. of M. Sample No. 1470 | | | | |
| Cut below 150° C. | 9.5 | 5.2 | 3.7 | 2.8 |
| Cut 150° to 300° | 32.7 | 32.3 | 34.8 | 34.0 |
| Cut above 300° | 52.9 | 56.0 | 56.0 | 57.5 |
| B. of M. Sample No. 1464 | | | | |
| Cut below 150° C. | 16.7 | 11.5 | 9.5 | 11.1 |
| Cut 150° to 300° | 28.3 | 30.8 | 31.2 | 30.2 |
| Cut above 300° | 50.5 | 53.5 | 53.5 | 52.5 |

(*a*) For the sake of comparison, the temperature ranges prescribed for the Engler method were used in all the distillations.
(*b*) Allen's "Commercial Organic Analysis," **3** (1910), 48.
(*c*) *Ibid.*, **3** (1910), 50.
(*d*) Redwood, "Petroleum and Its Products," **2** (1906), 536 and **2** (1913), 206.

Their report is summarized in Table I and shows a wide discrepancy in the amounts of the various products obtained by the various methods of analysis in use among petroleum chemists, the greatest differences being in the case of the "naphtha" (cut below 150° C.).

### SCOPE OF THE PRESENT REPORT

It is not intended to discuss here the advantages and disadvantages of specific methods now in use.[1]

Abundant and satisfactory data are available with regard to the effects of the various methods of distillation on mixtures of two or three constituents.[2] No results of a similar nature seem to have been obtained for crude petroleum, and it would appear to be of utmost importance to secure such data in beginning a study like the present one.

Results of distillations differ mainly on account of the variable amounts of condensation occurring in the spaces between the surfaces of the boiling liquids and the outlets of the flasks or retorts used. We have considered three general cases.

1—When condensation is nil.

2—When condensation is moderate.

3—When condensation occurs in large amount, and there is thorough contact between vapors and condensed liquid.

In an apparatus designed by Allen and Jacobs[3] for the distillation of California crude oils, the first condition is fulfilled: vapors, as they leave the liquid surface, pass unchanged in composition to the condenser. The Allen and Jacobs method is by no means

[1] Published with the permission of the Director of the Bureau of Mines. An extended abstract of bulletin now in preparation on the above subject. This bulletin will contain full details of construction of apparatus, methods used, and experiments reported herewith.

[1] See Allen's "Commercial Organic Analysis," *loc. cit.*; Redwood, "Petroleum and Its Products," *loc. cit.*; Holde, "Untersuchung der Kohlenwasserstoffole und Fette," 4th ed., **1913**, pp. 29–38.

[2] See Sydney Young, "Fractional Distillation," **1903**, Chapters X and XI.

[3] "Physical and Chemical Properties of the Petroleums of the San Joaquin Valley of California," Irving C. Allen and W. A. Jacobs, *Bull.* **19**, Department of the Interior, Bureau of Mines.

the only one by which this end can be attained but on account of availability and convenience it has been selected as representative of the general case.

Each of the various methods studied by Whitaker and Metzger secures a moderate degree of separation. The Ubbelohde is most generally in use and has therefore been chosen as representative.

The extreme maximum limit of separation is a difficult and perhaps impossible one to attain, on account of mechanical and chemical difficulties connected with the distillation of crude petroleum. The literature[1] which discusses still-heads and dephlegmators is very profuse. As representative of the class of apparatus furnishing maximum condensation, a Hempel column of moderate height has been selected, chiefly on account of its availability and simplicity.

In the past, petroleum chemists have strongly favored methods of the Ubbelohde type, on account of their convenience, and because it was thought that the results obtained did not differ very greatly from those of distillations involving thorough fractionation. The unsatisfactory behavior of California oils, when examined by these methods, lead to the development of the Allen and Jacobs still.

## MECHANISM OF THE PROCESS OF DISTILLATION

The distillation of crude petroleum, while offering numerous difficulties from a mechanical point of view, is, nevertheless, free from complications due to the formation of "binary" and "ternary" mixtures. These mixtures, which may be either of maximum or of minimum boiling point, are known to occur only with constituents of differing chemical natures. The inherent resemblances among all the hydrocarbons of any one crude oil render negligible the possibility of any difficulty in this direction. The composition of the vapor leaving the liquid at any time is, therefore, a simple function of the partial pressures of the constituents present and of their relative quantities.

To prevent changes in the composition of the vapor it is necessary only to prevent the escape of heat through the walls of the distilling vessel. The Allen and Jacobs method accomplishes this by warming the walls of the flask with an enclosing electric heater.

In a simple distilling flask the process of cooling is irregular and takes place by conduction through the walls of the vessel. It seems perfectly possible that a considerable current of vapor may pass practically unchanged from the surface of the liquid to the outlet.

The Hempel column is one of the simplest and most effective devices for bringing the vapor into contact with a conducting medium and with the condensed liquid which is running back. For its efficiency relative to that of other still-heads and for its specific advantages and disadvantages, the discussions published by Young[2] and Golodetz[2] furnish satisfactory information.

[1] Sydney Young, "Fractional Distillation," *loc. cit.*; see also A. Golodetz, "Fractional Distillation in the Laboratory and New Rectifying Apparatus," *Chem. Eng.*, **35** (1912), 102 and 142.

[2] *Loc. cit.*

## GENERAL SCHEME OF EXPERIMENTAL PROCEDURE

All distillations were made with portions of a ten gallon sample of Pennsylvania crude oil, taken from one of the pipe-lines running into the city of Pittsburgh. Primary distillations were conducted by each of the three methods indicated above. Cuts were made at intervals of 25° C. and fractions between the same temperature limits in each series were combined and reserved for redistillation. Specific gravities were measured for the individual cuts and also for the combined fractions, the latter figures representing an average of all the single determinations.

Redistillations were made with portions of the combined 25° fractions: 5° cuts were made in these cases over appropriate temperature ranges and individual specific gravities determined.

The whole series of experiments represents some 50 primary distillations and about 40 redistillations. Over 800 specific gravity determinations were made. It is felt therefore that the measurements have been sufficiently comprehensive to establish conclusively the relative amounts of fractionation secured by the three types of general distillation methods selected for study.

The procedure adopted for the study of degrees of fractionation is believed to be one which will be found of much service for other similar cases. It furnishes a very satisfactory means of estimating the degrees of homogeneity of distillation cuts obtained from complex mixtures containing constituents which cannot be readily identified by chemical or physical measurements.

## GENERAL DETAILS OF PROCEDURE

The mechanical details involved in quantitative distillation are of great importance and deserve considerable discussion, though they will probably be of but slight interest to those who have not worked with the various methods now in vogue.

HEATERS—A heater of the type shown in Fig. I was used with a 220 volt alternating current in series with an ammeter and a water rheostat. In some cases the temperature of the vapor in the Hempel apparatus was carried up to 325° C. which required a current density of from 3 to 4 amperes.

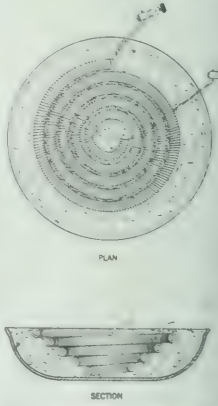


FIG. I—ELECTRIC HEATER FOR OPEN FLASK DISTILLATIONS

CONDENSER—A type of condenser had been developed which meets in a satisfactory manner the needs of the work at present in progress. In distilling a crude oil, volatile products come over at first, and to prevent their loss efficient cooling is necessary; *viz.*, a temperature of 0° C. or lower. For the heavy lubricants driven over during a vacuum distillation, an air con-

denser gives too much cooling and there is trouble on account of lag or even clogging. The remedy for the latter difficulty is, of course, to raise the temperature of condensation and thus reduce the viscosity of the distillates.

Allen and Jacobs[1] used a vertical Liebig condenser (this position minimizing lag) and ran through the

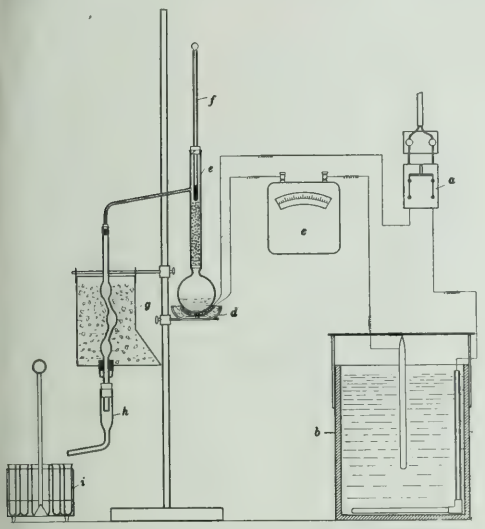


FIG. II—DISTILLING APPARATUS COMPLETE
*a*—Switch at Electric Mains. *b*—Water Rheostat. *c*—Ammeter. *d*—Heater. *e*—Distilling Flask with Hempel Column. *f*—Thermometer. *g*—Condenser with Three-bulbed Tube and Ice-filled Jacket. *h*—Adapter. *i*—Metal Rack Containing Receiving Tubes Packed in Ice.

jacket ice water during the first stage of a distillation and warm water during the period when lubricants were driven over. Their procedure has lately been modified by the elimination of running water as a cooling medium. An open-topped brass jacket[2] has been substituted and this is filled at the beginning of a distillation with cracked ice or a freezing mixture. Later a source of heat can be supplied and the water held at any temperature necessary to ensure sufficient mobility in the distillates. A device of this sort has long been used in tar distillation,[3] although there the advantageous upright position of the condenser has not been adopted.

RECEIVERS—The distillates were collected in 5 in. test tubes which were, when necessary, immersed in cracked ice or a freezing mixture. All measurements were made on a basis of percentage by weight.

SPECIFIC GRAVITY MEASUREMENTS—When cuts amounted to as much as 15 to 20 cc., an ordinary Westphal balance with a 5 cc. plummet was employed.

The great bulk of our specific gravity determinations were made with a type of pycnometer[1] which seems particularly adapted to the present needs. This is simply a capillary pipette with an ellipsoidal bulb of capacity between 1 and 2 cc.

Dimensions approximating those given in Fig. III have been found satisfactory though they are not necessarily ideal.

The tubes of oil were brought to the desired temperature in a cooling bath and the calibrated pycnometers filled to the mark[2] by suction, using a bit of rubber tubing as a mouthpiece. The tube is then dried and weighed. From the figures obtained gravities are calculated by one subtraction and one division.

When one of the pycnometers is filled, its contents are held strongly in place by capillary forces and there is little possibility of displacement except in the cases of the most mobile naphthas which must be handled with considerable care.

The surface for evaporation is negligibly small and no protecting caps are necessary. For work within a limit of error of 0.1 per cent it is necessary to weigh only to milligrams and a cheap balance may be used where one of the analytical type is not available. The ordinary horn-pan balance can be made to serve the purpose if it is carefully handled.

RATE OF DISTILLATION—All distillations have been conducted at a uniform rate of one drop per second, the count being made for the lower end of the upright condenser. The drops ran between 35 and 50 to the gram, drop weights varying during the course of a distillation. This rate is undoubtedly slower than is necessary but has been in use for several years in this laboratory and on that account has been provisionally adopted for the present series of experiments. The

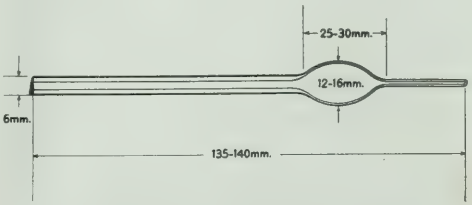


FIG. III—PYCNOMETER OF CAPILLARY PIPETTE TYPE
Modified for Petroleum Work from Design of Drushel

rate of 2 to 2.5 cc. per minute, generally used by petroleum chemists, is about twice as rapid.

TEMPERATURE MEASUREMENT appears to be a problem in itself and no pretense is made at present of considering it satisfactorily settled. Thermocouples

[1] *Bull.* 19.

[2] An admirable substitute for the brass jacket of special design is one of the cylindrical cans commonly used as commercial containers for benzol, alcohol and the like. By cutting out the bottom and inverting it is possible to obtain ready-made a jacket which possesses nearly all the desired qualities. The stopper which connects the inner glass tube must be wired in, and in applying heat some care must be exercised to avoid burning this stopper. It should be noted that the shape of the bulbs of the inner tube and their staggered arrangement (shown in Fig. II) are details of importance.

[3] See catalogues of firms dealing in chemical supplies.

[1] Pycnometers of this type were designed by Professor W. A. Drushel for use in a course in Qualitative Organic Analysis given in the Kent Chemical Laboratory of Yale University. The details here described are not those originally evolved but have been worked out with special reference to the needs of the petroleum chemist. A discussion concerning the more general case will be published later by Professor Drushel.

[2] To obtain a maximum of accuracy it is necessary to fill the bulb and let it run out once or twice in order to bring the glass to the temperature of the oil. This detail, however, can generally be omitted as the error due to the difference between the coefficients of cubical expansion of liquid and glass is not great enough to be of importance.

have both advantages and disadvantages. They were used for distillations with enclosed heaters. Standardized thermometers were employed in all other cases. The normal corrections for the stem projecting above the neck of the flask were figured by the usual formula.[1] These values were further corrected by estimation for the portion of the stem at uncertain temperature between the outlet of the flask and the stopper. It is believed that the temperatures used have been very nearly correct and at any rate all cuts have been made on an even basis, which is the essential consideration in the present connection.

### SPECIFIC METHODS

ALLEN AND JACOBS METHOD[2]—The fundamental idea in the development of this method was that no condensation should occur in the vapor space of the

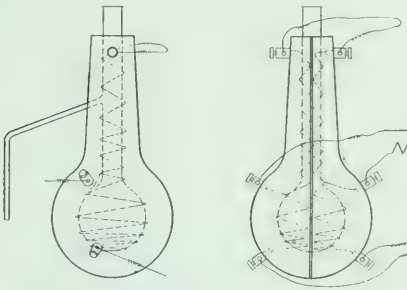


FIG. IV MODIFIED ALLEN AND JACOBS HEATER
*a*—Wires Connecting with Electric Mains *b*—Variable Resistance Shunted across Top of Bulb

distilling flask. To attain this end a heater[3] was used which was effective over the entire surface of the flask. If the temperatures of liquid and vapor are equal at the beginning of a distillation then the temperature of the latter is lower at the end. The best attainable arrangement was one which gave equality at the middle point of the temperature range.

A possible way of attaining uniform temperature throughout the flask would be by an equal degree of insulation for all parts of the flask. So far, however, the method followed has been to vary the relative amounts of heat supplied to bulb and neck during the course of a distillation by equipping the neck of the heater with an excess of wire and shunting a variable resistance across the top of the bulb (Fig. IV). By adjusting this resistance at intervals it is possible to maintain a proper ratio between the amounts of electrically generated heat supplied to the various parts of the distilling flask.

If temperatures in all parts of the flask are equal, it is obvious that it makes no difference which thermometer or thermocouple is read in making the cuts. It is also obvious that if the temperature of the vapor is higher than that of the liquid, no condensation will occur and the vapor must go unchanged in composition from liquid surface to outlet. This, it will be remembered, is the essential condition of the method. It therefore follows that it is possible to make cuts on a basis of the temperature of the liquid so long as the vapor is ever so slightly superheated. The superheating should not be excessive, in order that the possibility of cracking in the vapor phase may be eliminated. The mechanical difficulty of maintaining one temperature within, for example, twenty degrees of another, is decidedly less than that involved in preserving exact equality.

In order to verify the above theoretical considerations actual experiments were made with the two systems, with the results shown in Table 2.

TABLE 2 COMPARISON OF TWO MODIFICATIONS OF THE ALLEN AND JACOBS METHOD

| Temp. °C. | Per cent Distillate A | B | |
|---|---|---|---|
| 150 | 3.8 | 3.5 | In Experiment A the vapor was |
| 175 | 7.3 | 7.1 | kept 6 to 26° hotter than that |
| 200 | 7.6 | 7.7 | of the liquid. |
| 225 | 7.3 | 7.5 | |
| 250 | 6.9 | 6.8 | In Experiment B temperatures |
| 275 | 6.5 | 6.7 | of vapor and liquid were kept |
| 300 | 6.3 | 6.3 | within 1 or 2° of each other. |

UBBELOHDE METHOD—The Engler-Ubbelohde method is so familiar that it needs little further discussion. Experience has indicated the necessity of considerable nicety of manipulation in order to ensure moderately satisfactory agreement between the results of duplicate distillations. The difficulty seems to be due to extreme sensitiveness to slight variations in external conditions.

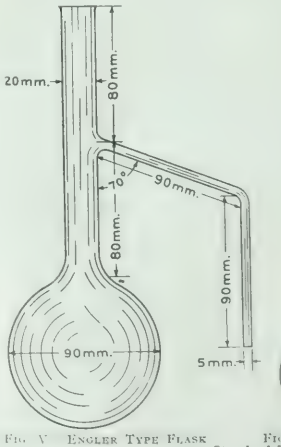


FIG. V ENGLER TYPE FLASK USED IN UBBELOHDE DISTILLATIONS

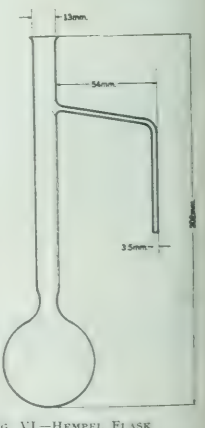


FIG. VI—HEMPEL FLASK Standard for Creosote Distillations. Forestry Service of the U. S. Department of Agriculture

In the present work the method was slightly modified in order to make the results comparable with

[1] Sydney Young, *Op. cit.*, p. 12.

California petroleums have an asphaltic base and are, as a rule, viscous, tarry liquids. They are particularly liable to hold water in an emulsified condition and often distil badly in the Engler flask. The method of Allen and Jacobs is particularly effective in obviating difficulties due to the presence of water. The enclosed heater prevents any condensation in the neck of the flask and renders impossible the near-explosions which occur when drops of water fall back into the boiling oil. For an example of what the method can do in the way of distilling a difficult mixture see *Bull.* **19**, 35. The oil treated contained 33 per cent water and 30 per cent asphaltum, brittle at room temperature.

[3] A full description of the heater and the method of its construction is given in *Bull.* **19**. A series of experiments, described in the bulletin, resulted in the adoption of a system of wiring which seemed to give the desired result, *viz.*, even temperature throughout the entire distilling flask during the whole course of a distillation; it was later observed by Mr. A. S. Crossfield, of this Bureau, that this result can be attained only approximately by a fixed system of wiring.

those of the Hempel and enclosed heater distillations. The upright condenser was used, 25° cuts were made, and the rate of distillation was slower than that generally prescribed. The flask used was of 250 cc. capacity and of the dimensions shown in Fig. V.

HEMPEL DISTILLATIONS—For the primary series of distillations, one of the standard creosote flasks[1] of the Forest Service, U. S. Department of Agriculture, was used[2] (Fig. VI).

These flasks have the fractionating column made in one piece with the bulb, which obviates the considerable difficulty of securing a tight joint between a short-necked bulb and an attached Hempel column. They also have the advantage of being a standard article that can be purchased from the regular stock of the larger chemical supply houses.

TABLE 3—ALLEN AND JACOBS METHOD
No Condensation
TYPICAL DISTILLATIONS

| Temp. °C. | Per-centages A | B | C | Specific gravities A | B | C | Average of 13 distillations % | Sp. gr. |
|---|---|---|---|---|---|---|---|---|
| 150 | 4.5 | 4.5 | 4.9 | 0.712 | 0.709 | 0.711 | 4.7 | 0.715 |
| 175 | 8.1 | 7.8 | 7.7 | 0.729 | 0.728 | 0.730 | 7.6 | 0.733 |
| 200 | 7.2 | 7.2 | 7.4 | 0.748 | 0.748 | 0.748 | 7.3 | 0.751 |
| 225 | 7.2 | 6.9 | 7.0 | 0.757 | 0.763 | 0.763 | 7.1 | 0.764 |
| 250 | 6.9 | 6.7 | 6.8 | 0.768 | 0.776 | 0.777 | 6.7 | 0.777 |
| 275 | 6.5 | 6.4 | 6.4 | 0.787 | 0.788 | 0.787 | 6.4 | 0.785 |
| 300 | 6.3 | 6.3 | 6.7 | 0.798 | 0.797 | 0.796 | 6.3 | 0.798 |
| 325 | 6.1 | 6.4 | 6.3 | 0.810 | 0.806 | 0.808 | 6.5 | 0.809 |

TABLE 4—UBBELOHDE METHOD
Moderate Condensation
TYPICAL DISTILLATIONS

| Temp. °C. | Per-centages A | B | C | Specific gravities A | B | C | Average of 25 distillations % | Sp. gr. |
|---|---|---|---|---|---|---|---|---|
| 125 | 6.9 | 6.1 | 5.8 | 0.702 | 0.703 | 0.702 | 6.5 | 0.709 |
| 150 | 6.8 | 6.4 | 6.7 | 0.734 | 0.733 | 0.733 | 6.7 | 0.736 |
| 175 | 7.3 | 7.2 | 7.4 | 0.753 | 0.749 | 0.752 | 6.9 | 0.753 |
| 200 | 7.0 | 7.0 | 6.8 | 0.773 | 0.764 | 0.767 | 6.5 | 0.767 |
| 225 | 7.4 | 7.2 | 7.2 | 0.779 | 0.778 | 0.778 | 6.9 | 0.779 |
| 250 | 7.1 | 7.8 | 7.6 | 0.793 | 0.788 | 0.790 | 6.9 | 0.790 |
| 275 | 6.2 | 7.6 | 9.0 | 0.804 | 0.802 | 0.804 | 6.7 | 0.801 |
| 300 | 6.2 | 7.2 | 5.9 | 0.812 | 0.813 | 0.816 | 6.8 | 0.813 |

TABLE 5—HEMPEL DISTILLATIONS
Maximum Condensation
TYPICAL DISTILLATIONS

| Temp. °C. | Per-centages A | B | C | Specific gravities A | B | C | Average of 13 distillations % | Sp. gr |
|---|---|---|---|---|---|---|---|---|
| 100 | 5.2 | 4.7 | 4.9 | 0.691 | 0.689 | 0.692 | 5.0 | 0.692 |
| 125 | 5.7 | 5.9 | 5.2 | 0.729 | 0.729 | 0.728 | 5.6 | 0.729 |
| 150 | 5.4 | 5.7 | 6.2 | 0.745 | 0.745 | 0.745 | 5.9 | 0.745 |
| 175 | 6.9 | 7.0 | 6.2 | 0.759 | 0.759 | 0.758 | 6.6 | 0.760 |
| 200 | 6.5 | 6.2 | 6.8 | 0.771 | 0.771 | 0.770 | 6.5 | 0.771 |
| 225 | 6.3 | 6.7 | 6.5 | 0.782 | 0.781 | 0.781 | 6.6 | 0.782 |
| 250 | 6.7 | 6.9 | 6.6 | 0.793 | 0.793 | 0.792 | 6.7 | 0.794 |
| 275 | 7.2 | 6.5 | 7.3 | 0.805 | 0.805 | 0.805 | 6.7 | 0.806 |

Aluminum beads[3] were found more satisfactory than glass. The matter of discovering optimum dimensions for these beads has not yet been studied. Those in use at present are of the type used in the steel industry, ellipsoidal in form and with diameters between $^1/_8$ and $^3/_8$ in.

In beginning a distillation, the flask[4] was counterpoised on a balance along with a spiral of iron gauze and the beads to be used. The charge of oil was then weighed in and the fractionating column adjusted. The spiral of gauze, which had a wire attached, was inserted so as to rest on the constriction at the base of the neck. The beads were then poured in, after which the thermometer was inserted and connections made with the condenser. At the end of a distillation the cooled flask was weighed entire and the difference between this weight and the original tare was a measure of the undistilled residue. To empty the flask the column of beads was loosened with a rod and removed by pulling on the wire attached to the spiral. The primary distillations in the Allen and Jacobs and the Ubbelohde series were made with original charges of 200 g.; for the Hempel primary distillations 300 g. were used.

PRIMARY DISTILLATIONS

For the whole thirteen experiments reported in Table 3 the average variation of the cuts from the mean, amounts to 0.17 per cent if figured on the basis of the original charge, and 2.6 per cent if figured on the more logical basis of the average cut (6.6 per cent for this series). This agreement is all the more impressive since the details of manipulation of this method have not yet been developed to the same degree of uniformity as those involved in the other two methods. It will also be noted that the first cut was made at 150° and that it was necessary to run the temperature up to 325° in order to distil off approximately 50 per cent of the oil.

The agreement among percentage figures in Table 4 is not particularly good although these experiments were perhaps the most uniform of the whole series. The average variation from the mean for the 25 distillations was 6.3 per cent of the average cut, the latter being 6.7 per cent of the original charge. Great care was exercised in manipulation and the only factor not under absolute control was the atmosphere of the room. Even this was regulated in large degree. No noticeable draughts were permitted and in addition the distilling flask was surrounded with a tin shield. The first cut was made at 125°; the last at 300°, at which temperature about 50 per cent of the oil had been distilled.

The results of the Hempel distillations, Table 5, checked better than those of the Ubbelohde though not as well as those of the Allen and Jacobs method. The mean variation was 5.0 per cent (per average cut of 6.2 per cent) as against 6.3 per cent for the Ubbelohde and 2.6 per cent for the enclosed heater method. The first cut was made at 100° and approximately 50 per cent of the oil had distilled over when the temperature of the vapor reached 275°. In several cases distillations were continued up to 325°, but there was strong evidence that "cracking" had begun as the increases in specific gravity of the cuts were less than the earlier course of the distillation had indicated as normal. Temperature measurements showed that the liquid in the Hempel flask was in the neighborhood of 75° hotter than the vapor at the outlet.

COMPARISON OF RESULTS OF PRIMARY DISTILLATIONS

The results of the three types of distillation methods can be better compared by a study of the curves in Figs. VII and VIII than by the data in Tables 3 to 6. Curves A, B, and C appear alike except that they are plotted from different ordinate axes.

TABLE 6—COMPARISON OF RESULTS OF PRIMARY DISTILLATIONS

| Condensation Temperature °C. | Maximum. Per cent | Sp. gr. | Moderate. Per cent | Sp. gr. | Minimum. Per cent | Sp. gr. |
|---|---|---|---|---|---|---|
| 100 | 5.0 | 0.692 | None | ... | None | ... |
| 100–125 | 5.5 | 0.729 | 6.5 | 0.709 | None | ... |
| 125–150 | 5.9 | 0.745 | 6.7 | 0.736 | 4.7 | 0.715 |
| 150–175 | 6.6 | 0.760 | 6.9 | 0.753 | 7.6 | 0.733 |
| 175–200 | 6.5 | 0.771 | 6.5 | 0.767 | 7.3 | 0.751 |
| 200–225 | 6.6 | 0.782 | 6.9 | 0.779 | 7.1 | 0.764 |
| 225–250 | 6.7 | 0.794 | 6.9 | 0.790 | 6.7 | 0.777 |
| 250–275 | 6.7 | 0.806 | 6.7 | 0.801 | 6.4 | 0.785 |
| 275–300 | ... | ... | 6.8 | 0.813 | 6.3 | 0.798 |
| 300–325 | ... | ... | ... | ... | 6.5 | 0.809 |

Curves A′ and B′ are identical with A and B except that they have been moved away from the ordinate

[1] These flasks were obtained through the courtesy of Professor Gellert Alleman of Swarthmore College, to whom we are also indebted for helpful suggestions regarding electric heaters.

[2] Dean and Bateman, *Bull.* 112, Forest Service of the U. S. Department of Agriculture.

[3] Provided by the kindness of Dr. David T. Day.

[4] In all our experiments, bits of porous tile were used to prevent bumping.

axis 37° and 25°, respectively. They are approximately coincident with C′ through a large portion of their course *but diverge at the lower end.* As this is

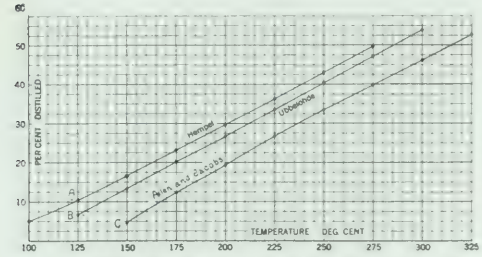


FIG. VII—PRIMARY DISTILLATIONS. PERCENTAGE-TEMPERATURE CURVES

the part which represents the "naphtha" cut, the differences are of considerable importance.

A study of the gravities of the cuts obtained by the different methods is particularly instructive (Fig. IX). Curves which represent approximately differential relations between gravity and percentage have been drawn by setting the specific gravity of each cut against its middle point on the percentage scale. It appears that, excepting the first portion of the curves, gravity-percentage relations obtained by different methods of distillation are nearly the same. Again, however, it must be noted that the discrepancies occur in regions which present commercial conditions have rendered most important.

These apparent similarities seem in a measure to explain the rather common supposition that one method is about the same as another if a little care is used in the interpretation of results. Furthermore, in the past, the lighter fractions were much less important than they are now and on this account chemists have been more or less indifferent toward the differences which do occur.

These similarities will be shown to be entirely superficial by the results of the redistillations, which indi-

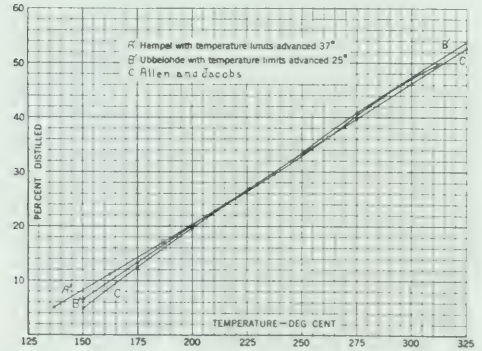


FIG. VIII—PRIMARY DISTILLATIONS. PERCENTAGE-TEMPERATURE CURVES

cate impressive differences among the degrees of separation attained by the three typical methods, and emphasize the danger of drawing conclusions on the assumption that there are more or less fixed relations among the results obtained by the different methods of analytical distillation.

### REDISTILLATIONS

Redistillations were made with initial charges of 100 g. The series of redistillation experiments may be summarized as follows:

1—Redistillations in Ubbelohde flask of cuts.

*a*—From Ubbelohde primary distillations.

2—Redistillations in a small-bulbed[1] Hempel flask of cuts obtained:

*a*—By Allen and Jacobs primary distillations;

*b*—By Ubbelohde primary distillations;

*c*—From redistillations under *1a;*

*d*—From distillations in Hempel flask.

The only general feature to which attention need be called in the redistillation data (Tables 7 to 12) is the matter of regularity. The 5° cuts represent such small percentages in many cases that they are of necessity subject to considerable error. These individual errors tend to neutralize each other, however,

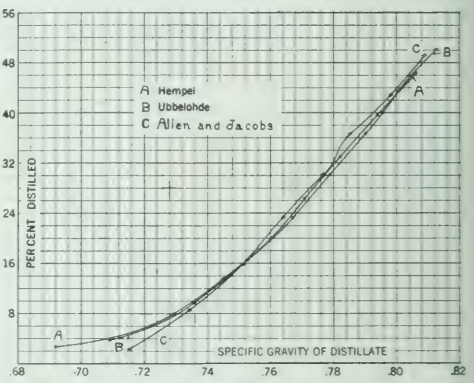


FIG. IX—PRIMARY DISTILLATIONS. PERCENTAGE-SPECIFIC GRAVITY CURVES

and a surprisingly good agreement will be noted among summation figures for the 25° intervals.

In Table 7 distillation begins nearly 100° below the lower limit of the original cut and from 18 to 20 per cent of the oil remains undistilled when the upper limit is reached. Here about 14 per cent of each cut comes over between the original limits. This means that when an oil is fractioned by the minimum condensation method the original temperature limits of the various cuts are but remotely related to those discovered on redistillation.

The cuts from the Ubbelohde primary distillations (Table 8) do not extend out over quite so wide a range of temperature and gravity as do the ones represented in Table 7. They do, however, indicate a considerable lack of homogeneity in the fractions obtained by the original distillation, for only about 25 per cent of each cut comes over between the original limits.

It is to be noted that a redistillation of Ubbelohde

[1] A Hempel flask with a neck like that of the creosote standard, but with a smaller bulb, on account of the reduced size of the charge. Credit for the construction of special glassware is due to Mr. F. E. Donath, glassblower in the Pittsburgh laboratory of the Bureau of Mines.

cuts in the original apparatus (Table 9) indicates a higher degree of fractionation than that to be noted in Table 8. This difference illustrates the necessity of making all redistillations in one standard apparatus when figures for the comparison of different methods are desired. The 5° cuts in Table 10 are larger than those appearing in Tables 7 and 8 and there are narrower ranges of temperature and specific gravity.

The Hempel cuts (Table 11) show a greater degree of homogeneity than occurs in any of the other series of redistillations. The maximum cut in every case but one is only 5° lower than that between the original limits. About 55 per cent of each cut again distils over within the original limits.

A distillation in a Hempel apparatus of moderate size is considerably more efficient than a distillation and redistillation by the Ubbelohde method.

values were obtained by using the lower temperature limit of each cut as a basis and averaging up the 5° fractions equally distant from this. Such a procedure is not strictly logical but it permits the drawing, for each method, of a single curve which represents with sufficient accuracy the characteristics of the method.

In Figure X, the cut represented in each case is that coming over before, and not after, the temperature represented. The ideal curve would be the one entirely between the original temperature limits. Even the Hempel curve approaches this condition but distantly, though its superiority over the others is marked. Perhaps most impressive is the clear demonstration of the fact that a single Hempel distillation gives a degree of fractionation considerably higher than that attained by two successive Ubbelohde distillations.

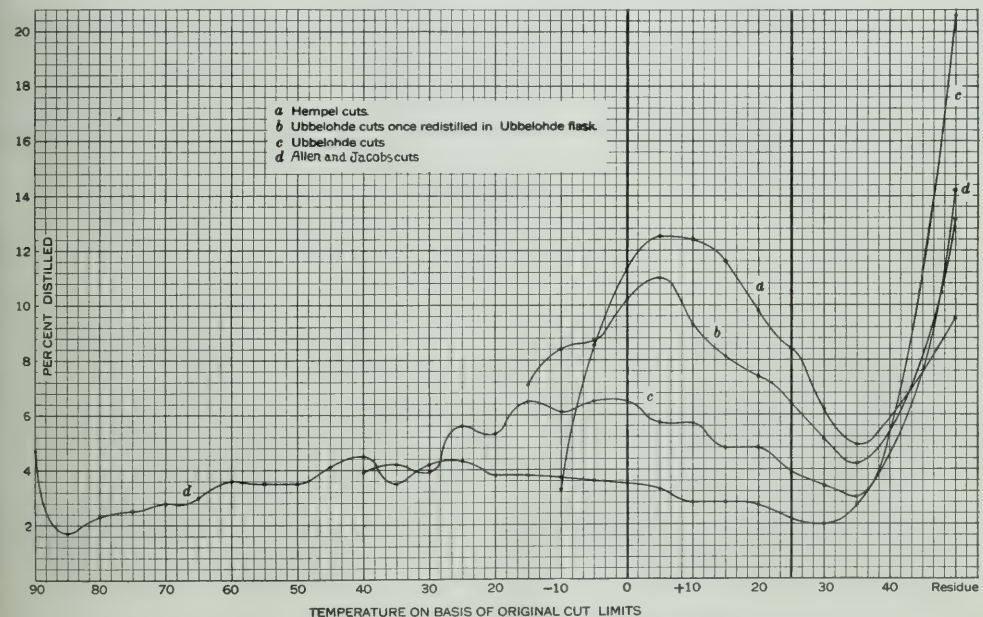


FIG. X—REDISTILLATIONS. PERCENTAGE CUT-TEMPERATURE CURVES

The Ubbelohde method produces fractionation which is considerably sharper than that obtained by the use of the Allen and Jacobs still.

### GENERAL DISCUSSION OF RESULTS

All the main points of interest from the various tables are summarized in Table 12, which is sufficient to show the wide differences among the degrees of separation attained by different methods of distillation. It is evident that the ideal distillation would be the one giving the largest possible maximum cut, the limits of which coincided with those of the primary distillation. Curves have been plotted to show the various relations.

PERCENTAGE AND TEMPERATURE—Each of the curves in Figs. X and XI represents an average for one of the methods of primary distillation. The percentage

This has been proven several times[1] in the past and the Hempel column studied by Young was rated as equivalent to four open-flask distillations. The one used in the present experiments was probably equivalent to about three.

The curves in Figure XI were plotted from the same data as those used for Fig. X, but summation values instead of individual cuts are represented. Here the ideal curve would be the one having the sharpest slope and the narrowest range on the axis of abscissas.

Figure XII is a graphic representation of the results collected in Summary Table 12.

PERCENTAGE AND GRAVITY—The gravity measurements furnished a very nice index of the homogeneity

[1] Dean and Bateman, *Op. cit.*; Sydney Young, *Op. cit.*, p. 179.

## REDISTILLATIONS OF ORIGINAL CUTS OBTAINED BY THE THREE METHODS STUDIED (SEE PAGE 190)

TABLE 7—REDISTILLATIONS OF ALLEN AND JACOBS CUTS IN HEMPEL FLASK

| Cut: 150–175 | | 175–200 | | 200–225 | | 225–250 | | 250–275 | | 275–300 | | 300–325° C. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr.: 0.733 | | 0.750 | | 0.768 | | 0.777 | | 0.785 | | 0.798 | | 0.809 | |
| °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. |
| ... | ... | ... | ... | ... | ... | ... | ... | 155 | 6.8 | 0.747 | 180 | 4.0 | 0.766 |
| 60 | 2.0 | 0.642 | 85 | 3.4 | 0.683 | 110 | 3.3 | 0.720 | 135 | 4.9 | 0.739 | 160 | 2.1 | 0.757 |
| 65 | 1.3 | 0.662 | 90 | ... | ... | 115 | 1.8 | 0.730 | 140 | 1.5 | 0.747 | 165 | 2.1 | 0.758 |
| 70 | 1.6 | 0.670 | 95 | 3.4 | 0.715 | 120 | 3.1 | 0.733 | 145 | 2.4 | 0.748 | 170 | 2.7 | 0.762 |
| 75 | 1.6 | 0.680 | 100 | 3.1 | 0.716 | 125 | 3.2 | 0.736 | 150 | 2.3 | 0.752 | 175 | 2.8 | 0.764 |
| 80 | 2.2 | 0.685 | 105 | 2.9 | 0.723 | 130 | 4.0 | 0.738 | 155 | 3.0 | 0.755 | 180 | 2.5 | 0.766 |
| 85 | 3.1 | 0.693 | 110 | 3.8 | 0.725 | 135 | 2.8 | 0.742 | 160 | 3.0 | 0.757 | 185 | 2.5 | 0.767 |
| 90 | 3.2 | 0.700 | 115 | 5.2 | 0.729 | 140 | 3.3 | 0.743 | 165 | 3.2 | 0.759 | 190 | 3.8 | 0.768 |
| 95 | 3.9 | 0.707 | 120 | 4.1 | 0.733 | 145 | 3.2 | 0.747 | 170 | 3.5 | 0.760 | 195 | 3.2 | 0.771 |
| 100 | 5.4 | 0.714 | 125 | 2.6 | 0.735 | 150 | 3.9 | 0.752 | 175 | 3.6 | 0.763 | 200 | 2.8 | 0.772 |
| 105 | 4.6 | 0.718 | 130 | 5.3 | 0.737 | 155 | 4.0 | 0.753 | 180 | 3.8 | 0.765 | 205 | 3.3 | 0.773 |
| 110 | 6.4 | 0.723 | 135 | 4.7 | 0.741 | 160 | 4.2 | 0.755 | 185 | 3.7 | 0.767 | 210 | 4.3 | 0.775 |
| 115 | 3.1 | 0.728 | 140 | 3.1 | 0.753 | 165 | 4.4 | 0.757 | 190 | 3.8 | 0.768 | 215 | 3.9 | 0.777 |
| 120 | 5.2 | 0.731 | 145 | 4.4 | 0.747 | 170 | 3.8 | 0.758 | 195 | 4.1 | 0.769 | 220 | 3.8 | 0.781 |
| 125 | 4.9 | 0.733 | 150 | 4.2 | 0.750 | 175 | 5.3 | 0.763 | 200 | 3.2 | 0.772 | 225 | 4.4 | 0.781 |
| 130 | 4.2 | 0.735 | 155 | 4.2 | 0.757 | 180 | 4.5 | 0.764 | 205 | 3.5 | 0.773 | 230 | 4.4 | 0.784 |
| 135 | 4.0 | 0.739 | 160 | 3.3 | 0.754 | 185 | 4.2 | 0.765 | 210 | 3.6 | 0.775 | 235 | 3.7 | 0.787 |
| 140 | 3.3 | 0.742 | 165 | 3.8 | 0.757 | 190 | 3.4 | 0.765 | 215 | 3.8 | 0.777 | 240 | 3.9 | 0.788 |
| 145 | 3.8 | 0.746 | 170 | 3.8 | 0.759 | 195 | 3.3 | 0.768 | 220 | 3.8 | 0.779 | 245 | 3.4 | 0.792 |
| 150 | 3.1 | 0.748 | 175 | 3.3 | 0.761 | 200 | 2.4 | 0.772 | 225 | 3.6 | 0.783 | 250 | 3.1 | 0.796 |
| 155 | 2.9 | 0.751 | 180 | 3.6 | 0.763 | 205 | 3.3 | 0.773 | 230 | 3.5 | 0.785 | 255 | 3.4 | 0.796 |
| 160 | 2.8 | ... | 185 | 2.7 | 0.765 | 210 | 2.8 | 0.777 | 235 | 2.9 | 0.787 | 260 | 2.8 | 0.798 |
| 165 | 3.3 | 0.754 | 190 | 2.5 | 0.768 | 215 | 2.9 | 0.778 | 240 | 3.2 | 0.789 | 265 | 2.6 | 0.800 |
| 170 | 2.7 | 0.757 | 195 | 2.1 | 0.770 | 220 | 2.2 | 0.779 | 245 | 2.9 | 0.790 | 270 | 2.2 | 0.802 |
| 175 | 3.4 | 0.761 | 200 | 2.5 | 0.770 | 225 | 2.0 | 0.783 | 250 | 2.4 | 0.793 | 275 | 2.2 | 0.803 |
| 180 | 1.6 | 0.763 | 205 | 2.0 | 0.773 | 230 | 2.4 | 0.784 | 255 | 2.3 | 0.795 | 280 | 1.7 | 0.807 |
| 185 | 2.5 | 0.764 | 210 | 2.0 | 0.776 | 235 | 2.7 | 0.787 | 260 | 3.0 | 0.797 | 285 | 2.9 | 0.808 |
| Res. | 13.0 | 0.782 | Res. | 13.8 | 0.793 | Res. | 13.5 | 0.806 | Res. | 15.5 | 0.814 | Res. | 13.0 | 0.822 |
| Max. } cut } | 95–120 | | 125–150 | | 150–175 | | 170–195 | | 205–230 | | 235–260 | | 250–270° C. |
| | 24.7 | | 22.6 | | 21.7 | | 19.0 | | 19.8 | | 20.3 | | 20.1 per cent |
| Orig. cut: 14.1 | | | 13.4 | | 13.2 | | 14.9 | | 14.9 | | 14.6 | | 13.6 per cent |

TABLE 8—REDISTILLATION OF UBBELOHDE CUTS IN HEMPEL FLASK

| Cut: 125–150 | | 150–175 | | 175–200 | | 200–225 | | 225–250 | | 250–275 | | 275–300° C. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr.: 0.736 | | 0.753 | | 0.767 | | 0.779 | | 0.796 | | 0.801 | | 0.813 | |
| °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. |
| ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 0.794 |
| 85 | 3.8 | 0.629 | 110 | 3.3 | 0.723 | 135 | 3.3 | 0.742 | 160 | 3.8 | 0.758 | 185 | 4.8 | 0.771 |
| 90 | 2.5 | 0.698 | 115 | 5.8 | 0.732 | 140 | 6.8 | 0.747 | 165 | 4.4 | 0.762 | 190 | 2.7 | 0.773 |
| 95 | 3.5 | 0.707 | 120 | 4.9 | 0.734 | 145 | 3.4 | 0.749 | 170 | 4.1 | 0.763 | 195 | 5.1 | 0.775 |
| 100 | 9.1 | 0.708 | 125 | 3.4 | 0.737 | 150 | 4.5 | 0.753 | 175 | 4.6 | 0.766 | 200 | 5.8 | 0.777 |
| 105 | 3.6 | 0.718 | 130 | 4.5 | 0.740 | 155 | 6.5 | 0.753 | 180 | 6.3 | 0.767 | 205 | 5.2 | 0.778 |
| 110 | 9.9 | 0.726 | 135 | 4.6 | 0.742 | 160 | 5.7 | 0.757 | 185 | 7.0 | 0.768 | 210 | 6.2 | 0.779 |
| 115 | 5.2 | 0.729 | 140 | 5.6 | 0.744 | 165 | 7.9 | 0.759 | 190 | 6.3 | 0.769 | 215 | 5.7 | 0.781 |
| 120 | 7.0 | 0.731 | 145 | 4.9 | 0.748 | 170 | 7.2 | 0.761 | 195 | 5.5 | 0.771 | 220 | 7.0 | 0.782 |
| 125 | 6.0 | 0.732 | 150 | 3.7 | 0.750 | 175 | 6.8 | 0.763 | 200 | 6.4 | 0.773 | 225 | 6.6 | 0.785 |
| 130 | 6.4 | 0.736 | 155 | 6.4 | 0.753 | 180 | 5.5 | 0.765 | 205 | 5.0 | 0.774 | 230 | 5.3 | 0.787 |
| 135 | 6.6 | 0.738 | 160 | 5.1 | 0.753 | 185 | 6.2 | 0.767 | 210 | 6.1 | 0.776 | 235 | 5.4 | 0.788 |
| 140 | 4.7 | 0.743 | 165 | 5.7 | 0.757 | 190 | 4.5 | 0.767 | 215 | 4.9 | 0.778 | 240 | 4.7 | 0.792 |
| 145 | 5.0 | 0.747 | 170 | 4.6 | 0.759 | 195 | 4.3 | 0.768 | 220 | 4.5 | 0.781 | 245 | 4.7 | 0.793 |
| 150 | 3.1 | 0.748 | 175 | 4.4 | 0.763 | 200 | 3.3 | 0.771 | 225 | 3.9 | 0.782 | 250 | 4.0 | 0.795 |
| 155 | 3.9 | 0.749 | 180 | 2.8 | 0.764 | 205 | 3.6 | 0.775 | 230 | 3.6 | 0.784 | 255 | 3.5 | 0.797 |
| 160 | ... | ... | 185 | 2.9 | 0.765 | 210 | 2.7 | 0.777 | 235 | 3.4 | 0.787 | 260 | 3.2 | 0.801 |
| Res. | 20.1 | | Res. | 16.8 | 0.786 | Res. | 19.1 | 0.793 | Res. | 21.4 | 0.800 | Res. | 21.7 | 0.810 |
| Max. } cut } | 105–130 | | 140–165 | | 150–175 | | 175–200 | | 205–230 | | 225–250 | | 255–280° C. |
| | 34.5 | | 29.3 | | 34.1 | | 31.2 | | 31.0 | | 33.3 | | 28.8 per cent |
| Orig. cut: 25.8 | | | 25.2 | | 23.8 | | 24.1 | | 24.1 | | 23.7 | | 21.2 per cent |

TABLE 9—REDISTILLATION OF UBBELOHDE CUTS IN UBBELOHDE FLASK

Results Not Comparable with Any of Other Series

| Cut: 125–150 | | 150–175 | | 175–200 | | 200–225 | | 225–250 | | 250–275 | | 275–300° C. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr.: 0.736 | | 0.753 | | 0.767 | | 0.779 | | 0.790 | | 0.801 | | 0.813 | |
| °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. |
| 95 | 1.9 | 0.702 | 120 | 1.7 | 0.739 | 145 | 1.2 | 0.747 | 170 | 2.5 | 0.763 | ... | ... |
| 100 | 4.0 | 0.706 | 125 | 4.0 | 0.733 | 150 | 2.5 | 0.750 | 175 | 2.2 | 0.764 | 200 | 3.4 |
| 105 | 7.6 | 0.716 | 130 | 9.1 | 0.738 | 155 | 7.6 | 0.754 | 180 | 6.5 | 0.765 | 205 | 4.1 |
| 110 | 13.1 | 0.719 | 135 | 13.6 | 0.741 | 160 | 10.4 | 0.756 | 185 | 11.2 | 0.768 | 210 | 13.1 |
| 115 | 8.1 | 0.724 | 140 | 7.5 | 0.744 | 165 | 9.8 | 0.758 | 190 | 9.9 | 0.770 | 215 | 9.8 |
| 120 | 9.4 | 0.730 | 145 | 8.0 | 0.746 | 170 | 11.6 | 0.760 | 195 | 9.2 | 0.771 | 220 | 8.4 |
| 125 | 7.7 | 0.734 | 150 | 8.2 | 0.748 | 175 | 7.9 | 0.762 | 200 | 7.7 | 0.772 | 225 | 9.1 |
| 130 | 7.5 | 0.736 | 155 | 6.5 | 0.749 | 180 | 6.9 | 0.764 | 205 | 7.7 | 0.774 | 230 | 7.4 |
| 135 | 6.8 | 0.738 | 160 | 6.4 | 0.753 | 185 | 6.8 | 0.765 | 210 | 6.2 | 0.775 | 235 | 5.7 |
| 140 | 3.9 | 0.741 | 165 | 6.3 | 0.756 | 190 | 5.5 | 0.767 | 215 | 5.7 | 0.776 | 240 | 5.3 |
| 145 | 4.6 | 0.746 | 170 | 3.9 | 0.758 | 195 | 4.4 | 0.768 | 220 | 4.1 | 0.782 | 245 | 5.2 |
| 150 | 4.0 | 0.747 | 175 | 4.0 | 0.760 | 200 | 3.8 | 0.771 | 225 | 4.0 | 0.783 | 250 | 4.1 |
| 155 | 3.2 | 0.751 | 180 | 3.4 | 0.762 | 205 | 2.9 | 0.772 | 230 | 3.3 | 0.784 | 255 | 6.4 |
| 160 | 3.0 | 0.753 | 185 | 2.7 | 0.765 | 210 | 3.3 | 0.775 | 235 | 3.0 | 0.788 | 260 | 6.4 |
| Res. | 14.6 | 0.764 | Res. | 14.1 | 0.776 | Res. | 15.0 | 0.786 | Res. | 16.6 | 0.802 | Res. | 17.6 |
| Max. } cut } | 100–125 | | 125–150 | | 150–175 | | 180–205 | | 205–230 | | 230–255 | | 260–285° C. |
| | 45.9 | | 46.4 | | 47.3 | | 45.7 | | 47.8 | | 46.3 | | 42.1 per cent |
| Orig. cut: 26.8 | | | 27.1 | | 27.4 | | 27.7 | | 27.7 | | 26.5 | | 26.6 per cent |

| 0.797 | 220 | 1.2 | 0.783 | 245 | 3.4 | 0.797 |
|---|---|---|---|---|---|---|
| 0.797 | 225 | 2.9 | 0.787 | 250 | 1.5 | 0.800 |
| 0.798 | 230 | 5.6 | 0.788 | 255 | 7.0 | 0.800 |
| 0.799 | 235 | 8.3 | 0.790 | 260 | 5.4 | 0.802 |
| 0.792 | 240 | 12.2 | 0.791 | 265 | 8.3 | 0.803 |
| 0.778 | 245 | 10.2 | 0.794 | 270 | 11.8 | 0.805 |
| 0.778 | 250 | 8.4 | 0.796 | 275 | 8.6 | 0.807 |
| 0.780 | 255 | 7.2 | 0.797 | 280 | 7.1 | 0.809 |
| 0.788 | 260 | 5.3 | 0.800 | 285 | 6.3 | 0.809 |
| 0.790 | 265 | 5.5 | 0.802 | 290 | 4.0 | 0.812 |
| 0.782 | 270 | 4.8 | 0.803 | 295 | 5.3 | 0.814 |
| 0.793 | 275 | 3.7 | 0.806 | 300 | 3.9 | 0.815 |
| 0.797 | 280 | 3.2 | 0.808 | 305 | 3.5 | 0.816 |
| 0.797 | 285 | 2.5 | 0.808 | 310 | 3.0 | 0.818 |
| 0.806 | Res. | 18.8 | 0.819 | Res. | 20.5 | 0.826 |
| 0.808 | 290–315 | | 315–340 | | 340–365° C. | |
| | 46.3 | | 42.1 per cent | | | |
| | 26.5 | | 26.6 per cent | | | |

TABLE 10—REDISTILLATION OF CUTS (UBBELOHDE REDISTILLED IN UBBELOHDE) IN HEMPEL FLASK

| Cut: 100–125 | | 125–150 | | 150–175 | | 175–200 | | 200–225 | | 225–250 | | 250–275° C. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr.: 0.723 | | 0.742 | | 0.756 | | 0.768 | | 0.779 | | 0.790 | | 0.801 | |
| °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. |
| ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 180 | 3.4 | 0.768 | ... |
| 80 | 2.1 | 0.681 | 105 | 2.2 | 0.724 | ... | ... | ... | ... | ... | ... | ... | ... |
| 85 | 2.1 | 0.698 | 110 | 4.0 | 0.728 | 135 | 4.3 | 0.743 | 160 | 7.6 | 0.759 | 185 | 7.9 |
| 90 | 8.8 | 0.709 | 115 | 12.4 | 0.730 | 140 | 10.6 | 0.747 | 165 | 8.7 | 0.763 | 190 | 9.2 |
| 95 | 6.5 | 0.711 | 120 | 9.1 | 0.733 | 145 | 9.5 | 0.750 | 170 | 10.3 | 0.763 | 195 | 8.2 |
| 100 | 13.4 | 0.716 | 125 | 9.7 | 0.737 | 150 | 8.5 | 0.752 | 175 | 11.0 | 0.766 | 200 | 9.7 |
| 105 | 13.5 | 0.722 | 130 | 12.2 | 0.739 | 155 | 11.7 | 0.754 | 180 | 11.9 | 0.766 | 205 | 9.2 |
| 110 | 8.8 | 0.724 | 135 | 6.6 | 0.742 | 160 | 9.7 | 0.756 | 185 | 9.0 | 0.766 | 210 | 8.2 |
| 115 | 7.9 | 0.729 | 140 | 8.0 | 0.746 | 165 | 9.3 | 0.757 | 190 | 8.0 | 0.767 | 215 | 7.1 |
| 120 | 7.1 | 0.731 | 145 | 7.3 | 0.749 | 170 | 8.1 | 0.761 | 195 | 7.3 | 0.769 | 220 | 7.5 |
| 125 | 7.7 | 0.733 | 150 | 5.9 | 0.752 | 175 | 6.4 | 0.763 | 200 | 5.6 | 0.770 | 225 | 5.4 |
| 130 | 5.7 | 0.736 | 155 | 5.4 | 0.753 | 180 | 5.0 | 0.765 | 205 | 5.0 | 0.773 | 230 | 5.5 |
| 135 | 4.3 | 0.737 | 160 | 3.1 | 0.755 | 185 | 4.3 | 0.766 | 210 | 4.7 | 0.773 | 235 | 4.3 |
| Res. | 10.1 | 0.751 | Res. | 9.7 | 0.763 | Res. | 11.8 | 0.772 | Res. | 13.3 | 0.785 | Res. | 13.9 |
| Max. } cut } | 85–110 | | 110–135 | | 135–160 | | 165–180 | | 185–210 | | 215–240 | | 240–265° C. |
| | 51.0 | | 53.0 | | 50.0 | | 50.2 | | 44.5 | | 45.3 | | 46.6 per cent |
| Orig. cut: 45.0 | | | 43.0 | | 45.2 | | 41.8 | | 37.4 | | 41.3 | | 41.7 per cent |

TABLE 11—REDISTILLATION OF CUTS IN HEMPEL FLASK

| Cut: 100–125 | | 125–150 | | 150–175 | | 175–200 | | 200–225 | | 225–250 | | 250–275° C. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr.: 0.727 | | 0.744 | | 0.758 | | 0.770 | | 0.780 | | 0.791 | | 0.804 | |
| °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. | °C. | % Gr. |
| ... | ... | 110 | 2.7 | 0.728 | 135 | 2.0 | 0.744 | ... | ... | ... | ... | ... | ... |
| 90 | 1.9 | 0.692 | 115 | 3.7 | 0.733 | 140 | 2.6 | 0.748 | 165 | 3.6 | 0.762 | 190 | 2.5 |
| 95 | 9.3 | 0.711 | 120 | 8.3 | 0.735 | 145 | 9.1 | 0.750 | 170 | 11.1 | 0.765 | 195 | 8.5 |
| 100 | 13.1 | 0.717 | 125 | 12.0 | 0.737 | 150 | 11.1 | 0.753 | 175 | 12.0 | 0.765 | 200 | 11.5 |
| 105 | 14.1 | 0.723 | 130 | 13.2 | 0.741 | 155 | 11.3 | 0.753 | 180 | 13.6 | 0.767 | 205 | 12.4 |
| 110 | 10.8 | 0.727 | 135 | 12.8 | 0.743 | 160 | 12.1 | 0.755 | 185 | 13.5 | 0.768 | 210 | 14.5 |
| 115 | 10.5 | 0.729 | 140 | 11.8 | 0.747 | 165 | 13.3 | 0.757 | 190 | 11.0 | 0.768 | 215 | 12.6 |
| 120 | 10.3 | 0.730 | 145 | 9.7 | 0.748 | 170 | 10.5 | 0.762 | 195 | 9.4 | 0.770 | 220 | 9.5 |
| 125 | 9.8 | 0.732 | 150 | 8.3 | 0.751 | 175 | 8.8 | 0.763 | 200 | 6.9 | 0.773 | 225 | 8.3 |
| 130 | 6.7 | 0.734 | 155 | 5.6 | 0.753 | 180 | 6.2 | 0.764 | 205 | 5.3 | 0.777 | 230 | 6.6 |
| 135 | 4.2 | 0.741 | 160 | 4.8 | 0.755 | 185 | 4.3 | 0.765 | 210 | 4.5 | 0.777 | 235 | 4.8 |
| Res. | 8.7 | 0.748 | Res. | 7.2 | 0.763 | Res. | 8.6 | 0.772 | Res. | 8.8 | 0.786 | Res. | 9.8 |
| Max. } cut } | 95–120 | | 120–145 | | 145–170 | | 165–190 | | 195–220 | | 220–245 | | 245–270° C. |
| | 58.8 | | 59.5 | | 58.3 | | 61.2 | | 60.4 | | 59.0 | | 59.6 per cent |
| Orig. cut: 55.5 | | | 55.8 | | 56.0 | | 54.4 | | 52.2 | | 55.4 | | 56.6 per cent |

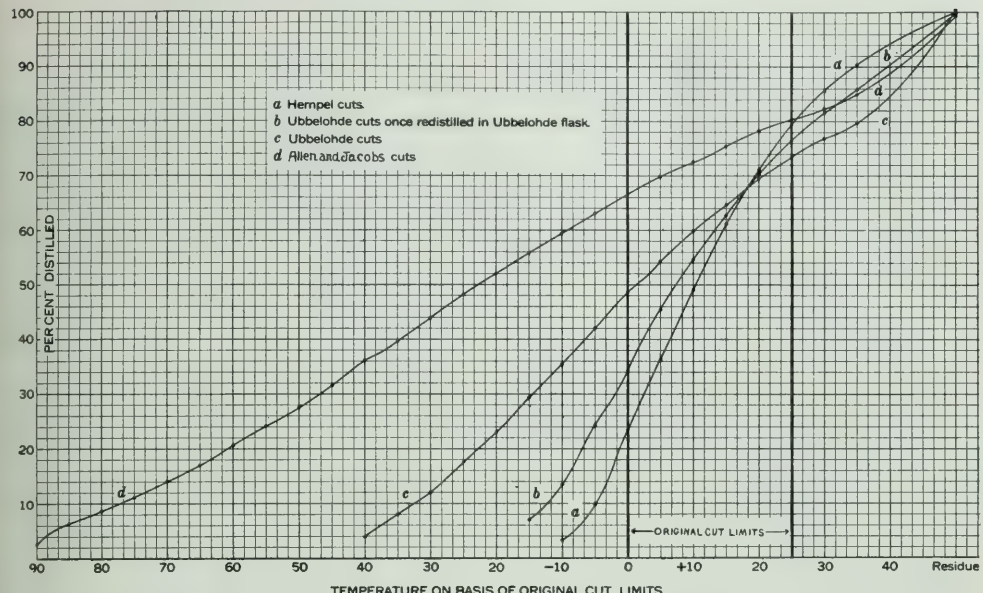


FIG. XI—REDISTILLATIONS. TOTAL PERCENTAGE-TEMPERATURE CURVES

of the 25° cuts of the original distillations. There appears to be no very satisfactory way of obtaining average curves for each series; hence, typical single curves are given, Fig. XIII, each representing the relations between percentage and gravity discovered on redistilling the middle original cut of each series.

To put these curves on a comparable basis the gravities were plotted relative to their differences from that measured for the original cut. The lines particular points were chosen because they just avoided the irregular extremities of each of the curves.

Table 13 indicates a fact which does not appear on consideration of the percentage-temperature relations; *i. e.*, the degree of separation obtained by any particular method of distillation is not a constant and characteristic factor but increases as the temperature scale is ascended. Redistillations increase in efficiency in a similar proportion. Consequently the

TABLE 12—SUMMARY TABLE OF MAXIMUM AND ORIGINAL CUTS AND REDISTILLATIONS IN HEMPEL FLASK

| ORIGINAL LIMITS OF CUT ° C. | ORIGINAL CUTS Percentage redistilled within original limits | | | | MAXIMUM CUTS Temperature limits of maximum cuts ° C. | | | | MAXIMUM CUTS Percentage redistilled between maximum cut limits | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Allen and Jacobs | Ubbelohde- lohde | Ubbelohde- lohde | Hempel | Allen and Jacobs | Ubbelohde | Ubbelohde- Ubbelohde | Hempel | Allen and Jacobs | Ubbelohde- lohde | Ubbelohde- Ubbelohde | Hempel |
| 100–125 | .. | .. | 45.0 | 55.5 | ..... | .. | 85–110 | 95–120 | .. | .. | 51.0 | 58.8 |
| 125–150 | .. | 25.8 | 43.0 | 55.8 | ..... | 105–130 | 110–135 | 120–145 | .. | 34.5 | 53.0 | 59.5 |
| 150–175 | 14.1 | 26.2 | 45.2 | 56.0 | 95–120 | 140–165 | 135–160 | 145–170 | 24.7 | 29.3 | 50.0 | 58.3 |
| 175–200 | 13.4 | 23.8 | 41.8 | 54.4 | 125–150 | 150–175 | 165–190 | 165–190 | 22.6 | 34.1 | 50.2 | 61.2 |
| 200–225 | 13.2 | 24.4 | 37.4 | 57.2 | 150–175 | 175–200 | 185–210 | 195–220 | 21.7 | 31.2 | 44.5 | 60.4 |
| 225–250 | 14.9 | 24.1 | 41.3 | 55.4 | 170–195 | 205–230 | 215–240 | 220–245 | 19.0 | 31.0 | 45.3 | 59.0 |
| 250–275 | 14.9 | 23.7 | 41.7 | 56.6 | 205–230 | 225–250 | 240–265 | 245–270 | 19.8 | 33.3 | 46.6 | 59.6 |
| 275–300 | 14.6 | 24.2 | .. | .. | 235–260 | 255–280 | .... | . . | 20.3 | 28.8 | .. | . |
| 300–325 | 13.6 | .. | .. | .. | 250–275 | ..... | .... | . | 20.1 | .. | .. | . |
| Average | 14.1 | 24.6 | 42.2 | 55.9 | ..... | ..... | ..... | ..... | 21.2 | 31.7 | 45.8 | 59.5 |

marking this value have been superimposed and used as the ordinate axis. The angle made by the average course of each of these curves with this axis indicates the homogeneity, or lack of homogeneity, of the cut it represents. The superiority of the Hempel method is impressively shown when this factor is considered.

It happens that the relation of percentage and gravity can be shown clearly and completely by numbers and Table 13 will be found instructive. The data given, obtained by interpolation on the curves, of which those in Fig. XIII are examples, represent increases in specific gravity between points marking 10 and 85 per cent in the course of each redistillation. These

state of affairs is, that measurements are being made of a continuously increasing value by a method, the efficiency of which varies very nearly in the same ratio.

TABLE 13—VARIATIONS IN SPECIFIC GRAVITY SHOWN BY REDISTILLATIONS

Values Given Represent Increases between Points Marking 10 and 85 Per Cent of the Distillates

| Temperature limits of original cut | INCREASES IN SPECIFIC GRAVITY Allen and Jacobs | Ubbelohde | Ubbelohde- Ubbelohde | Hempel |
|---|---|---|---|---|
| 100–125° | ... | .... | 0.029 | 0.024 |
| 125–150° | ... | 0.047 | 0.026 | 0.018 |
| 150–175° | 0.075 | 0.043 | 0.020 | 0.014 |
| 175–200° | 0.058 | 0.032 | (0.013) | 0.012 |
| 200–225° | 0.052 | 0.030 | 0.018 | 0.010 |
| 225–250° | 0.047 | 0.030 | 0.018 | 0.010 |
| 250–275° | 0.050 | 0.027 | 0.020 | 0.010 |
| 275–300° | 0.044 | 0.025 | ... | ... |
| 300–325° | 0.043 | ... | ... | ... |

By considering a relation which is independent of temperature we are able to detect and estimate the

magnitude of the progressions in the degree of fractionation furnished by the various methods. A closer study of Table 13 brings out points which may, in a later connection, prove important. For the present it is sufficient to note that there are increases and that

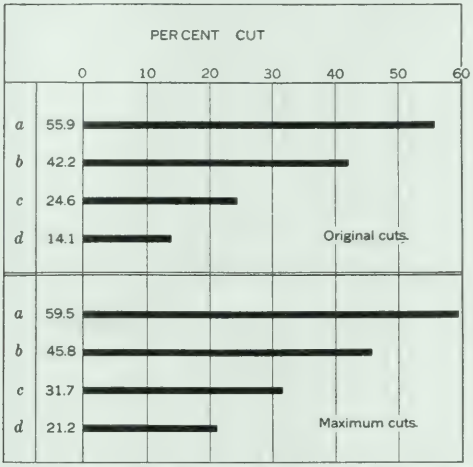


FIG. XII—REDISTILLATIONS RELATIVE MAGNITUDE OF ORIGINAL AND MAXIMUM 25° CUTS
*a*—Hempel Cuts. *b*—Ubbelohde Cuts Once Redistilled. *c* Ubbelohde Cuts. *d*—Allen and Jacobs Cuts.

the maximum degree of separation attained by the Ubbelohde method is lower than the minimum by the Hempel.

## GENERAL CONCLUSIONS

I—A low degree of separation is obtained by the most efficient of the three crude petroleum distillation methods studied.

Taking as an index the most favorable figures, those for the maximum cuts, it appears that only 60 per cent efficiency can be attained when something like 90 would be desirable. An increased efficiency might be obtained by using a longer Hempel column but this would make it so effective a reflux condenser that the higher boiling petroleum constituents could not be driven over without the occurrence of considerable cracking.

II—Distilling through a Hempel column of moderate height gives a degree of fractionation over twice and probably three times that attained by the use of the ordinary open flask.

III—The method of minimum condensation falls almost as far below the open flask as the latter is behind the Hempel in efficiency.

IV—The degree of separation obtained by any one method of distillation is not a constant factor but increases as the temperature scale is ascended.

The consideration of percentage-temperature relations fails to show this fact, which is theoretically so obvious that it hardly needs experimental proof. The figures for specific gravities, however, demonstrate the increases and furnish an approximate measure of their magnitude.

V—That the similarities between results obtained by various methods of analytical distillation are entirely superficial is shown by the series of refractionation experiments.

## SUPPLEMENTARY NOTE

The foregoing report represents the first section of a series of experiments dealing with the analytical distillation of petroleum. These experiments have been begun for the purpose of securing comprehensive data which will aid in the formulation of a standard method. The requirements of such a method have been provisionally outlined as follows:

1—The report of an analytical distillation must meet the needs of both the scientist and the oil technologist.

The results of a general laboratory distillation method need not and cannot be identical with those obtained in the refinery. No further proof is needed of this than a knowledge of the variations among commercial processes now in vogue. The end to be attained is a uniform and reliable method for comparing crude oils. By interpreting the results obtained by such a method in the light of knowledge of his own processes the refiner should be able to estimate with sufficient exactness the commercial value of any given crude oil.

2—The method of distillation must minimize, or, if possible, eliminate "cracking."

*The purpose of a distillation is to ascertain what is already in an oil.* The determination of what can be made from it is another and a different problem.

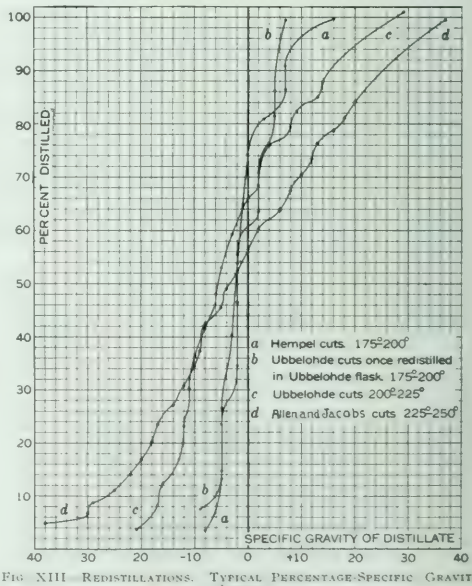


FIG. XIII REDISTILLATIONS. TYPICAL PERCENTAGE-SPECIFIC GRAVITY CURVES

3—The method must be satisfactory from the point of view of the laboratory worker.

*a*—It must not be too tedious nor require too skilful a technique.

*b*—Checks must be easily obtainable.

*c*—Apparatus must be standard and easily obtainable, or the method must not depend upon the details of construction of the apparatus used.

The present report furnishes only partial information with regard to any of these requirements. It does, however, help to put our knowledge of the process of crude oil distillation on a firmer basis and furnishes necessary comparative data with regard to the mechanism of three typical distillation methods.

The next phase of the problem to be studied is that of "cracking" and it is proposed to determine in an empirical way the temperature and time factors which fix its minimum limit.

A third section of the work will deal with a correlation of technical requirements and will also furnish information with regard to the specific advantages of the known distillation methods.

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## THE GERMICIDAL EFFICIENCY OF DENTAL CEMENTS

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### INTRODUCTION

Dental cements, which are used by the dental profession because of their bactericidal properties, are known as "Copper Cements" or "Copper Oxyphosphates." Their advantage over other dental cements lies in the increased germicidal power secured by the use of certain compounds of copper. These cements reach the dentist in the form of a liquid and powder. There are several types of "copper cement" on the market, these being characterized largely by their color. The powders of the cements now in use appear as white, red, black, or varicolored compounds.

The liquid supplied with the majority of these cements consist essentially of concentrated solutions of orthophosphoric acid, $H_3PO_4$, modified by the addition of hydrated oxide of alumina, $Al_2(OH)_6$. Occasionally other metallic salts, such as iron and nickel, are added. Hydrated oxide of alumina is used as a modifier in order to control the reaction of the liquid on the powder when the two are combined by spatulation. White copper cement powder consists of calcined oxide of zinc, magnesia and bismuth, the copper being added in the form of cuprous iodide, $Cu_2I_2$, cupric phosphate, $CuHPO_4$, cupric silicate, $CuSiO_3$, or other light colored copper salts. Black copper cement powder consists of either black copper oxide, CuO, and cobalt oxide, or black copper oxide and zinc oxide with or without other oxides such as magnesia and bismuth. Red copper cement powder consists essentially of zinc oxide and cuprous oxide, $Cu_2O$, other oxides such as magnesia and bismuth being occasionally present. Red pigments are also added to improve the color, which is not a deception, provided sufficient cuprous oxide is used to give the cement mass the requisite germicidal power. The varicolored cement powders consist essentially of zinc oxide, magnesia, and bismuth, with a small proportion of light colored copper compounds such as cupric silicate, cupric phosphate, or other light colored copper salts. Pigments are added to obtain the various shades.

These various dental cements are mixed for use by the dentist on a glass slab, upon which the powder and liquid are separately placed, the powder being subsequently incorporated in small amounts at a time, with a nickel-plated or agate spatula, until a certain consistency is obtained. The proper consistency is dependent upon the character of the individual cement, and is generally given by the manufacturer in the descriptive matter accompanying the package of cement.

Very little information is contained in dental literature on the subject of germicidal efficiency of dental cements, and the little information which has been circulated is very often of a misleading character, having been presented largely for advertising purposes.

It is possible to measure the germicidal efficiency of material of this character in precisely the same way as it is possible to measure the germicidal efficiency of disinfectants. It is therefore obvious, especially in view of the varied composition of these cements, that a thorough investigation of this subject is of immediate interest to the dental profession, as well as to chemists and bacteriologists who may be called upon to report on the germicidal power of dental cements. The object of this paper is to show the comparative germicidal power of these cements, and also some of the compounds used in their production.

### EXPERIMENTAL—GERMICIDAL EFFICIENCY TESTS

SERIES I—CUPROUS OXIDE, CUPRIC OXIDE, AND CALCINED ZINC OXIDE—The object of these tests was to determine, if possible, the comparative germicidal efficiency of the red and black copper oxide, as compared with calcined zinc oxide.

Saliva was obtained from one individual by means of chewing unflavored gum.

Glass beads were added to 50 cc. of saliva, in a sterile 4 oz. glass-stoppered bottle, and the bacteria separated by shaking for a period of 10 minutes; 10 cc. of the saliva were transferred to each of five sterile 1 oz. glass-stoppered bottles; 1 cc. of the saliva was removed from each bottle, and the various dilutions plated in standard agar. One gram of each of the samples to be tested was added to the bottles in the order described below. The fifth bottle remained as a control on the number of bacteria present in the saliva during the test. All five bottles were shaken and then incubated at 37° C. for 24 hours. The bottles were then removed from the incubator and shaken thoroughly for one minute, and the sediment caused by the samples under examination was allowed to settle for 5 minutes. At the end of this time 1 cc. was removed from each of the five bottles and various dilutions plated in standard infusion agar. The plates in both series of determinations were incubated at 37° C. for a period of 48 hours, with the results given in Table I.

The results of these tests indicate that the amount of red copper oxide and black copper oxide which was dissolved by the saliva was sufficient to produce practical sterilization, and that the zinc oxide in itself, while not sufficient to produce practical sterilization, shows a germicidal efficiency of 96.2 per cent.

CUPROUS OXIDE, CUPRIC PHOSPHATE, AND CUPROUS IODIDE, IN ADMIXTURES WITH CALCINED ZINC OXIDE

SERIES 2—The object of this test was to determine, if possible, the relative germicidal efficiency of cupric phosphate and cuprous iodide in comparison with cuprous oxide when these different compounds of copper were mixed with calcined oxide of zinc. The manner in which these tests were conducted was precisely the same as used in Series 1 and the results given in Table I show that the cuprous oxide and cuprous iodide in the quantities used, and in the presence of zinc oxide, produce practical sterilization in 24 hours. It is also shown that the cupric phosphate is less efficient under similar conditions than cuprous oxide or cuprous iodide.

SERIES 3—These tests were conducted with the object of determining still more definitely what the effect of cuprous oxide, cupric phosphate, and cuprous iodide would be in the presence of smaller quantities of these copper compounds in admixture with calcined zinc oxide. The tests were conducted in the same manner as in Series 2, except that 20 cc. of saliva were used for one gram of the powder, instead of 10 cc. for one gram, as in Series 2. The object of making this greater dilution was to reduce the quantity of powder in proportion to the saliva, so that the germicidal efficiency obtained in the different materials would be more pronounced.

TABLE I—TESTS OF COPPER COMPOUNDS AND ZINC OXIDE

| | Per cent copper compound | Per cent calcined zinc oxide | No. LIVING BACTERIA PER CC. Just before addition of 1 g. of sample | After incubation for 24 hrs. at 37° C. | Germicidal efficiency per cent |
|---|---|---|---|---|---|
| SERIES 1: | | | | | |
| Copper Oxide red | 100 | None | 9,000,000 | Less than 100 | 99.9 |
| Copper Oxide black | 100 | None | 8,200,000 | Less than 100 | 99.9 |
| None | | 100 | 10,500,000 | 394,000 | 96.2 |
| Control Saliva (Blank) | | | 9,400,000 | 12,900,000 | .. |
| SERIES 2: | | | | | |
| Cuprous Oxide | 1 | 99 | 8,800,000 | Less than 50 | 99.9 |
| | 5 | 95 | 9,500,000 | Less than 50 | 99.9 |
| | 10 | 90 | 8,400,000 | Less than 50 | 99.9 |
| Cupric Phosphate | 1 | 99 | 12,900,000 | 142,000 | 98.9 |
| | 5 | 95 | 10,300,000 | 200 | 99.9 |
| | 10 | 90 | 9,000,000 | 130 | 99.9 |
| Cuprous Iodide | 1 | 99 | 10,900,000 | Less than 50 | 99.9 |
| | 5 | 95 | 13,000,000 | Less than 50 | 99.9 |
| | 10 | 90 | 11,900,000 | Less than 50 | 99.9 |
| Control Saliva (Blank) | | | 10,700,000 | 8,900,000 | .. |
| SERIES 3: | | | | | |
| Cuprous Oxide | 0.1 | 99.9 | 5,600,000 | 550,000 | 90.1 |
| | 0.5 | 99.5 | 5,100,000 | 17,900 | 99.6 |
| | 1.0 | 99.0 | 5,500,000 | 100 | 99.9 |
| Cupric Phosphate | 0.1 | 99.9 | 7,400,000 | 12,600 | 99.8 |
| | 0.5 | 99.5 | 6,100,000 | 8,900 | 99.8 |
| | 1.0 | 99.0 | 6,200,000 | 41,000 | 99.3 |
| Cuprous Iodide | 0.1 | 99.9 | 5,900,000 | 335,000 | 94.3 |
| | 0.5 | 99.5 | 7,600,000 | Less than 100 | 99.9 |
| | 1.0 | 99.0 | 7,000,000 | 5,100 | 99.9 |
| Control Saliva (Blank) | | | 3,900,000 | 18,300,000 | .. |

The results indicate that these compounds of copper produce a marked effect in increasing the germicidal power. It will, however, be observed that the period of incubation of 24 hours is too long, or else that the dilutions are not sufficiently great to give definite information as to the germicidal efficiencies of the various compounds.

The object of this work was largely to determine whether an increase in germicidal efficiency could be obtained with small quantities of copper compounds. The results of the tests, given in Table I, show without question that the various compounds of copper used in the tests show powerful germicidal action. It is, however, necessary to conduct these tests under the conditions in which the compounds will actually exist when used in a dental cement, since in the three series just described, the powders alone have been tested, and not the powders mixed into a cement mass with a balanced liquid and allowed to set. For this reason the work on the uncombined powder was discontinued, and a further series of tests were conducted with the powder in combination with an appropriate liquid as a cement.

VARYING PERCENTAGES OF CUPROUS IODIDE ADDED TO A DENTAL CEMENT, COMPARED WITH TWO COPPER CEMENTS AND ONE CEMENT FREE FROM COPPER

SERIES 4—The tests were conducted in the same manner as Series 3, except that the periods of exposure were 1 hour and 24 hours. The powders were prepared by combining the cement powders with the liquid, allowing the mass to set between glass plates for 48 hours, and then reducing the mass in an agate mortar, after which the powder was carefully sifted through a No. 25 bolting silk. The results are given in Table II.

They show that the various additions of cuprous iodide to Caulk's Crown & Bridge & Gold Inlay Cement produce complete sterilization in 1 and in 24 hours. It will be noted that Caulk's Crown & Bridge & Gold Inlay Cement, which does not carry any copper, is markedly germicidal. Ames' New Process Oxyphosphate of Copper also produces complete sterilization in 1 and in 24 hours. Smith's Copper Cement is shown to be deficient in germicidal power, since it fails to produce practical sterilization in 1 hour. An analysis of Smith's Copper Cement shows that it contains the equivalent of 0.755 per cent copper oxide, CuO, which is apparently present either as copper hydrate or copper silicate. This quantity of copper and the nature of the compound is such that high germicidal power cannot be obtained from the quantity which is used.

SERIES 5—This series is a duplication of Series 4, except that the exposure periods were reduced to 5 minutes, 15 minutes, and 1 hour, in order to more clearly show the germicidal efficiency, since, as observed in the case of Series 4, the various percentages of cuprous iodide did not show any difference, for the simple reason that the exposure period of 1 hour is sufficient to destroy all of the bacteria, whereas a shorter exposure period will not do so.

The results of Series 5 are given in Table II, where they are also expressed in terms of germicidal efficiency, which represents the percentage of organisms originally present which were killed by the cement.

A study of the data found in Series 5 shows that the addition of 1 to 5 per cent of cuprous iodide to Caulk's Crown & Bridge & Gold Inlay Cement gives practical sterilization in 5 minutes exposure and complete sterilization in 15 minutes exposure.

Ames' New Process Oxyphosphate of Copper apparently shows a higher efficiency when mixed with a nickel spatula than when mixed with an agate spatula. With the exception of the results obtained with this cement when mixed with an agate spatula, it is evi-

dent that practical sterilization is obtained in 5 minutes exposure and complete sterilization in 15 minutes exposure.

Smith's Copper Cement shows incomplete sterilization throughout, and it is also seen that a slightly higher efficiency is obtained with this cement when mixed with a nickel, than when mixed with an agate spatula. This is true in both the 5-minute and 15-minute exposure. There is apparently a slightly higher efficiency when mixed with an agate spatula in the 1-hour exposure, but in this case the results are so closely identical that the conclusion appears warranted that this cement will give in precisely the same manner as with Ames' New Process Oxyphosphate of Copper, a slightly higher efficiency when mixed with a nickel spatula.

Caulk's Crown & Bridge & Gold Inlay Cement, while showing a slightly lower efficiency than Smith's Copper Cement in the 5-minute and 1-hour exposure, apparently shows approximately the same efficiency in the 15-minute exposure, and as far as the general results show there is but little difference between this cement and Smith's Copper Cement, as far as the germicidal efficiency is concerned. It must be remembered, however, that Caulk's Crown & Bridge & Gold Inlay Cement is not a copper cement, and therefore it will be seen that Smith's Copper Cement is deficient in the germicidal power to be expected of a copper cement.

### SERIES OF COPPER CEMENTS NOW ON THE MARKET

SERIES 6—These tests were conducted with the cement mixed in all cases by means of an agate spatula. In other respects the technique was the same as that employed in the tests in Series 5. The results, given in Table II, show that Caulk's White Copper Cement, Caulk's Red Copper Cement, and Ames' New Process Oxyphosphate of Copper Cement are almost identical in germicidal power. Decido Copper Cement and Fellowship Oxyphosphate of Copper Cement require 15 minutes exposure in which to secure the germicidal efficiency obtained from Caulk's White Copper Cement, Caulk's Red Copper Cement, and Ames' New Process Oxyphosphate of Copper Cement in only 5 minutes exposure. This shows that Decido Copper Cement and Fellowship Oxyphosphate of Copper Cement are both much weaker in germicidal power than these cements. Smith's White Copper Cement shows the lowest germicidal power of the entire series.

### TESTS OF THREE CEMENTS AND ONE MIXTURE

SERIES 7—Caulk's Copr-Zinc is a preparation containing 10 per cent cuprous iodide, and therefore has 5 times the concentration of Caulk's White Copper Cement. It is not used alone as a cement, but is used in the proportion of one part of Copr-Zinc to four parts of Crown & Bridge & Gold Inlay Cement.

The plates in each case after incubation were counted and then photographed, and are shown in the accompanying photographs, Nos. 1, 2 3, 4, 5 and 7.

The technique followed in Series 7 varied slightly from that followed in the other tests, particularly in that only 15-minute exposures were made, and that the powder and saliva were thoroughly shaken immediately before plating. Only one dilution was plated, representing 1/10,000 cc. of the original saliva. Individual controls were eliminated, one control serving for this series. The photographs show very plainly the growth of colonies in the saliva itself, as well as in the saliva exposed to Caulk's Crown & Bridge & Gold Inlay Cement and Smith's Copper Cement. It will, however, be observed that in the case of Caulk's Crown & Bridge & Gold Inlay Cement to which Copr-Zinc was added, and Ames' New Process Oxyphosphate of Copper Cement, the plates were both sterile.

Table II—Germicidal Efficiency Tests on Several Cements with Varying Periods of Exposure

| Sample | Series 4: No. of Living Bacteria per Cc. Just before addition of 1 g. of sample | Series 4: After exposure of 1 hr. | Series 4: After exposure of 24 hrs. | Series 5: No. of Living Bacteria per Cc. Just before addition of 1 g of sample | Series 5: After exposure of 5 min. | Series 5: After exposure of 15 min. | Series 5: After exposure of 1 hr. | Per cent germicidal efficiency after exposure of 5 min. | Per cent germicidal efficiency after exposure of 15 min. | Per cent germicidal efficiency after exposure of 1 hr. |
|---|---|---|---|---|---|---|---|---|---|---|
| Series 4 and 5: Ames' New Process Oxyphosphate of Copper: | | | | | | | | | | |
| Mixed with Nickel Spatula | 7,000,000 | 0 | 0 | 6,800,000 | 11,000 | 0 | 0 | 99.8 | 100 | 100 |
| Mixed with Agate Spatula | 9,000,000 | 0 | 0 | 5,000,000 | 210,000 | 100 | 0 | 95.8 | 99.9 | 100 |
| Smith's Copper Cement: | | | | | | | | | | |
| Mixed with Nickel Spatula | 15,000,000 | 2,000,000 | 0 | 7,900,000 | 3,400,000 | 3,000,000 | 1,000,000 | 56.9 | 62.0 | 87.3 |
| Mixed with Agate Spatula | 15,000,000 | 770,000 | 0 | 5,300,000 | 3,400,000 | 2,800,000 | 500,000 | 35.8 | 47.1 | 90.5 |
| Caulk's Crown & Bridge & Gold Inlay Cement Containing Per Cent Cuprous Iodide: | | | | | | | | | | |
| 1 | 14,000,000 | 0 | 0 | 5,200,000 | 143,000 | 0 | 0 | 95.3 | 100 | 100 |
| 2 | 10,000,000 | 0 | 0 | 6,000,000 | 39,000 | 0 | 0 | 99.4 | 100 | 100 |
| 3 | 7,400,000 | 0 | 0 | 5,000,000 | 2,500 | 0 | 0 | 99.9 | 100 | 100 |
| 4 | 8,900,000 | 0 | 0 | 8,000,000 | 200 | 0 | 0 | 99.9 | 100 | 100 |
| 5 | 12,000,000 | 1,800 | 0 | 10,000,000 | 2,500 | 0 | 0 | 99.9 | 100 | 100 |
| 0 | 11,000,000 | 4,500,000 | 0 | 7,000,000 | 5,000,000 | 3,800,000 | 2,000,000 | 28.5 | 45.7 | 71.4 |
| Control Saliva (Blank) | 12,000,000 | 10,000,000 | 17,400,000 | 6,000,000 | 8,000,000 | 7,000,000 | 8,000,000 | .. | ... | ... |
| Series 6: | | | | | Series 6 | | | | | |
| Smith's White Copper Cement | | | | 9,000,000 | 11,000,000 | 3,000,000 | 1,500,000 | 0 | 66.6 | 83.3 |
| Caulk's White Copper Cement | | | | 10,000,000 | 360,000 | 100 | 0 | 96.3 | 99.9 | 100 |
| Caulk's Red Copper Cement | | | | 7,000,000 | 200,000 | 0 | 0 | 97.1 | 100 | 100 |
| Ames' New Process Oxyphosphate of Copper Cement | | | | 10,000,000 | 400,000 | 0 | 0 | 96.0 | 100 | 100 |
| Decido Copper Cement | | | | 10,000,000 | 9,000,000 | 400,000 | 200,000 | 10.0 | 96.0 | 98.0 |
| Fellowship Oxyphosphate of Copper Cement | | | | 7,000,000 | 7,000,000 | 250,000 | 200,000 | 0 | 96.4 | 97.1 |

### METHODS IN USE FOR DETERMINING THE BACTERICIDAL PROPERTIES OF DENTAL CEMENTS

The experimental part of this paper clearly shows that the germicidal power of a dental cement can be determined. It is evident that a standard or uniform method of testing should be employed in work of this character, and unless the technique is given, it is obvious that such work would be of little value.

### AUTHOR'S METHOD

The following method has been developed as a result of the experimental work given in this paper:

PREPARATION OF THE CEMENT—The manufacturers of dental cements almost invariably give the instructions to be followed in the mixing of a given cement, and therefore it is only fair that these instructions

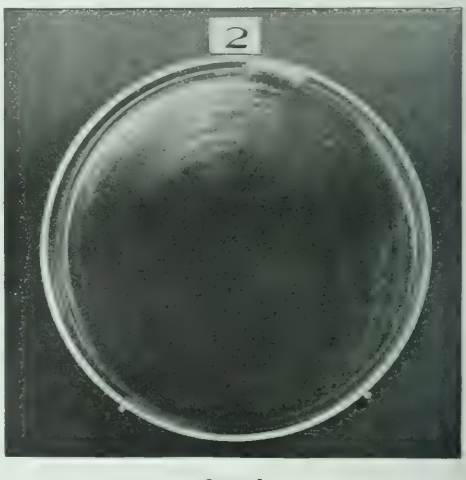
be rigidly observed. The cement is therefore mixed in accordance with the instructions, using whatever character of spatula is recommended, and the cement mass placed between glass plates, separated by glass guides so as to form a disk of the cement. It is then allowed to set for a period of 48 hours, after which it is powdered in an agate mortar and carefully bolted through No. 25 bolting silk. Metallic sieves should never be used for the purpose. A sufficient number of mixes are made to yield approximately 3 g. of powder. This powder is placed in a glass vial and is now ready for the test for germicidal efficiency.

SALIVA is obtained from one or more individuals by means of chewing paraffin. The individual is instructed to rinse the mouth with water, and then to chew a piece of paraffin, rejecting the saliva until the mass of paraffin is soft and adherent, after which the saliva is collected in a sterile glass-stoppered bottle until a sufficient quantity has been obtained. If the saliva from more than one individual is collected, it is all finally mixed and strained through several thicknesses of sterile cheese-cloth, in order to remove large particles from the saliva. Sterile glass beads are then added to the strained saliva and the bacteria separated by shaking vigorously.

TECHNIQUE—Twenty cc. of saliva are measured into a sterile 1 oz. glass-stoppered bottle and the bottle placed in a water bath maintained at a temperature of 37° C. One gram of the prepared cement powder is weighed on a clock glass, and held in readiness for its addition to the saliva. The bottle containing the saliva is then shaken for one minute, 1 cc. withdrawn and plated in the proper dilution as an individual control. One gram of powder is then added to the bottle, the bottle thoroughly shaken for one minute, and transfers made at intervals of 5 and 15 minutes, proper dilutions of these transfers being plated. During the exposure period, the bottles are shaken for a minute at intervals of 5 minutes, the final shaking of one minute being made before the final transfer. The proper dilution is then plated in nutrient agar-agar and incubated at 37° C. for 48 hours. If more than one test is to be conducted at one time, it is simply necessary to repeat the above procedure. Experience with this method has shown that dilutions of 1/10,000 cc. invariably yield plates which can be properly counted, although in some instances a dilution of 1/100,000 cc. is preferable in the case of the saliva itself.

NOTES—The object of using a hardened cement, one in which the chemical reactions involved have reached equilibrium, is that in this condition all of the cements to be compared have reached a fixed state. The results are not influenced by such factors as the setting time. A cement which could only act germicidally in a plastic condition, loses this property on setting, and would obviously be of no permanent value. Any liqud disinfectant applied to the cavity before inserting the cement would do as much work. It is the continued giving off of germicidal salts after the cement mass has set, which is the important factor. This is accomplished through the gradual yet infinitesimal solubility of the cement. A cement which is germicidal in the hardened state will certainly be germicidal in the plastic state, if not more so. From a practical standpoint, it would be impossible to determine germicidal efficiency accurately by using a cement in the plastic state. *First:* It would be almost impossible to use a fixed and uniform amount of such a plastic in all of the tests; any variation in the amount of the plastic would introduce a variable. *Second:* It would be practically impossible to control the state of the mix, since this is continually varying while in the plastic state, and therefore, another varia-

SERIES 7
Petri dish showing colonies of bacteria from 1 10,000 cc of saliva.
1022 colonies or 10,220,000 bacteria per cc.

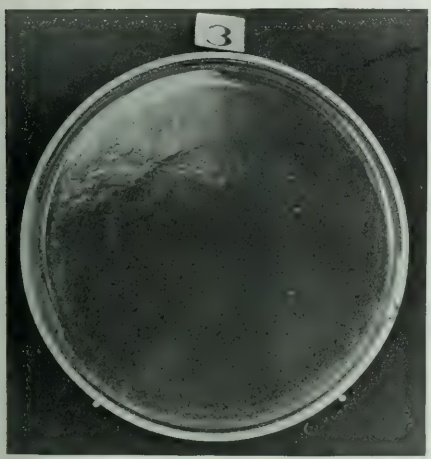



SERIES 7
Petri dish plated with 1/10,000 cc. of saliva exposed to Caulk's Crown & Bridge & Gold Inlay Cement with Copr-Zinc added.
No colonies. Germicidal efficiency = 100 per cent

ble would be introduced. It is necessary to work with fixed conditions in order to obtain comparative results.

The object of using the cement in the powdered condition in which the particles of powder are of as uniform size as it is possible to obtain them by careful sifting, is that a given weight of such a powder will represent a fairly uniform surface area of the cement. Since all of the cements in the tests are prepared in exactly the same manner, it is evident that this introduces a fixed condition.

Saliva is used in the tests, since in this manner the various mouth organisms are used instead of a pure culture of one organism. Saliva is the proper media to be employed in tests of this kind, since it represents exactly the fluid with which the cement comes in contact in the mouth. The exposure of masses of




SERIES 7

Petri dish showing colonies of bacteria from 1/10,000 cc. of saliva exposed to Caulk's Crown & Bridge & Gold Inlay Cement. 660 colonies or 6,660,000 bacteria per cc. Germicidal efficiency = 35.4 per cent

cement to ordinary culture media does not represent the conditions to be obtained in the mouth.

It will be remembered that culture media is always acid in reaction, whereas the saliva is normally slightly alkaline. Bacteriologists adjust the acidity of culture media to a reaction of "(+ 1)" a symbol used to indicate that 1 per cent of normal sodium hydroxide solution is required to bring it to the phenolphthalein neutral point. If saliva is tested in accordance with the standard method adopted by bacteriologists for ascertaining the reaction of culture media, it will be found that the saliva will not be acid to phenolphthalein, but alkaline. It is thus evident that saliva is the proper media to be used for tests of this character, since all tests where nutrient agar-agar, or nutrient bouillon is used, must of necessity fail to represent the conditions which exist in the mouth, because the reaction and chemical composition of saliva and culture media are entirely different.

The importance of shaking the saliva and the cement powder immediately before withdrawing a sample for plating will be realized when we consider that if the sample is merely allowed to settle, the cement powder, in settling, may carry down with it some living bacteria, or else the bacteria may be unequally distributed.

OTHER METHODS

The following quotations are taken from a paper by Ames,[1] entitled "Possible Sterilizing Properties of Filling Materials." Were it not for the fact that this paper has been widely circulated among the dental profession, it would hardly be necessary to discuss it at all, because of its pseudo-scientific character.

The following statements bearing directly on the subject of germicidal properties are made by Ames in this paper:

1—"The results obtained after placing hardened cement

SERIES 7

Petri dish showing colonies of bacteria from 1/10,000 cc. of saliva exposed to Smith's Copper Cement. 760 colonies or 7,600,000 bacteria per cc. Germicidal efficiency = 25.6 per cent

pellets in media are apt to be misleading, because the greater the density and integrity of the mass, the less readily will germicidal salts be given off."

2—"In a liquid medium such as beef bouillon, a tendency to form a copper salt distinctly blue is easily seen when a pellet of a high percentage copper oxid cement is placed in sterile medium, with no visible tendency, when a pellet containing, for instance, 50 per cent each of copper oxid and zinc oxid modified with smaller additions of any copper salt is so placed. In a tube of inoculated bouillon the same blue color will appear and if extreme care is exercised to avoid agitation of the fluid medium, there will be inhibition about the pellet at the bottom of the test tube. If only a low percentage of copper compound be contained in the pellet, no inhibition or color will be noticeable."

3—"Pellets of cement subjected to various media, both sterile and inoculated, give evidence of their comparative germicidal potency. When bacteria will thrive throughout an amount of liquid media containing pellets of zinc oxid cements, pellets compounded of 25 per cent to 75 per cent of copper oxid with zinc oxid, with pellets of some so-called copper cements

[1] *The Dental Review*, June, 1914.

composed of zinc oxid and a small percentage of iodid of copper, and even pellets of oxychlorid of zinc, and when the media in the test tube to the level of the top of a pellet of a high per cent copper oxid cement will remain sterile and clear excepting a copper salt color, we have evidence of comparative germicidal properties."

4—"Bouillon experiments are otherwise very unsatisfactory, as the conditions differ entirely from those we are trying to explain. Agar as media offer slightly better opportunity to obtain tooth and filling conditions. Various schemes by which pellets and agar have been inoculated and brought into contiguity, have been tried. The method most nearly duplicating the tooth and filling condition has been the filling of the smallest Wassermann test tube with melted and inoculated agar, to within about one-eighth of an inch of the top and chilling the tube and contents. While this agar is yet cold, the cement in question is inserted in a plastic state, to fill the remaining portion of the tube. A mass of cement placed upon inoculated agar in a Petri dish does not as closely duplicate the tooth and filling conditions, but the comparative inhibition is more apparent."

SERIES 7
Petri dish plated with 1/10,000 cc. of saliva exposed to Ames' New Process Oxyphosphate of Copper Cement. No colonies.
Germicidal efficiency = 100 per cent

SERIES 7
Control plate. No colonies.

Quotation 1 shows that Ames is opposed to testing a cement in the hardened state. It must, however, be remembered that a cement inserted into the tooth cavity hardens in a very short time; hence, if the mass is not germicidal in the hardened state, it will fail to accomplish the purpose for which it is used. A cement which could act germicidally only in a plastic condition would lose this property in setting, and obviously be of no permanent value, since any disinfectant applied to the cavity before inserting the cement will do as much work. The cement remains in the plastic condition in the tooth cavity for a very short time, whereas it remains there in a hardened condition for a period of years, and it follows that the proper condition in which the cement should be tested is in the hardened state, and not in the plastic form, since the dentist does not rely upon the initial sterilization secured by inserting the plastic mass into the cavity, but upon the permanent sterilization secured by the gradual, although infinitesimal solubility of the hardened cement mass.

The first part of Quotation 2 is intended to show that in the nutrient beef bouillon, hardened pellets of cement composed of a high percentage of copper oxide, when placed in the sterile bouillon, will form a distinctly blue color in the bouillon, due to the solution of copper salts, whereas a pellet composed of 50 per cent each of copper oxide and zinc oxide modified with smaller additions of any copper salt, fail to show this blue color. This is simply a function of the solubility of the cement, and if anything, it merely shows that a high percentage of copper oxide cement is less resistant, or more soluble in nutrient bouillon, than one composed of a smaller percentage of copper oxide, and admixed with zinc oxide. The second part of this quotation is intended to show that, owing to the presence of this blue copper salt, there will be inhibition of bacterial growth about the pellet at the bottom of the test tube, but that with a low percentage of a copper compound, no inhibition or color will be noticeable. It would certainly be necessary to exercise extreme care to avoid agitation of the nutrient bouillon, if this inhibition is to be observed, but the important point is that even if it were possible to make this observation, the test does not show the germicidal efficiency of the material. Again, the chemical composition of nutrient bouillon is entirely different from that of the saliva, so that a test of this character can have absolutely no value.

Quotation 3 infers that the comparative germicidal potency of various copper cements can be determined by placing hardened pellets of the cement mass in nutrient bouillon by observing whether bacteria will thrive throughout the liquid media. It is inferred in this quotation that those copper cements composed of copper oxide and zinc oxide, and also those composed

of zinc oxide with a small amount of cuprous iodide, and even oxychloride of zinc cements, show no germicidal power, and that only those cements which contain a high percentage of copper oxide have germicidal power, because the media "will remain sterile and clear, excepting a copper salt color." The experimental part of this paper clearly shows how absurd this statement is, since it is shown conclusively that those materials which Ames infers to have no germicidal power, on the contrary, have very high germicidal efficiency—as great as can be obtained with cements composed largely of copper oxide. Assuming for the moment that the statement is based upon accurate observation, it is evident that the test is of a qualitative character, giving no information whatever as to germicidal efficiency.

Quotation 4 also fails to present a method which would be of any value in determining germicidal

In explaining these plates, Ames makes the following statement:

"In applying these cements in the fresh state, to inoculated agar, there is one case, No. 1, the typical copper coloration with marked inhibition of bacterial reproduction, and in the other, No. 3, no coloration and inhibition, only to the extent that would be expected from the corresponding zinc salts, which we know from clinical observation is so slight as to be negligible. "

No. 1 refers to a copper cement composed largely of copper oxide, and No. 3 refers to a white copper cement. It will be noted that Ames claims that the white copper cement gave "inhibition only to the extent that would be expected from the corresponding zinc salts." The experimental part of this paper shows that there is a vast difference between a white copper cement and one which is free from copper, and the very fact that Ames is forced to use the expression, "only to the extent that would be

SERIES 8

SERIES 8

efficiency. The assumption that the filling of the smallest Wassermann test tube with melted and inoculated agar will most nearly duplicate the tooth and the filling condition, is certainly not impressive, mainly on account of the fact that agar is entirely different in physical and chemical character from the tooth substance, and the mere crowding of a mass of cement into a space approximating the size of a tooth cavity does not duplicate the tooth and the filling conditions. Here again the tests used are based upon the observation of comparative inhibition of bacterial growth, and not upon the determination of the percentage of organisms destroyed in exposure, and for this reason the tests fail to give any information on the germicidal efficiency of the materials.

In addition to the above statements, Ames shows two plates in which were embedded freshly mixed cement upon agar inoculated with staphylococcus.

expected from the corresponding zinc salts," shows that the test is of purely qualitative character and gives no information as to germicidal efficiency. There is a vast difference between an ordinary oxyphosphate of zinc cement and an oxyphosphate of zinc cement containing cuprous iodide. What does "inhibition only to the extent to be expected from corresponding zinc salts" mean in the absence of a definite statement as to what the zinc salts will accomplish? Absolutely nothing! We must have some definite standard of comparison.

Many ambiguous statements of similar character appear throughout this paper of Ames, and were it not for the wide circulation which it has received among the dental profession, it would not be given any consideration in connection with this paper.

SERIES 8—Plates 1 and 2 have been prepared in this laboratory to show the results which may be ex-

pected from the use of a plastic or solid mass of cement embedded in inoculated agar in order to show the germicidal properties.[1]

Plate 1 is a photograph of a Petri dish containing agar inoculated with saliva upon which two mixes of plastic masses of cement were placed. The plate was incubated for 48 hours. The upper mix of cement is Caulk's Crown & Bridge & Gold Inlay Cement and the lower is Caulk's Crown & Bridge & Gold Inlay Cement and Caulk's Copr-Zinc (four parts of the former to one part of the latter, by weight). Colonies of bacteria are seen over the entire plate. There is a sterile area around each cement mix. the actual measurement on the original plate showing sterility within the radius of from 6 to 8 mm. in both cases. It would have been impossible to specify the comparative germicidal properties of these two cements from this test, since it failed to show any marked difference in the germicidal power. Reference to the photographs shown in Series 7 of the experimental part of this paper plainly shows that the same materials vary widely in germicidal power.

Plate 2 is a photograph of a Petri dish containing agar inoculated with saliva into which two solid cylinders of cement were inserted. The photograph shows the bacterial colonies to approach the cement mass much more closely than in the case of the plastic mass. This is exactly what one would expect, owing to the insolubility of the set cement as compared with the solubility of the unset or plastic mass. The upper mix of cement in this plate is Caulk's Crown & Bridge & Gold Inlay Cement, and the lower is Caulk's Crown & Bridge & Gold Inlay Cement and Caulk's Copr-Zinc (four parts of the former to one part of the latter, by weight). Here again it would have been impossible to state whether one cement was more germicidal than the other, since reference to the photographs shown in Series 7 of the experimental part of this paper plainly shows these two materials to vary widely in germicidal power.

SUMMARY

Dental cements known as "copper cements" vary widely in chemical composition. The several types sold to the dental profession are at present described almost entirely by the color of the powder, and include red, white, black, and varicolored cements. The color of these cements is largely due to the compounds of copper used in their production, although pigments are used to improve the color. Such additions may be considered to be legitimate if the cement shows the requisite germicidal power.

Cuprous oxide, cupric oxide, and zinc oxide have marked germicidal properties. The addition of cuprous oxide, cupric phosphate, and cuprous iodide, to zinc oxide, enhances the bactericidal properties of the zinc oxide.

The addition of varying amounts of cuprous iodide to a "copper-free" dental cement shows that the germicidal efficiency is increased in proportion to the quantity added. The addition of 1 per cent of cuprous iodide to a dental cement increases considerably the germicidal efficiency.

Commercial "copper cements" show wide differences in germicidal efficiency, the color of the cement having no relation to its bactericidal properties.

Tests for germicidal properties of dental cements in "plastic" or "set" condition are unsatisfactory if such mixes are placed in inoculated bouillon or agar-agar, owing to the difference in chemical composition of the nutrient culture media and the saliva. Visual tests for inhibition of bacterial growth are purely qualitative tests and fail to demonstrate the comparative germicidal efficiency of these materials. The comparative germicidal efficiency of "copper cements" can be ascertained only by methods which determine the number of living organisms killed on exposure to the cement under fixed conditions.

Much misleading information has been circulated in regard to the germicidal properties of "copper cements." This has been based upon ignorance of the manufacturer, or upon pseudo-scientific or inconclusive tests.

CONCLUSIONS

The germicidal efficiency of a dental cement is merely one of the properties which are of importance. Many other physical properties such as resistance to saliva, hardness, crushing strength, constancy of volume, etc., are also of importance. The relation of the germicidal efficiency to these other properties is being investigated in this laboratory, and the results will be published in future papers.

Many of the bacteriological tests contained in this paper were conducted while the author was still associated with the Lederle Laboratories, as Assistant Director of the Department of Chemistry. The author desires to acknowledge his indebtedness to Dr. H. D. Pease, Director of the Department of Bacteriology of the Lederle Laboratories, and to his assistants, for having conducted many of the tests.

LABORATORIES OF THE L. D. CAULK COMPANY
MILFORD, DELAWARE

[1] This method is in quite common use for testing dental cements.

## DRYING PROPERTIES OF LINSEED OIL TREATED WITH COBALT, LEAD AND MANGANESE ELAEOSTEARATES[1]

By Louis E Wise and Robert A. Duncan

Received December 15, 1914

Since the manganese, lead and cobalt linoleates have been successfully used in the preparation of siccatives in the manufacture of boiled oil, it seemed of interest to attempt the preparation of the corresponding salts of $\alpha$-elaeostearic acid, a probable isomer of linolic acid,[2] and to study the drying properties of linseed oil which had been treated with these soaps.

$\alpha$-Elaeostearic acid, which occurs as the triglyceride in Chinese wood oil, gives the oil its characteristic properties of gradually crystallizing on exposure to light[3] and of gelatinizing when heated to about 200° C. The free acid is an unstable, crystalline compound,

[1] This is a brief abstract of the thesis submitted by Robert A. Duncan in partial fulfilment of the requirements for the degree of M.A. in the graduate school of the University of Missouri.

[2] Kametaka, *J. Chem. Soc.*, **88**, 1042.

[3] Cf. Ware and Schumann, THIS JOURNAL, **6** (1914), 806.

m. p. about 48° C., resinifying rapidly in air and changing readily into its $\beta$-isomer, m. p. 71°, when its ethereal or alcoholic solutions are exposed to light. Since some of the derivatives of elaeostearic acid also readily undergo change on exposure to light and air, due precautions were taken in the preparation of the metallic elaeostearates. One hundred grams of commercial Chinese wood oil (with a saponification number of 190) were heated with about 100 cc. of 20 per cent alcoholic KOH for $^1/_2$ hour, in a darkened flask under a reflux condenser, a slow stream of hydrogen being conducted through the reaction mixture during the saponification. On cooling, the potassium soap[1] separated in the form of radiating clusters of white needles. The product was recrystallized five times from 90 per cent alcohol, and dried in a darkened Drexel bottle at 100° C., in a current of dry hydrogen, or *in vacuo*. All filtrations were made by suction and solutions were never exposed to direct sunlight. The dried, powdered soap, when decomposed by acids yielded $\alpha$-elaeostearic acid (melting at 44° C.). In spite of all precautions taken the potassium soap was never obtained in absolutely pure state.

The lead elaeostearate was prepared by treating a clear, aqueous solution of the potassium soap with an aqueous lead acetate solution, rapidly filtering the resulting insoluble precipitate, washing thoroughly with water, and drying the product *in vacuo*, over fused $CaCl_2$. The manganous and cobaltous soaps were prepared by very similar methods using $MnCl_2$ and, $CoCl_2$, respectively.

The metallic soaps all undergo marked decomposition at 50–60° C. and resinify rapidly on exposure to air. The dry lead soap is a white powder,[2] containing 28 per cent of lead whereas the theoretical percentage lead in lead elaeostearate is 27.05. The manganese soap is also a nearly white powder containing 9.96 per cent manganese, the calculated percentage in manganous elaeostearate being 8.97 per cent. The cobalt soap, when first precipitated from its solution, formed a pale pink curd which rapidly darkened to a rich purple. The dried soap, which was apparently not homogeneous, contained 9.05 per cent cobalt, whereas the theory for cobaltous elaeostearate requires 9.56 per cent. All of these heavy metal soaps, when dissolved in linseed oil, cause a marked increase in the rate of drying of the oil.

In order to obtain comparative data in our drying tests, four 10-gram samples of a good commercial linseed oil were placed in test tubes and treated as indicated below:

| Sample | Mixed with |
|---|---|
| A | 0.2957 g. manganese elaeostearate |
| B | 0.3695 g. lead elaeostearate |
| C | 0.2990 g. cobalt elaeostearate |
| D | 0.1072 g. litharge |

Both *B* and *D* contained 0.1 g. (or 1 per cent) lead whereas *A* contained 0.9265 g. manganese and *C* contained 0.0287 g. cobalt. The mixtures contained *equivalent* amounts of the "drier." since in each case the ratio *equivalent weight of metal : weight of metal in weight of drier taken* was constant. These mixtures together with a control *E* (which contained simply 10 g. of linseed oil) were then heated for 6 hours in an electric oven at 350–375° F., and shaken at intervals during the period of heating. The oils were allowed to cool and settle, and were later used in the drying tests.

In carrying out these tests, glass plates of uniform size weighing about 25 g. each were used. An exact area of 42.9 sq. cm. was marked off on each plate by means of a glass cutter and the plates were carefully cleansed, dried and weighed to the nearest 0.1 milligram. Thin films of oil taken from Samples *A*, *B*, *C*, *D* and *E* were then spread as uniformly and as rapidly as possible over the exact areas outlined on the plates. The latter were again weighed without delay and laid horizontally in a ventilated, dust-free glass cabinet, which was exposed to diffused daylight. At frequent intervals (every few hours during the first few days) the plates were accurately and rapidly weighed and replaced in the cabinet, the room temperature at the time of weighing being invariably recorded. The 5 drying tests, which were run in duplicate, extended over a period of nearly 450 hours.

Since, in these tests, the oil films were by no means identical in thickness and in order to assure ourselves that these differences did not materially affect the rate of drying or gain in weight,[1] we undertook a similar series of drying tests (using a boiled oil containing 1 per cent lead, as litharge) in which oil films covered identical areas but varied considerably in thickness. Our results, Table I, indicate that during the drying process the percentage gain in weight at the end of definite time intervals, is practically independent of the film thickness.

TABLE I—EFFECT OF FILM THICKNESS ON RATE OF DRYING

| Time of drying Hours | Temp. at time of weighing ° C. | Weight in Grams of Film I | II | III | Per Cent Gain in Weight of Film I | II | III |
|---|---|---|---|---|---|---|---|
| 0 | 23 | 0.0221 | 0.0326 | 0.0485 | 0.0 | 0.0 | 0.0 |
| 1.5 | 24 | 0.0225 | 0.0333 | 0.0495 | 1.8 | 2.1 | 2.0 |
| 5.5 | 21.5 | 0.0231 | 0.0344 | 0.0510 | 4.6 | 5.4 | 5.0 |
| 8.5 | 21 | 0.0240 | 0.0352 | 0.0522 | 8.7 | 7.8 | 7.5 |
| 11.5 | 21 | 0.0247 | 0.0364 | 0.0541 | 11.9 | 11.4 | 11.3 |
| 23 | 23 | 0.0255 | 0.0379 | 0.0562 | 15.6 | 15.9 | 15.8 |
| 25 | 27 | 0.0256 | 0.0377 | 0.0562 | 16.1 | 15.3 | 15.8 |
| 30 | 23 | 0.0254 | 0.0376 | 0.0559 | 15.2 | 15.0 | 15.2 |
| 35.5 | 19 | 0.0251 | 0.0374 | 0.0555 | 13.9 | 14.4 | 14.4 |
| 47 | 22 | 0.0250 | 0.0373 | 0.0554 | 13.5 | 14.1 | 14.2 |
| 50 | 22 | 0.0253 | 0.0374 | 0.0556 | 14.8 | 14.4 | 14.6 |
| 59 | 25 | 0.0253 | 0.0376 | 0.0557 | 14.8 | 15.0 | 14.8 |
| 70.5 | 25 | 0.0251 | 0.0372 | 0.0553 | 13.9 | 13.8 | 14.0 |
| 79 | 25 | 0.0251 | 0.0372 | 0.0553 | 13.9 | 13.8 | 14.0 |
| 84 | 25 | 0.0250 | 0.0372 | 0.0553 | 13.5 | 13.8 | 14.0 |
| 95.5 | 27 | 0.0251 | 0.0370 | 0.0553 | 13.9 | 13.2 | 14.0 |
| 108 | 18(a) | 0.0241 | 0.0361 | 0.0543 | 9.3 | 10.5 | 11.8 |
| 122 | 20 | 0.0243 | 0.0364 | 0.0544 | 10.2 | 11.4 | 12.0 |
| 132.5 | 20 | 0.0245 | 0.0364 | 0.0545 | 11.1 | 11.4 | 12.2 |
| 147.5 | 24 | 0.0244 | 0.0364 | 0.0545 | 10.7 | 11.4 | 12.2 |
| 180 | 18 | 0.0244 | 0.0364 | 0.0545 | 10.7 | 11.4 | 12.2 |
| 250 | 22 | 0.0245 | 0.0362 | 0.0541 | 11.1 | 10.8 | 11.4 |

(a) At the end of 108 hours, the sudden decrease in weight of the oil films may have been influenced by the drop in temperature.

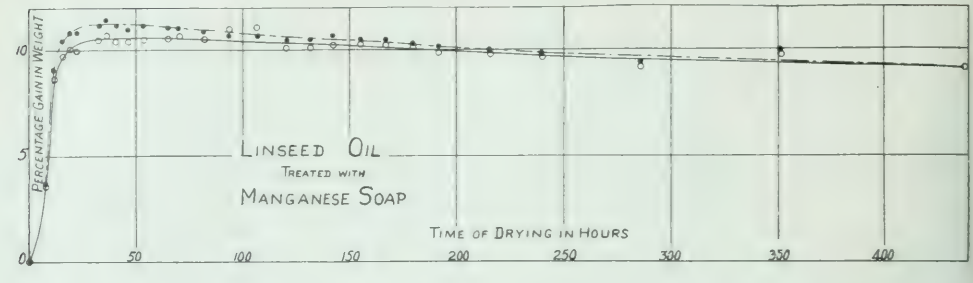
In the accompanying graphs the abscissas represent the hours of drying, while the ordinates represent the percentage increase (or decrease) in the weight of oil film. In all cases smooth curves have been drawn, the two curves of each set representing the results of duplicate drying tests. In the case of untreated oil, these duplicates do not check closely, whereas in the other cases the curves are very nearly coincident. Since Gardner[2] has shown that a drying oil film loses large

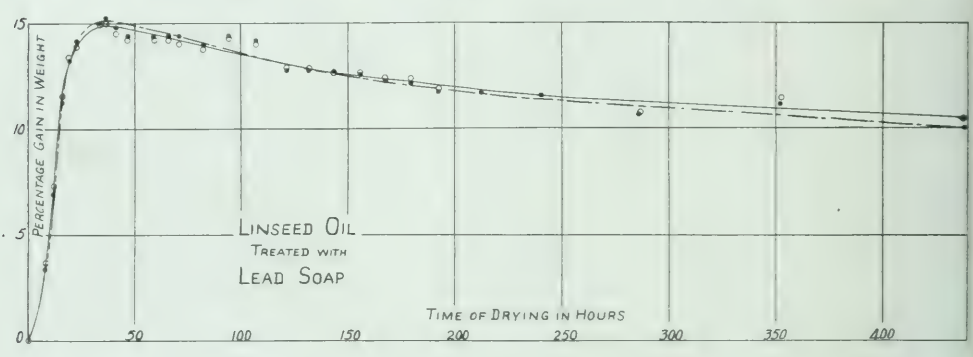
[1] Cf. Cloez, *Compt. rend.*, **83**, 934.

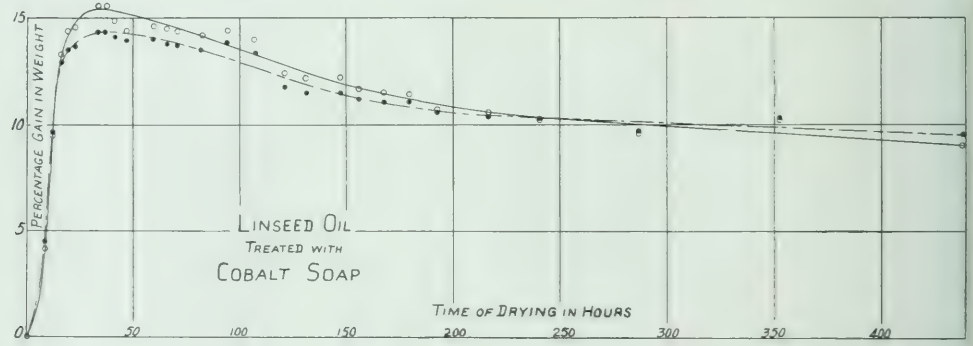
[2] Cf. Cloez, *Loc. cit.*, who prepared this soap. His analysis showed 27.74 per cent lead.

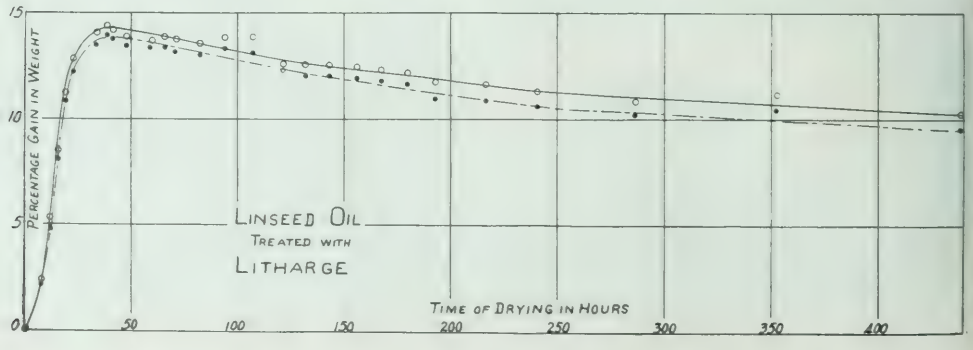
[1] This had been previously indicated by Lippert, *Z. angew. Chem.*, **1898**, p. 42.

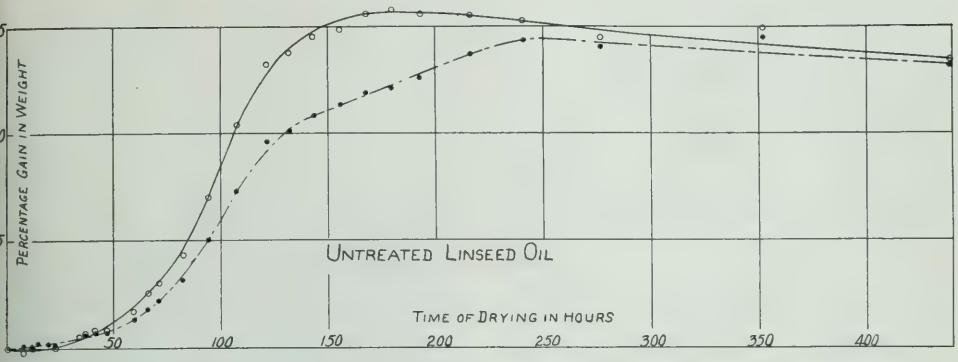
[2] THIS JOURNAL, **6**, 91.


PERCENTAGE GAIN IN WEIGHT
0
5
10
LINSEED OIL
TREATED WITH
MANGANESE SOAP
TIME OF DRYING IN HOURS
50
100
150
200
250
300
350
400


PERCENTAGE GAIN IN WEIGHT
0
5
10
15
LINSEED OIL
TREATED WITH
LEAD SOAP
TIME OF DRYING IN HOURS
50
100
150
200
250
300
350
400


PERCENTAGE GAIN IN WEIGHT
0
5
10
15
LINSEED OIL
TREATED WITH
COBALT SOAP
TIME OF DRYING IN HOURS
50
100
150
200
250
300
350
400


PERCENTAGE GAIN IN WEIGHT
0
5
10
15
LINSEED OIL
TREATED WITH
LITHARGE
TIME OF DRYING IN HOURS
50
100
150
200
250
300
350
400




amounts of carbon dioxide and traces of organic compounds,[1] soon after exposure to air the weight[2] of the film at any stage of the drying process is dependent on the resultant of the gain due to oxygen absorption and these losses. The drying process is a continuous one and there can be no definite point on any of the curves at which this process may be termed *complete*. We are, however, inclined to agree with Lippert that the highest point on the curve may be advantageously used in judging the relative rates of drying. When this maximum is reached the film is tough and elastic, the surface may be termed "dry" and we are probably justified in saying that the most rapidly drying oil film reaches its maximum weight in the shortest space of time.

The curves indicate clearly that the addition of the three elaeostearates greatly increases the rate of drying of linseed oil. The three sets of curves are quite similar and indicate very similar drying properties. The film containing the manganous soap probably dries most rapidly.[3] Its maximum gain in weight is the lowest of the series. The litharge and lead elaeostearate drying curves resemble each other very closely although the latter shows a somewhat greater gain during the first stage of the drying process. The general similarity of these curves leads us to the conclusion that the drying action depended solely on the presence of the lead, and was quite independent of the non-metallic radical in the drier. The cobalt soap-oil film has drying properties similar to those of the oil film treated with lead soap, but loses more rapidly than the latter after the maximum gain in weight has been reached.

In conclusion we beg to thank the Standard Varnish Works of Staten Island, N. Y., for supplying the Chinese wood oil used in this work.

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[1] Klein has very recently shown that Gardner's results do not prove the presence of carbon monoxide in the vapors given off by drying linseed oil films. Cf. THIS JOURNAL, **7**, 99.

[2] Cf. Sabin, *Ibid.*, **3**, 84

[3] This point is more clearly indicated in an unpublished set of curves representing the results of drying tests with the same linseed oil treated with these soaps at 250–70°. The curves are somewhat steeper than those given herein.

## VARIATIONS OF THE PHYSICAL CHARACTERISTICS OF A PETROLEUM RESIDUUM WITH INCREASING PERCENTAGES OF GRAHAMITE

By H. ROSSBACHER

Received November 23, 1914

In the technology of asphaltic materials the fluxing of asphaltites such as Grahamite and Gilsonite in asphaltic or semi-asphaltic petroleum residuum plays a very important rôle. It is well known that the effect of increasing the proportion of the asphaltite is to raise the melting point and lower the penetration of the product. The object of this paper is to present a graphic representation of the alteration of the physical characteristics of a sample of Mexican residuum on fluxing with it increasing percentages of Grahamite.

### DESCRIPTION OF EXPERIMENTS

Typical samples of Mexican residuum and Grahamite were taken (Table I); the flux was weighed into a copper beaker of about 250 cc. capacity and heated to 475–485° F. and the finely powdered Grahamite was added with stirring. Stirring and heating at the above temperatures were continued until the solution was complete. About an hour was the average time required, varying, of course, with the percentage of asphaltite to be fluxed. Percentages of Grahamite from 0 to 30 were used (Table II), the coarseness of the product in the latter case indicating that the limit of solubility was being approached.

TABLE I—MATERIALS USED IN EXPERIMENTS

| MEXICAN RESIDUUM | | GRAHAMITE | |
|---|---|---|---|
| Sp. gr. 77° F. | 1.0039 | Sp. gr. 77° F. | 1.1822 |
| Shutte 77° F. | 78″ | | Per cent |
| $CS_2$ insoluble | None | Fixed carbon | 53.77 |
| $CCl_4$ insoluble | 0.31 per cent | Ash | 1.17 |
| 88° Bé. naphtha insoluble | 21.50 per cent | $CS_2$ insoluble (hot) | 0.83 |
| Flash point | 457° F. | $CCl_4$ insoluble cold | 95.65 |
| Fire point | 505° F. | $CCl_4$ insoluble hot | 74.75 |
| | | 88° Bé. naphtha insoluble cold | 99.46 |
| Evaporation loss: | | 88° Bé. naphtha insoluble hot | 97.12 |
| 20 hours at 485° F. | 13.4 per cent | | |

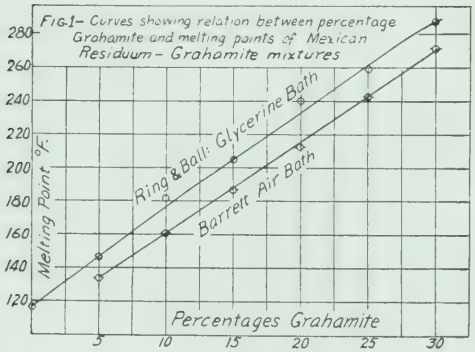
The "Ring and Ball" melting points noted in Table II and Fig. I were determined by the method developed in the Chicago laboratory of the Barrett Manufacturing Company. The melted sample is poured into a brass cylinder $^5/_8$ inch high, exterior diameter $^{13}/_{16}$ in., interior diameter $^3/_4$ in.: copper wire is soldered to the cylinder for suspending it in the bath. When the sample has cooled to room temperature it is cut off level with the top of the cylinder and a brass ball

TABLE II—PRODUCTS OBTAINED BY FLUXING GRAHAMITE WITH MEXICAN RESIDUUM

| MATERIALS AND MIXTURES | | | PER CENT | | MELTING POINT °F. | | | CHARACTER OF PRODUCT |
|---|---|---|---|---|---|---|---|---|
| | | | Fixed Carbon | Ash | Ring and Ball Water | Ring and Ball Glycerine | Barrett Air | |
| M | Mexican residuum | | 17.26 | tr. | 104 7 | 117.3 | Too soft | Semi-fluid |
| R | 485° F. 20 hr. residue | | 21.22 | 0.04 | Too hard | 191 5 | 179 0 | Tough |
| Per cent % loss on M. Gr. fluxing | | | | | | | | |
| A | 95 | 5 .. | ... | . | 130.3 | 145.4 | 133.0 | Soft Homogeneous |
| B | 90 | 10 .. | 20.34 | 0.08 | | 181.4 | 162.0 | Homogeneous |
| C | 85 | 15 2.15 | ... | .. | | 212.0 | 187.0 | Homogeneous |
| D | 80 | 20 1.90 | 22.72 | 0.24 | Too hard | 238.3 | 229.0 | Homogeneous |
| E | 75 | 25 1.15 | ... | .. | | 257.0 | 241.0 | Homogeneous |
| F | 70 | 30 1.25 | 26.62 | 0.24 | | 288.0 | 269.0 | Fairly homogeneous. Brittle |

$^3/_8$ in. in diameter and weighing $3^1/_2$ g. is placed on top of the sample which is then suspended in a 600 cc. beaker containing 400 cc. of glycerine, the bottom of the cylinder being 1 in. from the bottom of the beaker. A thermometer is suspended in the bath with the bottom of the bulb flush with the bottom of the cylinder. The bath is heated at the rate of 7° C. per minute with constant stirring. The temperature registered at the time the sample touches the bottom of the beaker is recorded as the melting point of the material. The rate of heating exercises a marked effect on the melting point and must be watched closely to obtain concordant results.

The reflux solubilities and the air melting points were made as described by S. R. Church.[1] The various other tests noted were made according to the methods



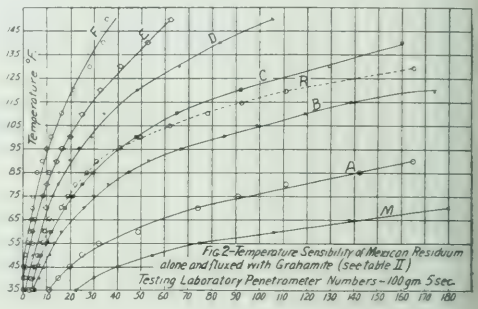

recommended by Prevost Hubbard[2] and by Clifford Richardson.[3]

## CONCLUSIONS

I—Fig. 1 shows a fairly regular increase of melting points of the fluxed products with increasing percentages of the asphaltite.

II—It is of interest to note in Fig. 2, that the temperature-penetration curve of the residue from a 485° F.–20 hour evaporation test of the original residuum follows very closely the curve given by the sample containing 15 per cent of the asphaltite.

III—The writer believes that too much emphasis is often placed on the melting point of an asphaltic material or on the penetration at one specified temperature. The flattening out of the temperature-penetration curves far below the so-called melting points emphasizes this point. A series of determinations plotted as in Fig. 2 may be of assistance in many




cases in predetermining and comparing the values of new "mixes."

NOTE—The writer is indebted to Mr. S. Drucker for the preparation of the graphs which accompany this article.

TECHNICAL DEPARTMENT, MORRIS AND COMPANY
UNION STOCK YARDS, CHICAGO

[1] THIS JOURNAL, 3 (1911), 227; 5 (1913), 195.
[2] "Dust Preventives and Road Binders."
[3] "The Modern Asphalt Pavement."

## INVESTIGATIONS ON THE OIL OF EUCALYPTUS GLOBULUS OF CALIFORNIA

BY CHARLES E. BURKE AND CHARLES C. SCALIONE

Received December 21, 1914

For many years considerable interest has been taken in California, in the *Eucalyptus globulus* (Blue gum), a tree which, while a native of Australia, has been transplanted and thrives well on many parts of the Pacific Coast. The fact that the tree grows very fast, and yields a hard wood makes it a tree particularly desirable in these localities which are almost destitute of hard woods.

Many difficulties have been met in seasoning the wood which has a great tendency to warp and check, but these have been largely overcome by experienced lumbermen and it is now easily possible with certain precautions to prepare from the Eucalyptus a good clean lumber, which for hardness and tensile strength compares very favorably with oak or hickory.

In Australia one of the valuable products of the tree has been the oil which is obtained by the distillation of the leaves; this oil finds extensive use in the arts and in medicine and is imported in large quantities annually from Australia into the United States. The United States Pharmacopeia describes the oil as:

"A colorless or pale yellow oil, having a characteristic or aromatic and somewhat camphoraceous odor, and a pungent, spicy, and cooling taste. Specific gravity, 0.905 to 0.925 at 25° C. Soluble in all proportions in alcohol; also soluble in three volumes of 70 per cent alcohol. Its alcoholic solution should be neutral to litmus. It is dextrogyrate, the angle of rotation being not more than +10° in a 100 mm. tube.

at a temperature of 25° C. If 2 cc. of the oil be mixed with 4 cc. of glacial acetic acid and 3 cc. of a saturated solution of sodium nitrite be gradually added, the mixture when gently stirred should not form crystals of phellandrene nitrite. It should become semi-solid on being stirred, when cold, with a third or a half of its volume of phosphoric acid of commerce of specific gravity 1.750 (presence of a due proportion of cineol)."

FIG. I—EUCALYPTUS GROVE ON THE CAMPUS OF THE UNIVERSITY OF CALIFORNIA. TREES APPROXIMATELY THIRTY YEARS OLD

The Australian oil fulfils these specifications but the Californian oil does not, and therefore the latter has not been utilized to any great extent. It is this fact that has led us to an examination of the Californian oil, to determine whether there is any difference in the crude oil from the same species of Eucalyptus grown in Australia and California, or whether the difference is simply in the method of refining.

Baker and Smith[1] after a very extensive research on the Eucalyptus oils of Australia state that "the constituents of the oil of *Eucalyptus globulus* are practically constant wherever the tree is grown; a sample of oil distilled from trees in New South Wales differed in no respect from the product of trees grown in Tasmania or Victoria. The amounts of the constituents may vary but the constituents found are always the same." Our work on the Californian oil has fully corroborated this statement, since we have found exactly the same constituents in the Californian oil that Baker and Smith found in the Australian oils. The amounts of the constituents vary so greatly, however, as to give the crude oils entirely different properties. This may be seen from the following comparison of the Australian oil and Californian oil.

| | CALIFORNIAN OIL | AUSTRALIAN[1] OIL |
|---|---|---|
| $D_{20}$ | 0.9052 | 0.913 |
| $[\alpha]_D^{20}$ | 14° 42 | 9° 2 |
| $N_D^{20}$ | 1.46053 | ? |

| | Insoluble in 70 per cent alcohol | Soluble in 1.5 volumes of 70 per cent alcohol |
|---|---|---|
| Free acid | 0.73 | 1.1 |
| Saponification No. | 2.5 | 1.0 |
| Acetylation No. | 56.0 | ? |

These data were obtained from leaves of the *Eucalyptus globulus* gathered on the University Campus and distilled with steam at a pressure of four pounds; these leaves gave a total yield of oil corresponding to 0.8 per cent of the total weight of the green leaves. Baker and Smith have obtained yields as high as 0.918 per cent; this of course varies somewhat with the season of the year. For the rest of our work, since we wished to make our analysis as valuable as possible commercially, we have used oil obtained from a commercial still in North Berkeley. This oil was obtained from a grove of almost pure Globulus but containing a sprinkling of other varieties and would more fairly represent the average Californian oil than an absolutely pure Globulus oil.

This oil was fractionally distilled and the following table shows the fractions obtained with the constants of each.

| Fraction No. | Temperature ° C. | Percentage oil in each | $D_{20}$ | $N_D^{20}$ | $[\alpha]_D^{20}$ |
|---|---|---|---|---|---|
| 1 | 85–100 | 3.1 | 0.866 | 1.4485 | 15.25 |
| 2 | 100–155 | 0.8 | 0.885 | 1.4606 | 20.11 |
| 3 | 155–165 | 6.5 | 0.887 | 1.4635 | 19.17 |
| 4 | 165–170 | 35.6 | 0.896 | 1.4635 | 16.00 |
| 5 | 170–180 | 30.0 | 0.909 | 1.4645 | 8.80 |
| 6 | 180–190 | 11.1 | 0.921 | 1.4675 | 3.81 |
| 7 | 190 up | 12.5 | 0.980 | .. | ... |

From the curves in Fig. II it will be seen that there are at least four constituents in the oil: the first distils between 85° and 155°, the second between 155° and 170°, the third between 170 and 180, and the fourth above 180.

BUTYRIC, ISOVALERIC, AND CAPRONIC ALDEHYDES—In the fraction boiling below 155° C. the strong irritating odor suggested the presence of aldehydes; on redistillation this part was easily divided into three fractions, the first distilling at 75–85°, the second at 85–100°, and the third at 100–140°. The first of these fractions readily formed an addition product with ammonia which after recrystallization from alcohol melted at 26–27° C. The second one also formed an

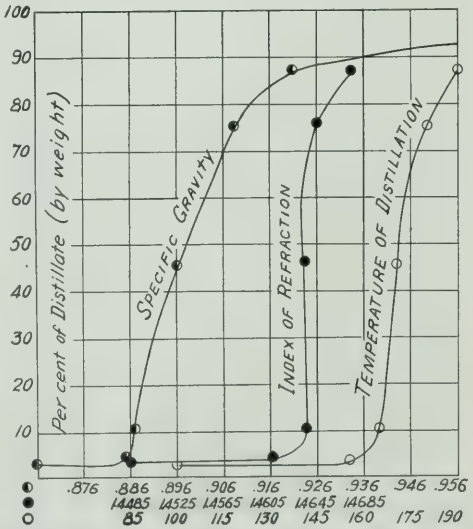



FIG. II—BOILING POINT, SPECIFIC GRAVITY AND INDEX OF REFRACTION CURVES FOR EUCALYPTUS OIL[1]

[1] "A Research on Eucalyptus with Particular Reference to Their Essential Oils," by Baker and Smith. Published by the Australian Government.

[1] See Burke and Scalione, THIS JOURNAL, 6 (1914), 804.

addition product with ammonia which after recrystallization melted at 52–53°. The first of these fractions was undoubtedly butyric aldehyde, and the second isovaleric aldehyde since the ammonia addition products of these two aldehydes melt at 29°, and 56°, respectively. The third fraction formed no addition products with ammonia but the boiling point and other physical properties indicated capronic aldehyde. A quantitative analysis of the fresh oil, by the sodium sulfite method of Sadtler and Burgess,[1] showed the total aldehyde content of the oil to be 6 per cent of the total volume.

PINENE—After the removal of the aldehydes the remainder of fractions 1, 2 and 3 was combined with fraction 4 and redistilled. The fraction distilling at 156–157° constituted approximately 20 per cent of the original volume of the oil and the following constants would seem to indicate that it was practically pure pinene.

| | Distillate 156–157° C. | PURE PINENE |
|---|---|---|
| $D_{20}$ | 0.8758 | 0.8767 |
| $[\alpha]_D^{20}$ | 34° | 20–49° |
| Boiling point | 156–157° | 156–157° |
| Melting point nitrosochloride | 102–103° | 102–103° |

A quantitative analysis for pinene was also made on the crude oil as follows: a weighed portion of the oil was fractionated and the fraction boiling at 130–176° retained; 5 cc. of the oil in this fraction were placed in a cassia flask and 50 per cent resorcinol solution was added to take up all the cineol and traces of aldehydes present; after the solution became clear the unabsorbed oil amounted to 21–22 per cent of the whole. This oil had the same properties as the pinene above which had been purified by distillation.

CINEOL—The remainder of the oil from the first fractions was added to fractions 5 and 6, and redistilled; after several fractionations a fraction was obtained which boiled at 176°. A comparison of the constants of this fraction with those of pure cineol shows that this fraction was cineol.

| | Distillate 176–177° | PURE CINEOL |
|---|---|---|
| Boiling point | 176–177° | 176 |
| $D_{20}$ | 0.930 | 0.9267 |
| $N_D^{20}$ | 1.457 | 1.4559 |
| Melting point iodol (after recrystallization) | 111° | 112° |

The iodol formed from this distillate after recrystallization melted at 111°. Cineol iodol melts at 112°. A quantitative analysis by the U. S. P. phosphoric acid method gave 47 per cent cineol by volume.

EUDESMOL AND GLOBUOL—The fraction boiling at 190° and up was placed in a shallow dish and allowed to stand for several days until crystals began to separate; these were removed, dried on a porcelain plate, dissolved in alcohol and after adding enough water to produce turbidity allowed to evaporate spontaneously until crystals separated. After another recrystallization soft white flaky crystals were obtained which gave the following constants:

B. p. = 255° M. p. = 80° $D^{20}$ = 0.988

$[\alpha]_D^{20}$ = + 31.21° in 12 per cent chloroform solution.

Assuming the formula proposed by Semmler and Tobias,[1] namely, a bicyclic alcohol with an unsaturated grouping, the theoretical molecular index of refraction would be 68.069; the observed molecular index of refraction was 68.001. The acetate prepared by a mixture of acetic anhydride and sodium acetate gave constants identical with those obtained by Tobias and Semmler. This and the general properties of the body seemed to indicate that we were dealing with an alcohol rather than an oxide as suggested by Baker and Smith.

In the higher boiling portions a body corresponding to globuol was separated. Semmler and Tobias consider that this body bears the same relation to eudesmol that borneol bears to isoborneol.

Considering the formulas of the two alcohols to be $C_{15}H_{26}O$ the acetylation number would indicate that the alcohols form 23.22 per cent of the total weight of the oil.

The complete analysis shows that the oil contains the following constituents in the given percentages:

| | |
|---|---|
| ALDEHYDES (butyric, isovaleric, and capronic) | 6 |
| PINENE | 21–22 |
| CINEOL | 47 |
| ALCOHOLS (eudesmol, globuol, with traces of free acids and esters) | 23 |

In order to determine whether or not the oil from the burrs, which are necessarily gathered in large quantities with the leaves, had any detrimental effect upon the oil as a whole, a quantity of the burrs were

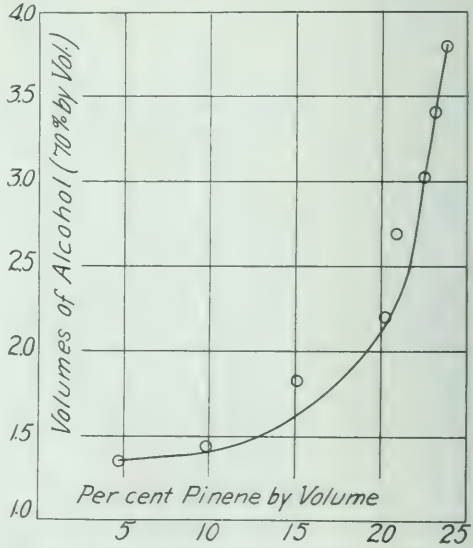



FIG. III—EFFECT OF PINENE UPON THE SOLUBILITY OF CINEOL

collected, ground and steam-distilled. The yield of oil corresponded to 0.2 per cent of the weight of the burrs. The oil thus obtained was of a lighter specific gravity and had a greater rotation than the leaf oil; it dissolved in 18 volumes of alcohol (70 per cent by weight) while the leaf oil dissolves in 15 volumes. This would seem to indicate that the burrs have a

[1] Burgess, *Analyst*, **29** (1904), 78.

[1] Semmler and Tobias, *Ber.*, **43** (2), (1913), 2026.

detrimental effect upon the oil and should be removed as far as possible.

The above analysis would seem to indicate that the chief difference between the Californian and Australian oils is in the exceedingly high content of pinene found in the Californian oil; this would account for the high rotation and low specific gravity of this oil. In order to determine the effect of the pinene upon the solubility in alcohol, pure pinene and cineol were mixed in definite proportions and the solubility in alcohol determined. Fig. III shows the effect of varying concentrations of pinene upon the solubility of cineol. It is readily seen that above certain percentages of pinene the mixture would become practically insoluble in 70 per cent alcohol.

SUMMARY

The above investigation has brought out the following facts:

I—The oil from the *Eucalyptus globulus*, from trees grown in California, has the same constituents as the oil of the Australian trees but in different proportions.

II—The reason why the Californian oil does not fulfil the U. S. P. requirements is probably due in great part to the exceptionally high pinene content.

Since Eucalyptus oil could be easily produced in large quantities in various parts of California and other Pacific coast states, a method of refining the oil so as to bring it up to the U. S. P. specifications would be particularly valuable. The investigation is being continued by the present authors with this idea in view.

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## THE SEPARATION OF GASES BY FRACTIONAL DISTILLATION IN A VACUUM AT LOW TEMPERATURES[1]

By G. A. BURRELL AND I. W. ROBERTSON

Received November 25, 1914

The authors have separated many gaseous mixtures by means of fractional distillation in a vacuum at low temperatures, and have found the method useful, accurate and applicable to a wide range of mixtures. Some of the latter are impossible to separate by other methods and some are exceedingly difficult. Hence there is presented in this paper a summary of the results so far obtained, with a discussion of the application of the method to mixtures other than those experimented with. To date three papers on the subject have been presented by the Bureau, as follows:

1—Gas analysis by fractional distillation at low temperatures.[2] In this paper was shown the separation of the paraffin hydrocarbons in natural gas.

2—The separation of the illuminants of mixed coal and water gas.[3] In this paper was shown the method of separating the paraffin hydrocarbons, olefine hydrocarbons and benzene in mixed coal and water gas.

3—The determination of gasoline vapor in air.[4] In this paper was shown a method for separating gasoline vapor from air.

PARAFFIN HYDROCARBONS—Any combination of the gaseous hydrocarbons, methane, ethane, propane and the two butanes, can be separated by first liquefying the mixture at the temperature of liquid air, removing the methane at that temperature, the ethane at a temperature not higher than —140° C., the propane at a temperature not higher than —120° C., the butanes at a temperature not higher than —95° C. leaving the pentanes or higher paraffins as a final residue.

OLEFINE HYDROCARBONS—Any combination of the gaseous olefine hydrocarbons, ethylene, propylene, and the butylenes, can be separated. The ethylene can be removed at a temperature not higher than —140° C., the propylene at a temperature not higher than —120° C., leaving the butylenes as a residue.

PARAFFIN AND OLEFINE HYDROCARBONS—Any combination of the paraffin and olefine gaseous hydrocarbons can be separated. The methane can be removed at the temperature of liquid air. The ethane and ethylene can be removed at a temperature not higher than —140° C. The propylene and propane can be removed at a temperature not higher than —120° C., leaving the butanes and butylene as a residue. The pairs of constituents can be analyzed as such by combustion in oxygen, and from this data the percentage of each one determined. The authors have separated ethylene and ethane, boiling point only 10° C. apart, but the operation is too tedious to be of practical value.

BENZENE VAPOR in air or in mixture with other gases, such as coal gas, can be separated at the temperature of liquid carbon dioxide (—78° C.). In the case of benzene vapor and other gases that represent the final or the only separation desired in mixtures, it is most convenient to measure their pressure after the removal of the other constituents. The volume present can be calculated from this pressure. For instance in the case of benzene vapor in air or coal gas, the mixture is introduced into the liquefaction bulb at atmospheric pressure. It is then cooled by surrounding the liquefaction bulb with liquid carbon dioxide and removing as much gas as is possible with a vacuum pump. Next the stopcock on the liquefaction bulb is closed, the refrigerant removed, and the pressure of the benzene read on a manometer attached to the liquefaction bulb. If $a$ represents the pressure of the atmosphere and $b$ the partial pressure of the benzene vapor, the percentage of benzene by volume becomes $100\ b/a$: water vapor is removed by absorbing same in phosphorus pentoxide.

GASOLINE VAPOR IN AIR—It was found necessary to adopt a temperature lower than that of liquid carbon dioxide in order to separate gasoline vapor from air, hence liquid air was used since it has to be used and time is consumed in obtaining temperatures between those of liquid carbon dioxide and liquid air. The partial pressure of the gasoline is determined in the same way as is that of the ben-

[1] Published by permission of the Director of the Bureau of Mines.
[2] *J. A. C. S.*, **36** (1914), 1537.
[3] THIS JOURNAL, **7** (1915), 17.
[4] *Ibid.*, **7** (1915), 112.

zene. From the partial pressure of the gasoline its volume is computed.

WATER VAPOR IN AIR can be determined in the same manner as gasoline or benzene vapor. A temperature of —78° C. (the temperature of liquid carbon dioxide) can be employed. At this temperature the vapor pressure of ice is practically nil.

APPLICATION OF METHOD TO OTHER MIXTURES—Aside from the separation of natural gases, illuminants in coal gas, gasoline, benzene and water vapor in air, the method should be useful in examining the various mixtures produced in the destructive distillation of different fuels, concerning which a large amount of experimental work is performed each year. The authors are coöperating with Dr. W. F. Rittman, of the petroleum laboratory of the Bureau, in the cracking of oils. The different gases produced by cracking oils and the pure liquid paraffins are being examined by the method of fractional distillation. In this way facts of fundamental importance regarding the "cracking" of oils will be learned.

In the case of fractional distillation of liquids at ordinary or elevated temperatures, the distillations have to be repeated several times in order to obtain the different fractions in a fairly free condition. The same is true of the fractional distillation of gases in a vacuum at low temperatures. The Bureau has redistilled some fractions four and five times to obtain gases that were analytically pure.

The apparatus required is such as can be easily obtained by many laboratories. A vacuum pump for withdrawing the gases, glass vessels for trapping them, a gas burette for measuring them, and pentane thermometers for measuring temperatures are easily procurable. Liquid air can be obtained at several different places in the United States, and liquid carbon dioxide in all large cities. The only special part of the apparatus is the liquefaction bulb and this is very simple. Precise thermometric measurements are not necessary and pentane thermometers accurate to 1 or 2° C. can be used.

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## A RAPID METHOD OF FRACTIONATING GASES AT LOW TEMPERATURES[1]

By G. A. BURRELL AND I. W. ROBERTSON

Received December 9, 1914

In this paper is shown a more rapid method of fractionating gases in a vacuum at low temperatures than hitherto used by the Bureau of Mines. The particular gas worked with was the artificial illuminating gas of New York City.

In previous experiments the authors continued to refractionate a particular fraction until the gases obtained were analytically pure. For instance, in working with natural gas, the first distillate was obtained at the temperature of liquid air. The distillate and residue were then refractionated until methane and nitrogen were obtained pure. The same procedure was followed in fractionating coal gas. At the temperature of liquid air, the first fraction consisted of methane, nitrogen, carbon monoxide, hydrogen, and oxygen with small quantities of ethane and ethylene. Also the residue contained some of the five gases first mentioned. Hence the distillate and residue were refractionated until the distillate was freed of ethane and ethylene, and none of the five gases remained in the final residue.

The procedure now adopted, which is faster and more economical of liquid air, consists, in the case of coal gas, for instance, of first removing as much gas as possible at the temperature of liquid air. Call this fraction *A*. The residue is then subjected to distillation at a temperature not higher than —140° C. Call the distillation so obtained *B*. Next fractionate the residue from *B* at a temperature not higher than —120° C. Call the distillate so otained *C*. Then fractionate the residue from *C* at a temperature not higher than —78° C. and call the distillate so obtained *D*. There are thus obtained four fractions, *A*, *B*, *C* and *D*, each containing some gases that belong properly to other fractions and which must be purified by further fractionating. As each distillate was obtained it was removed from the pump and transferred to another container. The residue in each case was left in the liquefaction bulb. For instance, after the first distillate was removed (at the temperature of liquid air), the liquid air was removed and the bulb surrounded with light gasoline of a temperature not higher than —140° C., and so on.

The following data show the results of fractionating the artificial illuminating gas of New York City:

FRACTIONATION ANALYSIS OF NEW YORK ILLUMINATING GAS

| | Cc. |
|---|---|
| Original volume of gas | 1007.6 |
| $CO_2$ removed by caustic potash | 32.3 |
| Volume taken for fractionation | 975.3 |

975.3 cc. Liquefied at temperature of liquid air

*A* — Residue

Distillate 817.4 cc

157.9 cc. Liquefied at —140° C.

*B* — Residue

Distillate 106.5 cc

51.4 cc. Liquefied at —120° C.

*C* — Residue

Distillate 25.3 cc.

26.1 cc. Liquefied at —78° C.

*D*

Distillate 13.8 cc

12.3 cc.

The above diagram shows the method of obtaining the first four distillates, *A*, *B*, *C* and *D*. Next the distillate *A* was reliquefied at the temperature of liquid air and the distillate from it removed. The residue, which was very small, was left in the liquefaction bulb and the distillate *B* added to it. The latter was then refractionated at a temperature not higher than —140° C. The distillate and residue so obtained were both refractionated again, because the pressure manometer showed that one fractiona-

[1] Published by permission of the Director of the Bureau of Mines.

tion was not enough. The final residue was left in the liquefaction bulb and the distillate *C* added to it, and so on. The last residue obtained at —78° C. was allowed to evaporate at room temperature and its pressure read. Previous experimentation had shown that at —78° C. practically the only gas remaining in coal gas is benzene.

There follows an analysis of the artificial illuminating gas of New York City as made by this method.

ANALYSIS OF NEW YORK CITY ILLUMINATING GAS

| | Per cent | | Per cent |
|---|---|---|---|
| $CO_2$ | 4.7 | $C_2H_4$ | 9.8 |
| $O_2$ | .. | $C_2H_6$ | 2.7 |
| CO | 29.8 | $C_6H_6$ | 1.6 |
| $H_2$ | 32.0 | $C_6H_6$ | 1.5 |
| $CH_4$ | 13.1 | $N_2$ | 1.7 |
| $C_2H_6$ | 2.8 | | |
| $C_3H_8$ | 0.3 | Total | 100.0 |

The various fractions were analyzed as described in a previous communication to THIS JOURNAL.[1]

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PITTSBURG

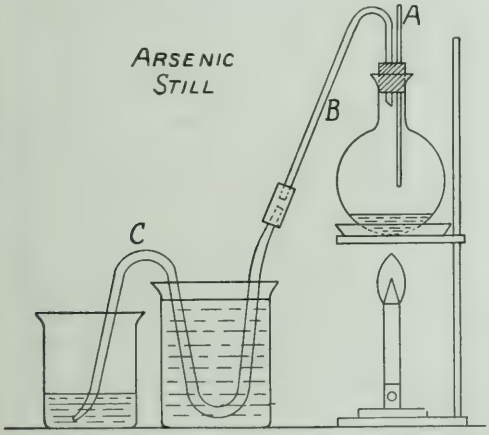
## RAPID ANALYSIS OF ALLOYS FOR TIN, ANTIMONY AND ARSENIC

By F. A. STIEF[2]

Received December 14, 1914

The iodine and permanganate titrations in the following method are well known, and used with many variations in many laboratories, but this combination method of determining tin, antimony and arsenic all on the same sample and without filtering, as well as many important details, is original.

METHOD—Dissolve 0.5 gram of the finely divided alloy, best in the form of thin foil-like shavings (sawings or very small drillings will do), in exactly




8 cc. concentrated sulfuric acid in a 300 cc. Florence flask covered with a small watch glass: boil the solution. Cool, add exactly 5 cc. of water; cool, add a bulk of about 0.5 cc. clean, granulated pumice stone, and exactly 20 cc. concentrated hydrochloric acid. Now insert in the flask a clean rubber stopper, carrying a centigrade thermometer (A) and a delivery tube (B). The thermometer should be about 1 inch from the surface of the liquid, so as to get the vapor temperature only, which should never go above 108° C. Connect the delivery tube to the figure S condenser (C) which has one of its curves nearly filled with water and submerged in cold water in a 500 cc. beaker, and its other free end dipping into about 75 cc. of water in a 300 cc. beaker.

The S condenser is about 18 inches long and $^1/_2$ inch inside diameter but tapers to about $^1/_4$ inch at the upper, and $^1/_8$ inch at the lower end to facilitate washing and make the bubbles of gas small as they emerge into beaker. This makes a perfect condensing apparatus in this case; it is very simple, easy to handle, has only one rubber connection besides the rubber stopper, and no cocks or corks that leak. Nothing is lost through it except air from the flask at the very start.

Distil from 10 to 15 minutes, boiling gently, and keeping the vapor temperature at 107° for at least 5 minutes. The arsenic, as $AsCl_3$, is all distilled over even if the alloy contains 5 per cent, which is rare.

ARSENIC—Wash out the condenser into the 300 cc. beaker, and add an excess of about 2 g. sodium bicarbonate to this solution which should now have a volume of about 200 cc., and be warmed to a temperature of about 27° C. Titrate with standard iodine solution and starch to deep blue, which color will take 0.2 cc. of iodine solution in a blank under the conditions used.

| STANDARD SOLUTIONS | Equivalent in grams of 1 cc. of solution IODINE | TIN | ARSENIC |
|---|---|---|---|
| Iodine | 0.010672 | 0.005000 | 0.003150 |
| | $KMnO_4$ | IRON | ANTIMONY |
| Permanganate | 0.0026315 | 0.004650 | 0.005000 |

ANTIMONY—Cool the solution left in flask, add about 130 cc. cold water and titrate with standard permanganate solution. The blank is 0.1 cc. About 4 cc. of hydrochloric acid must be present during this titration; usually enough is left in the flask from the distillation.

TIN—If the antimony was found to run below 14 per cent or 0.07 g., add enough dissolved $SbCl_3$ to the solution to make it contain just about 0.07 Sb. This is done to insure perfect reduction of the tin, and for the sake of making uniform the effect of the antimony on the titration of tin with iodine. Then add exactly 6 cc. concentrated sulfuric acid, 60 cc. concentrated hydrochloric acid and about 6 inches of clean, soft, No. 14, pure Fe wire ("hay" wire is best, used in 2-inch lengths, and cleaned with dilute hydrochloric acid just before using). Boil gently one-half hour, add 4 to 6 inches more wire, and boil one-half hour longer. Take off heat, wash down the inside of the flask with distilled water, fit a clean rubber stopper loosely in the flask, and allow about two minutes for all air to be expelled from the flask and replaced by hydrogen, water and hydrochloric acid vapors; then cork tightly, and quickly place in cold water. When cold (about 20° C. is best) pour the solution into a 500 cc. beaker (leaving the iron wires in the flask); put 150 cc. cold, recently boiled distilled water into the flask and pour this into the beaker. This should give a final volume of between 300–350 cc. Titrate quickly with standard

[1] Burrell, G. A. and Robertson, I. W., "The Separation of the Illuminants in Mixed Coal and Water Gas," THIS JOURNAL, 7 (1915), 17.

[2] Chemist, Hoyt Metal Company, Granite City, Illinois.

iodine solution to a strong blue color. The blank under these conditions is 0.4 cc. of the iodine solution.

NOTES—The author has tried all sorts of bought condensers but the laboratory-made "S"-shaped tube mentioned above is, for this particular purpose, an improvement upon them all. Any chemist who has tried to wash out a couple of "U" tubes with leaky rubber connections and corks will appreciate the difference.

Either tin or antimony alone may be determined without using the condenser. This method is so extremely simple, that tin, antimony and arsenic can all three be determined in two hours; this is far more than can be said of many other methods requiring many separations which cannot but make the results run low.

Arsenic consumes close to 1.5 times as much permanganate solution as antimony does. Hence, if the arsenic is not removed before the antimony determination, the results will be worthless. Most all alloys which contain antimony contain arsenic. The arsenic should be removed before the tin determination since it often causes high results in this case too. Thus it can be seen at once what an improvement this new combination method is over most of the old ways of determining tin and antimony with iodine and $KMnO_4$, since those methods make no allowance for the effect of arsenic.

Copper has no effect whatever on the antimony determination but when it is over about 3 per cent it is apt to interfere with the tin determination. The amount of iron found in alloys is usually entirely oxidized in the concentrated sulfuric acid to the ferric state so that it does not interfere. There are no other common metals that interfere.

About the only causes of errors in this method are too great a variation of the conditions stated and the use of impure chemicals.

### NEW METHOD OF ELIMINATING THE INTERFERENCE OF COPPER ON THE TIN TITRATION

When the tin is low and the copper high in an alloy the end point in the tin titration is usually a fading green instead of a permanent blue but if the tin is over about 70 per cent any percentage of copper in the balance of the alloy will not interfere. It was this peculiarity that led the author to believe that the potassium iodide in the iodine solution was the cause of the apparently inconsistent effect of the presence of copper. Therefore, when the tin is low and the copper high, just before titrating, add 0.5 to 1.0 g. "C. P." KI crystals and stir until nearly dissolved; then titrate at once (if let stand too long at this point some lead, etc., may be precipitated and cause low results). If properly done, this will entirely eliminate the effect of the copper and the results will be just as accurate as if no copper were present.

### NEW DIRECT RAPID METHOD FOR ANTIMONY AND TIN IN MATTES, SOLUBLE FURNACE PRODUCTS, CHILLED SLAGS, ETC., CONTAINING MUCH COPPER, IRON AND ARSENIC (NO SEPARATIONS)

To 0.5 gram of the substance in a 250 cc. beaker add 10 cc. concentrated $H_2SO_4$ (if high in silicon add about 15 cc. of water first). Keep the beaker covered and boil the solution for 15 minutes or longer after taking to fumes if water has been added. Cool, add 10 cc. water and 10 cc. hydrochloric acid and boil 2 minutes; then add at least 1.5 grams $KClO_3$ to thoroughly oxidize all metallic salts and heat to fumes to drive off all Cl in any form.

Add the $KClO_3$ cautiously. With experience, and by using sufficient water in the solution, explosions can be avoided. If there is an explosion usually only the cover glass is blown off. The author never used a flask in this part of the method for fear of what might happen. Now add close to 0.10 gram of sulfur to the solution and boil till nearly all of the sulfur is gone (about $^1/_2$ hr.) Cool, add 6 cc. $H_2O$, cool, add 20 cc. concentrated hydrochloric acid and about 0.5 cc. bulk of pumice stone; boil off the arsenic and determine the antimony and tin as in the first method, using KI in the tin titration if necessary. Just before boiling off the arsenic, the solution may be transferred to a flask with the aid of the 20 cc. or more of HCl as a wash but no extra water should be used.

NOTES—The success of this method depends upon the complete oxidation of the metallic salts and any carbon present and the complete reduction of the antimony and arsenic by the sulfur. All the metallic salts are oxidized by the $KClO_3$. Only the antimony and arsenic are reduced by the sulfur. Use enough sulfur but do not have more than 0.10 g. present after reduction for it may retain some antimony or tin. $K_2SO_4$ and $HNO_3$ may be used instead of $KClO_3$ to oxidize the solution. The use of $HNO_3$ is usually necessary when much carbon is present, but more sulfur is required to remove the last traces of the $HNO_3$. Carbon colors the concentrated $H_2SO_4$ solution brown or black and hence is easily detected.

Having sufficient potassium or sodium present to form double salts with the tin and antimony while evaporating the solution to fumes will prevent any volatilization of the latter two metals as chlorides.

In these methods the author has not found it necessary to use nickel to reduce the tin solution or $CO_2$ gas to prevent oxidation while cooling and titrating it.

Slags or ores containing insoluble stannic oxide or silicate must be previously fused with NaOH for the tin determination.

These two methods have been proved reliable by six years of experimenting and practical work and by checking results from Ledoux & Co., Mr. G. W. Thompson and many other chemists. In three-cornered checks on the same samples with Ledoux & Co. and Mr. G. W. Thompson, the author's results using the first method compared as favorably as those of the other workers.

Smelting works chemists who have to separate and determine tin or antimony in speiss and hard-head assay buttons, etc., containing much iron, copper and arsenic will perceive the value of the second method in its simplicity, rapidness and accuracy. But like most methods it requires considerable experience to operate it successfully and should not be condemned after a short trial.

Tables of experiments, check analyses and other details will be published later.

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## DETERMINATION OF COPPER IN STEEL[1]

By W. D. Brown

In view of the increased use of copper in steel as a preventive of corrosion and of the necessity of completing the determination in a very short time, a rapid and accurate method for the determination of copper in steel is essential to a steel works laboratory.

The precipitation of copper by potassium or ammonium thiocyanate solution has been used in the gravimetric determination of copper. Van Name[2] has shown that, under certain conditions of concentration, acidity, etc., the precipitation is complete. Treadwell and Hall[3] describe a method for the titration of cuprous thiocyanate (CuCNS) with potassium iodate; in this titration iodine is at first set free and absorbed by the chloroform added as an indicator, then oxidized by more iodate to iodine chloride, the violet color disappearing from the chloroform.

In the method submitted here potassium iodate is used in excess and the excess, after the addition of potassium iodide, is titrated with sodium thiosulfate.

METHOD—Five grams of steel are dissolved in 65 cc. of a mixture of 40 cc. nitric acid (1.20 sp. gr.) and 25 cc. sulfuric acid (1 : 1) and the solution evaporated to fumes of sulfur trioxide in a covered porcelain dish over a high flame; care must be taken that all nitric acid is expelled. The dish is removed from the heat and, when cold, 50 cc. of hot water are added and the solution boiled, transferred to a No. 5 beaker and diluted to 400 cc. with hot water. When all the ferric sulfate is in solution, 50 cc. strong ammonium bisulfite are added, while stirring, followed by 25 cc. of 5 per cent potassium thiocyanate. The solution is boiled until precipitation is complete, which requires five minutes, and filtered by suction through a 11 cm. No. 0 Munktell filter, the precipitate and breaker being washed with cold 1 per cent sulfuric acid solution. Paper and precipitates are transferred to a beaker, 20 cc. hydrochloric acid (1 : 1) are added, followed by standard potassium iodate solution (2 cc. for each 0.1 per cent copper expected). The paper is well macerated with a glass rod and water added to a volume of 500 cc.; the potassium iodide solution is now added (1 cc. of 10 per cent solution for each cc. of iodate added) and free iodine titrated with standard thiosulfate solution; the thiosulfate should be added rather slowly and the solution stirred vigorously, care being taken that no part of the solution is bleached before the whole. When the yellow color of free iodine has nearly vanished, 5 cc. starch solution are added and the titration continued until the blue is bleached. The difference between the iodate and thiosulfate represents the copper.

CALCULATIONS—The reactions and calculations are rather intricate. The iodate when in excess oxidizes the copper thiocyanate as follows (Treadwell and Hall):

(1) $4CuCNS + 7KIO_3 + 14HCl = 4CuSO_4 + 7ICl + 4HCN + 7KCl + 5H_2O$, from which it is seen that $7KIO_3$ oxidize 4Cu and an iodate solution made accordingly gave correct results on titration using chloroform. If now the solution be diluted and an excess of potassium iodide be added the iodine chloride (ICl) will be changed to free iodine according to the reaction:

(2) $7ICl + 7KI = 14I + 7KCl$; $7KIO_3$ oxidize 4Cu and at the same time liberate 14I, or $1KIO_3$ liberates 2I. The excess of $KIO_3$ has been reduced by potassium iodide according to the reaction:

(3) $KIO_3 + 5KI + 6HCl = 6KCl + 3H_2O + 6I$, from which it follows that one $KIO_3$ in excess liberates 6I whereas each $KIO_3$ which oxidizes copper liberates 2I or $1/3$ the former.

Therefore $1/3$ of the oxidizing power of potassium iodate is reclaimed on addition of potassium iodide. It was shown that $4Cu = 7KIO_3$ in concentrated acid solution (1). In dilute solution, after addition of potassium iodide, $4Cu = 2/3$ of $7KIO_3$ or $1Cu = 7/6\ KIO_3$.

For the above titration 1 cc. should equal 0.1 per cent copper on a 5 g. sample or 1 cc. = 0.005 g. copper. Then 1 cc. should contain $0.005 \times 7KIO_3/6Cu$ or 1000 cc. should contain 19.64 g. potassium iodate. A solution of potassium iodate was standardized with sodium thiosulfate against potassium permanganate which had been standardized against sodium oxalate and it was found that the "C. P." salt contained but 97 per cent of its theoretical oxidizing power, there being some potassium carbonate present as well as other impurities. Taking this into consideration the solution of potassium iodate is made by dissolving 20.2 g. salt and diluting to 1 liter. The solution of sodium thiosulfate is made by dissolving 137 g. per liter and is made to agree with the iodate solution if necessary. These solutions are best standardized against permanganate in the well known way.

RESULTS—On determining copper on a solution of copper sulfate containing the equivalent of 0.25 per cent copper, good results were obtained.

Results on a Copper-Steel Standard

| Laboratory | Method | Per cent Cu |
|---|---|---|
| 1 | Not given | 0.216 |
| 2 | Not given | 0.21 |
| 3 | Not given | 0.21 |
| 4 | Not given | 0.222 |
| | Electrolysis | 0.224 |
| 5 | Vol. and elec | 0.205 |
| 6 | Electrolysis | 0.21 |
| 7 | Electrolysis | 0.204 |
| 8 | Not given | 0.21 |
| 9 | Not given | 0.206 |
| | Not given | 0.214 |
| 10 | Not given | 0.21 |
| | Duquesne grav. CuO | 0.215 |
| | Duquesne vol. $KIO_3$, $Na_2C_2O_4$ std. | 0.213 |
| | AVERAGE | 0.212 |

Results by Steel Works Laboratories on a copper steel standard were as given above.

DUQUESNE WORKS, CARNEGIE STEEL CO.
DUQUESNE, PA.

## RECOVERY OF MOLYBDIC ACID[1]

By W. D. Brown

On account of the rise in price of molybdic acid, an attempt was made in the Duquesne Laboratory last

[1] Presented before the Pittsburg Section of the American Chemical Society, January 21, 1915.

[2] *Am. J. Sci.*, **10**, 451; **12**, 20, and Gooch's "Chemical Analysis," p. 108.

[3] "Analytical Chemistry," Vol. II (**1914**), p. 672; (**1910**), p. 599. See also *J. A. C. S.*, **30** (1908), 760.

[1] Presented before the Pittsburg Section of the American Chemical Society, on January 21, 1915.

May to recover it from the filtrates from determinations of phosphorus. Various methods were tried before the present one was settled upon as giving the best recovery with the least work and expense. The method consists of the precipitation of the molybdic acid from the ferric nitrate solution with an excess of phosphate. At first the theoretical amount of phosphorus was added to the cold solution and but $^1/_3$ the molybdic acid was recovered. At the present time five times the theoretical amount of phosphate is added to the boiling solution.

It has been the practice in this laboratory to make the acid in $^1/_2$ lb. lots of 85 per cent molybdic acid, making 3500 cc. of solution and in agreement with the adopted method of the U. S. Steel Corporation. The filtrates from 3500 cc. of ammonium molybdic solution are heated to boiling and a solution containing 200 g. commercial sodium phosphate added. The precipitate is allowed to settle and, after the solution is decanted, is transferred to a large-mouthed bottle. When sufficient yellow precipitate from several precipitations is obtained, it is washed by decantation, transferred to a dish, the water evaporated off and the precipitate dried on a sand bath.

According to the commonly accepted formula for the yellow precipitate, it contains 92 per cent $MoO_3$, and 210 g. would contain the same weight of acid as $^1/_2$ lb. of 85 per cent molybdic acid. Accordingly, for the precipitation of the molybdic acid solution 210 g. of yellow precipitate are weighed and 800 cc. water added, followed by 600 cc. ammonia. The solution is cooled and 35 g. magnesium nitrate, dissolved in 100 cc. water, are added to precipitate all the phosphorus. After the solution has stood for some time it is filtered and the precipitate is washed with 100 cc. water or dilute ammonia. The filtrate is added to 1900 cc. of 1 : 1 nitric acid, the total volume being 3500 cc., and containing the usual amount of ammonia and nitric acid.

In this laboratory the recovery has been only about 85 to 87 per cent. The cost of recovery of one pound of molybdic acid is about 10 cents: 7 cents for the sodium phosphate and 3 cents for the magnesium nitrate, the ammonia being required in the ammonium molybdate solution.

DUQUESNE WORKS, CARNEGIE STEEL CO.
DUQUESNE, PA.

## THE MODIFICATION OF STARCH BY GASEOUS HYDROCHLORIC ACID

By FRANCIS C. FRARY AND ARTHUR C. DENNIS

Received November 23, 1914

Very little information on the actual manufacture of dextrin from starch is available. Text-books[1] generally state that it is made clear either by heating starch alone to from 210 to 280° C., producing a brown product, or by moistening the starch with dilute nitric acid and heating at a lower temperature (110 to 150° C.). It appears to be well known that dilute acids and some other substances have the power of modifying starch more or less in the cold, producing so-called "thin-boiling" starch, without breaking down the granules so that they are dissolved by cold water. After such treatment the excess of the reagent may be washed out and the starch dried as usual. Among the substances recommended (and in most cases patented) for modifying starch are persulfates, bleaching powder, sodium peroxide, bichromates, ozone, formic acid, oxalic acid, tartaric acid, salts of the heavy metals (copper, nickel, cobalt, iron, etc.), carbon dioxide and formaldehyde.

A second step in the modification of starch consists in submitting it to such treatment as to rupture the cellulose envelopes of the granules, thus making the starch emulsify in cold water to form a liquid like ordinary boiled starch paste. If this be accomplished in the dry way, the form of the starch is unchanged, but upon mixing it with cold water it dissolves as if it had been boiled. Such pastes are made in this country by a number of manufacturers, the raw material being apparently a low grade of flour. The only information obtainable as to the process of manufacture is that it is a very cheap one, as the finished product sells for little more than the raw flour. From the appearance of some samples received by one of us, some of the plants are apparently using the well-known process of Anderson,[1] which consists in heating the starch in closed vessels to over 100° C., and then suddenly releasing the pressure. The granules are ruptured by the expansion of the steam in them. It is interesting to note that this patent of Anderson's for making soluble starch, preceded and seems to have been a preliminary step toward his more important patents for "puffing" grains.

Other patented treatments which appear to aim to produce the same modification of starch were also found. Fielding[2] treats starch with acid vapors and steam to produce a soluble starch. Thompson and Morrice,[3] and Thompson and Berge[4] use sulfurous acid at temperatures from 100 to 190° C., while Kindscher[5] used chlorine. Hartwig[6] also uses chlorine, specifying a treatment of from four to eight days' duration. Browning and Barlow[7] use hydrochloric acid gas, or a spray of the aqueous acid, passing it into a rotary converter containing the starch. To produce a soluble starch a temperature of 54° C. is recommended, while for dextrin the temperature is said to be 76 to 93° C.

From a general consideration of the question, it appeared that treating the starch with a small amount of gaseous hydrochloric acid and heating it, would be the simplest method of producing soluble starch, and experiments had been begun and favorable results secured by one of us before we found the patent of Browning and Barlow. Believing that their process would be of general interest and that a study of it might yield interesting information, a series of experi-

[1] Allen's "Commercial Organic Analysis," 3rd Ed., **1**. 49.

[1] U. S. Pat. 707,892; Brit Pat 13,353, June 12, 1912; *J. Soc. Chem. Ind.*, **21**, 1189.

[2] Eng. Pat. 20,488, Sept. 15, 1906; *J. Soc. Chem. Ind.*, **26**, 980.

[3] Fr. Pat. 383,499, U. S. Pat. 951,666; *C. A.*, **3**, 1104; **4**, 1556.

[4] Eng. Pat. 7,272, Apr. 27, 1891; *J. Soc. Chem. Ind.*, **11**, 448.

[5] Ger. Pat. 168,980; *J. Soc. Chem. Ind.*, **26**, 334; see also Ger. Pat. 149,588.

[6] U. S. Pat. 798,509; *J. Soc. Chem. Ind.*, **24**, 1024.

[7] Fr. Pat. 336,903; *J. Soc. Chem. Ind.*, **23**, 449.

ments was carried out to determine the relation between the quantity of acid present, the temperature used and the character of the product. Further study of the products and the relations at higher temperatures was contemplated, but was prevented by Mr. Dennis leaving the University. As there seems to be no prospect of our being able to complete the work at present, these preliminary results are published in the hope that they may be of value in indicating the course of the reaction.

The starch used was made by powdering ten pounds of common laundry starch until about 70 per cent of it passed a 100-mesh screen. The rest appeared to be tough and glutinous, and did not crush well, so it was rejected. After thoroughly mixing and allowing the sample to stand in a large glass-stoppered bottle, a moisture determination showed 12.7 per cent loss on drying at 105° C. The sample contained 0.20 per cent of ash. Care was taken to keep the bottle tightly closed in order to maintain the moisture content constant throughout the series.

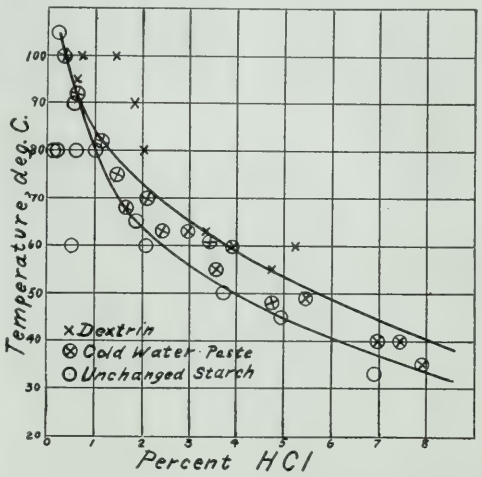
Twenty grams of starch were used for each experiment. The starch was placed in an improvised revolving mixer and dry hydrochloric acid gas (made from salt and sulfuric acid, and dried with sulfuric acid) was passed into the mixer. It was rapidly absorbed. The amount of acid absorbed was determined by titration of a 1 g. sample with $N/10$ alkali, using methyl orange and phenolphthalein as indicators.

For heating the starch a glass apparatus like a Liebig condenser was used, hot water being rapidly circulated through the jacket by means of a small centrifugal pump. For higher temperatures calcium chloride was added to the water. A bent glass tube revolving inside the inner tube stirred the starch thoroughly. Both ends of the inner tube were closed with rubber corks to prevent loss of moisture. The time of treatment was generally about thirty minutes. The results are presented in the accompanying table and curves.

TABLE I

| Time Min. | Temp. ° C. | Per Cent Acid Found by Phenolphthalein before | Phenolphthalein after | Methyl Orange before | Methyl Orange after | Cold water paste | Dextrin |
|---|---|---|---|---|---|---|---|
| 40 | 60 | 0.83 | 0.80 | .. | 0.47 | No | No(b) |
| .. | 80 | 0.33 | 0.33 | 0.18 | 0.11 | No | No(b) |
| 30 | 80 | 0.77 | 0.73 | 0.58 | 0.51 | No | Trace(c) |
| 30 | 90 | 0.77 | 0.69 | 0.54 | 0.47 | No | ... |
| 30 | 80 | 1.24 | 1.09 | 1.02 | 0.80 | Slight | Trace(c) |
| 30 | 80 | 0.15 | 0.15 | 0.11 | 0.03 | No | No(d) |
| 20 | 95 | 0.72 | 0.18 | 0.61 | 0.11 | No | Yes |
| 30 | 100 | 0.91 | 0.77 | 0.73 | 0.43 | No | Yes |
| 5 | 80–100 | 1.63 | .. | 1.42 | .. | No | Yes(e) |
| 10 | 100 | | | | | | |
| 20 | 90 | 2.10 | 1.96 | 1.81 | 1.67 | No | Yes(e) |
| 30 | 80 | 2.29 | 1.74 | 2.06 | 1.56 | No | Yes(e) |
| 30 | 70 | 2.47 | .. | 2.18 | .. | Yes | ... |
| .. | 65 | 2.06 | .. | 1.88 | .. | No | No |
| 30 | 60 | 5.52 | .. | 5.22 | 3.88 | No | Yes |
| 15 | 50 | 4.13 | 2.97 | 3.88 | 2.76 | Yes | Yes(f) |
| 20 | 60 | | | | | | |
| 30 | 100 | 0.40 | 0.36 | 0.33 | 0.25 | Yes | Yes(f) |
| 20 | 105 | 0.22 | .. | 0.15 | .. | Trace | No |
| 30 | 63 | 3.48 | .. | 3.27 | .. | No | Yes |
| 30 | 60 | 2.24 | .. | 2.07 | .. | Trace | ... |
| 30 | 82 | 1.26 | .. | 1.12 | .. | Some | ... |
| 30 | 61 | 3.45 | .. | 3.19 | .. | Yes | ... |
| .. | 75 | 1.63 | .. | 1.48 | .. | Yes | ... |
| 30 | 90–95 | 0.73 | .. | 0.58 | .. | Yes | ... |
| 30 | 60–65 | 3.27 | .. | 2.97 | .. | Yes | ... |
| 30 | 62–65 | 2.54 | .. | 2.40 | .. | Yes | ... |
| 30 | 54–56 | 5.08 | .. | 4.72 | .. | No | Yes(g) |
| 30 | 48–50 | 5.87 | .. | 5.45 | .. | Yes | ... |
| 30 | 39–41 | .. | .. | 7.44 | .. | Yes | ... |
| 30 | 35 | .. | .. | 7.91 | .. | Yes | ...(h) |
| 30 | 40 | .. | .. | 6.97 | .. | Yes | ...(h) |
| (a) | 20–25 | .. | .. | .. | 5.40 | Yes | ... |
| 30 | 48 | .. | .. | 4.72 | .. | Yes | ...(i) |
| 30 | 68 | .. | .. | 1.63 | .. | Yes | (j) |
| 30 | 33 | .. | .. | 6.90 | .. | Trace | No(k) |
| 30 | 55 | .. | .. | 3.52 | .. | Yes | No(l) |
| 30 | 50 | .. | .. | 3.70 | .. | No | No(m) |
| 30 | 45 | .. | .. | 4.94 | .. | No | No(n) |

(a) This was allowed to stand over night at room temperature, and is not included in the plot because of this long time of treatment.
(b) Slight opalescence with alcohol.
(c) Precipitate with alcohol.
(d) Opalescence with alcohol.
(e) Good dextrin.
(f) Sticks well.
(g) White, just converted.
(h) Some unchanged starch.
(i) Some unchanged starch.
(j) Much unchanged starch.
(k) Almost unchanged.
(l) About half converted.
(m) Very slightly changed.
(n) Almost unchanged.




It will be noticed that the acidity to phenolphthalein was greater than that to methyl orange, and where determinations of acidity were made after the treatment, decrease of acidity to both indicators was shown. In plotting the results, the acidity to methyl orange was used, as it is believed to more closely represent the acidity effective in the hydrolysis of the starch.

Under the conditions described, it is evident that for a given acidity there is a definite temperature range within which a half hour's heating will convert the starch to the soluble variety (called "Cold Water Paste" in the table); at higher temperatures the conversion to dextrin is rapid, and at lower temperatures little change takes place. Longer treatment at lower temperatures would undoubtedly effect some change, as indicated in one experiment in the table, where the acid starch was not heated at all, but simply allowed to stand over night at room temperature, and a cold water paste was obtained. Similarly, for a given temperature, the range of acidity within which a soluble starch is produced is definite, greater quantities of acid-producing dextrin and smaller quantities failing to produce the soluble starch. The smaller the amount of acid present, the higher the temperature required to convert the starch, and apparently the more difficult it would be to stop at the point where the soluble starch was formed.

The dextrins produced were generally very nearly white and had good adhesive power. The proportion of water present in the starch was so large that when the dextrin was formed it had a strong tendency to dissolve or melt in the water, forming lumps which

stopped the stirrer. In some of the first experiments, the treated starch was washed with cold water, and the behavior of the resulting solution noted in the table. The opalescence and precipitates with alcohol indicate that the reaction does not proceed in two definite, separate steps, but that dextrin begins to be formed in small quantities as soon as the soluble starch formation begins. Undoubtedly all products designated as "Cold Water Paste" contained a good deal of dextrin.

It would be comparatively easy to remove or neutralize the small amount of acid required if the conversion to dextrin were made at 100° or over, and it would appear that this would be an easy way of making a good white dextrin. If the starch were dried somewhat before use, less acid would probably be required and the product would not lump, hence would not need grinding. The method does not seem very well adapted to producing soluble starch, and it is evident that the temperatures given for this by Browning and Barlow require the use of larger quantities of acid than would be economically practicable, unless the time of treatment were much increased.

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## THE DIRECT AND THE INVERT POLARIZATION OF PURE SUCROSE[1]

By HERBERT S. WALKER

Considerable doubt has arisen in recent years as to the correctness of our present polarimetric methods of determining sucrose. At the last International Congress of Applied Chemistry a paper was presented by Bates and Jackson, indicating that the 100 point of the saccharimeter is approximately 0.1° too high. This subject was deemed of sufficient importance to warrant appointing a special committee for its investigation, to report at the next meeting of the Congress.

At the same session, on motion of Prof. Herzfeld, a committee was also appointed to re-determine the correctness of the factor 142.66 now used in the Clerget-Herzfeld method for the determination of sucrose by double polarization.

Since then, investigations by Steurwald, in Java, and Stanek, in Bohemia, tend to prove that the Clerget factor 142.66 is from 0.2 to 0.3 too low, Stanek claiming, however, that if the invert polarization be made within 5 minutes after completing the volume of the inverted solution, the original Herzfeld factor holds good, but owing to a slight muta-rotation of the invert sugar, a constant invert polarization is not reached until 15 to 20 minutes after completing to volume.

Both these investigators apparently find, or assume, the direct polarization of pure sucrose to be 100.0.

Since it will probably be several years before reports from the committee officially appointed to investigate these two subjects may be expected, the following experimental data may be of some interest:

An attempt was made to prepare pure sucrose by the customary method of precipitation from a hot, saturated solution by absolute alcohol, starting with the best grade of "domino" sugar. The sugar thus obtained was re-dissolved, re-precipitated, washed on a suction filter with alcohol, and finally air-dried

DETAILS OF EXPERIMENTS

SACCHARIMETER—S. & H. No. 8800, double field.

LIGHT—100 W, concentrated filament tungsten.

LIGHT FILTER—3 cm. of 3 per cent potassium bichromate solution.

100 POINT OF INSTRUMENT verified to 0.01° by comparison with a quartz plate standardized by the Bureau of Standards.

TUBE LENGTH measured by a standardized comparator to 0.03 mm.

FLASK used for making up solutions for direct polarization and for inversion made with special narrow neck—calibrated to 0.02 cc.

CONCENTRATION OF SOLUTIONS FOR DIRECT POLARIZATION—determined by weight as well as by volume, then calculated to grams solids per 100 cc., thus eliminating correction for moisture in the sugar and giving concentration exact to 0.01 g. per 100 cc., or 0.004° V.

VOLUME OF SOLUTION USED FOR INVERSION—checked by weight. After inversion and completion to volume, cooled solution was placed in the same "inversion tube" used for direct polarization and allowed to stand for approximately half an hour in the saccharimeter trough till it had assumed the same temperature as the instrument and the atmosphere, before reading.

WEIGHTS USED—corrected to 0.0001 g. by standard weights.

THERMOMETERS—corrected by gas thermometer.

"PROBABLE ERROR" OF READING INSTRUMENT (average of 10 readings)—For direct polarization 0.01° V. For invert polarization 0.02° V.

for several days. It was then found to contain: Moisture, 0.02 per cent; ash, 0.004 per cent; reducing sugars, less than 0.016 per cent (using Ost's solution).

The direct polarization of this sugar, using 26.000 g. dry sugar (weighed in air with brass weights) in 100 true cc. was, at 22.0° C., after adding 0.06 for temperature correction, 99.86. Adding 0.02 as a correction for reducing sugars and ash would give 99.88 as the polarization of 26 g. pure sucrose dissolved in 100 true cc. solution at 20° C.

Fifty cc. of the solution used for direct polarization were then inverted by the Herzfeld method and eventually polarized at 22.2° C. Using the factor 142.66, the calculated per cent sucrose of this sugar, corrected for reducing sugars and ash, was 100.07.

As a check on the above determination, a sample of pure sucrose was obtained from the Bureau of Standards, Washington, D. C. Its certified analysis was as follows: Moisture, 0.002 per cent.; ash, 0.002 per cent; invert sugar, less than 0.003 per cent. Its direct polarization, then, should exceed 99.99°.

At 23.95° C. the direct polarization actually found was, corrected for temperature, 99.90. Its sucrose by the Clerget-Herzfeld method, using the factor 142.66, was 100.09, showing a difference between direct polarization and "sucrose by Clerget" of 0.19 per cent.

From the last experiment it appears that the Clerget factor, if designed to give a reading of 100 per cent

[1] Paper presented at the Annual Meeting of the Hawaiian Chemists' Association, October 22, 1914.

for pure sucrose with the present sugar scale, should be increased from 142.66 to 142.78, while if it is intended to give the same figure as the direct polarization of pure sucrose, regardless of the scale used, which is more logical, it should be further increased to 142.92.

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## THE NITROGEN AND FAT IN SHORT STAPLE COTTONSEED

By C. A. Wells and F. H. Smith

Received December 21, 1914

The cotton plant breeders of the past have directed their efforts mainly towards increasing the yield and length of lint of cotton as well as its power of resistance, while the question of next importance, *i. e.*, the relative percentage of nitrogen and fat in different types of seed, has received little consideration. The manufacture and preparation of cottonseed oil and its products and of cottonseed meal constitute important industries within themselves. Modern and intelligent management of these industries is beginning to demand a more thorough understanding of the properties of the different varieties of seed. Already there is a wide-spread and growing endeavor on the part of the manufacturer to purchase seed containing a high percentage of fat and nitrogen, particularly the latter.

A study has been made in this laboratory of the commercially important chemical constituents of eighteen varieties of short staple cottonseed. These varieties were selected as typical for the upland sections of Alabama, Georgia and other states similarly situated. They were grown upon the same kind of soil (a red clay) which had been uniformly fertilized. This was deemed necessary because experience had indicated that both the type of soil and nature of fertilizer may affect the nitrogen and oil content of the seed. The cotton was ginned in one gin under conditions as nearly uniform as possible and the remaining lint was removed by hand with a scalpel. Even though tedious, this was essential because, as will be shown in Table I, the lint not removed from the seed by the gin may vary from 97 to 214 lbs. per 1000 lbs. of seed, so that it is inaccurate to base analytical results upon the original weight of seed, as has often been done, without proper consideration for the unremoved lint. The hulls were removed by hand and the kernels analyzed, using the Gunning-Arnold-Dyer modification of the Kjeldahl method for nitrogen, allowing for nitrates, and the vacuum-sulfuric acid procedure for moisture. It was not found feasible to determine the moisture in kernels or in cottonseed meal by the usual method of drying in an oven, because decomposition took place even at 60°. Similarly it was found necessary to dry the flasks containing the ether extracts by immersing them deeply into the boiling water of the water bath instead of drying on the water bath or in the drying oven.

The analytical results are given in Table I in order of nitrogen-ascendency in two groups of nine varieties each.

Table I—Percentage Composition of Upland Short Staple Cotton-seed

| No. | Variety | Seed lint | Delinted Seed Hulls | Delinted Seed Kernels | Kernels Moisture | Kernels Fat | Kernels Nitrogen |
|---|---|---|---|---|---|---|---|
| 1 | Niel's big boll | 19.13 | 35.00 | 65.00 | 7.06 | 41.10 | 5.16 |
| 2 | Mexican big boll | 16.61 | 33.90 | 66.10 | 9.75 | 36.20 | 5.21 |
| 3 | Caldwell's big boll | 20.30 | 36.90 | 63.10 | 7.83 | 39.80 | 5.21 |
| 4 | Cook's reimproved | 16.49 | 34.80 | 65.20 | 7.74 | 40.00 | 5.22 |
| 5 | Sunbeam | 18.09 | 34.20 | 65.80 | 6.42 | 40.35 | 5.23 |
| 6 | Cleveland big boll | 18.12 | 34.40 | 65.04 | 6.56 | 43.50 | 5.26 |
| 7 | Kimbrough | 21.43 | 36.50 | 63.50 | 9.29 | 48.04 | 5.32 |
| 8 | Poulnot | 12.96 | 34.60 | 65.40 | 7.80 | 44.06 | 5.39 |
| 9 | Willet's perfection | 18.34 | 35.30 | 64.70 | 6.60 | 41.20 | 5.49 |
| | Average | 17.94 | 35.07 | 64.87 | 7.67 | 41.58 | 5.27 |
| 10 | Schley | 9.74 | 34.3 | 65.7 | 6.89 | 42.70 | 5.63 |
| 11 | Pevy's improved | 10.75 | 33.30 | 66.70 | 8.67 | 42.72 | 5.65 |
| 12 | Cook's improved | 17.45 | 35.70 | 64.30 | 6.53 | 37.80 | 5.69 |
| 13 | Jarman K. sunbeam | 19.50 | 37.40 | 62.60 | 7.16 | 35.20 | 5.75 |
| 14 | Willet's ideal | 20.35 | 35.60 | 64.40 | 6.51 | 42.30 | 5.82 |
| 15 | Cook's No. 675 Ala. Exp. Station | 20.84 | 36.60 | 63.40 | 8.85 | 37.60 | 6.00 |
| 16 | Wanamaker's ext. big boll —storm proof | 14.92 | 35.20 | 64.80 | 7.58 | 35.50 | 6.15 |
| 17 | King & triumph hybrid | 13.46 | 36.70 | 63.30 | 8.04 | 43.43 | 6.20 |
| 18 | Hite's early prolific | 13.24 | 33.33 | 66.7 | 7.48 | 37.26 | 6.22 |
| | Average | 15.58 | 35.32 | 64.52 | 7.52 | 39.39 | 5.90 |

Attention has been called already to the difference in lint which the process of ginning may leave on the seed. From Table I it will be seen, also, that the fat in the kernels may vary from 35.2 to 48.04 per cent and the nitrogen from 5.16 to 6.22 per cent. If the average be taken for the two arbitrarily chosen groups of nine varieties each as given in the table, it will be seen that the fat varies only slightly, especially if consideration is had for the difference in lint on the seed, while the nitrogen shows a variation of approximately 10 per cent. Thus a ton of mixed cottonseed from the second group would contain 8.3 lbs. more nitrogen and 13.6 lbs. less oil than a ton of seed made up similarly from Group 1. This amount of nitrogen has a value of approximately $2.00 and the oil a value of about 50 cents for the expressible portion with a slight feeding value for the non-expressible portion, leaving a balance of approximately $1.50 a ton in favor of the high nitrogen seed. This means a great saving on the total of 5,000,000 tons of cottonseed crushed annually in the South. It will be interesting in the future to ascertain if the variations noted here are constant or if they change with the seasons.

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## UNSAPONIFIABLE MATTER IN GREASES

By E. Twitchell

Received November 30, 1914

The following method of determining unsaponifiable matter in greases has been in use under my direction in the laboratory of the Emery Candle Co. for five or six years.

Five grams of the sample (or preferably of the fatty acid prepared for "titer test," as this is cleaner) are saponified with alcoholic potash in a dish and evaporated nearly to dryness. A little alcohol is added and then water, and the solution obtained is washed into a separatory funnel. The ratio of alcohol to water in this soap solution should be about 1 : 4, and the total volume of the soap solution 150 to 200 cc. The soap solution is shaken twice with ether, using about 50 cc. each time. The ether extracts are united, washed once with water, then shaken

with dilute hydrochloric acid, washed again with water, transferred to a weighed dish, evaporated, dried at 110° C. and weighed. This residue consists chiefly of unsaponifiable matter, but contains fatty acids as the ether has dissolved some soap which is afterwards decomposed by the hydrochloric acid. It is therefore taken up with neutral alcohol and titrated with standard alkali solution. The fatty acids thus found, calculated as oleic acid, are deducted from the weight before obtained.

A third treatment with ether will extract so little more that for ordinary analytical work it may be omitted.

If the fatty acids obtained from the grease, instead of the grease itself, have been used, the result must of course be calculated on the original grease.

This method differs from that of Allen and Thomson, given by Lewkowitsch[1] as his preferred method, only in some details: chiefly the simple and accurate way of correcting for soap dissolved in the ether. Having this correction, it is not necessary to be sparing in the use of alcohol for fear of causing the ether to dissolve soap, but enough may be used to cause an almost instantaneous separation in the funnel of perfectly clear and sharply marked ethereal and aqueous layers. A determination of unsaponifiable matter can be easily completed in 1½ hours. Ether has been found to be the best general solvent for a variety of unsaponifiable matters found in fats and the objection that it dissolves some soap disappears when using this method.

The uncertainty as to the molecular weights of the fatty acids found by titration in the residue would lead to error, but when the small percentage of these fatty acids calculated on the original sample of grease is considered it will be seen that this error is entirely negligible, and the fatty acids may be calculated as oleic acid, or, an average molecular weight, as that of tallow fatty acids, may be taken.

The above method of determining unsaponifiable matter, when compared with other methods, has never given lower results. In some cases the results are higher, especially than those obtained where petroleum ether is used as the solvent. That the results are not too high has been repeatedly proven by a careful examination of the extract, particularly for neutral fat and for ethyl esters which might possibly have been formed from a little alcohol remaining in the ether when it is shaken with hydrochloric acid.

The details of this method were worked out by Mr. C. Foerster, who has used it in this laboratory, not only in the daily analysis of greases, but also with good results in extracting fats containing other than the usual kinds of unsaponifiable matter.

WYOMING, OHIO

## A NEW METHOD FOR THE DETERMINATION OF THE TOTAL FATTY ACIDS AND OTHER ETHER-SOLUBLE CONSTITUENTS OF FEEDSTUFFS

By J B. RATHER[2]

Received October 27, 1914

Determination of fats by direct saponification of the sample has been proposed by Liebermann and Szekely[1] and by Kumagawa and Suto.[2] These methods are open to several objections, chief among which are that they make no adequate provision for the removal of non-fatty material from the extracts, and that the methods, giving results comparable with ether extracts of the same samples, yield products not only impure but incompletely extracted.

While it has long been known that ether does not extract all of the ether-soluble constituents of plant and animal products, the extraction is generally considered to be complete enough for practical purposes.

Dormeyer[3] states that ether extraction of meat is far from complete at the end of 100 hours. Browne[4] states that pepsin digestion of steer feces renders a larger amount soluble in ether than can be obtained from untreated samples. Fraps and Rather[5] show that chloroform extracts considerable ether-soluble matter from hays which have previously been extracted with ether, and that this extract contains fatty acids.

We have been unable to find any mention in the literature of the use of *alcoholic* soda or potash as a solvent for fats in plant or animal products.

### EXPERIMENTAL

A method was developed for the determination of total fatty acids and other ether-soluble constituents of feedstuffs. The experimental evidence on which the method is based may be found elsewhere.[6] The following factors were considered in the development of the method (alcoholic soda method): 1—Completeness of saponification; 2—unsaponified material in the fatty acids; 3—fatty acids in the unsaponified material; 4—completeness of the extraction of the fatty acids by petroleum ether; 5—completeness of extraction of the saponified residue; 6—saponified residue in fatty acids; 7—saponified residue in the unsaponified material; 8—washing required to remove hydrochloric acid after liberating acids in unsaponified material; 9—the checking of duplicate determinations run at different times; 10—completeness of direct saponification; and 11—completeness of the extraction of the ether-soluble matter from the alcoholic soda extract.

The following determinations were made on twelve samples of hays and excrements from them, and on twelve samples of concentrated feeding-stuffs: ether extract by the Official Method;[7] constituents of the ether extract by the Precipitation Method;[8] and ether-soluble constituents by the Alcoholic Soda Method given below. The Precipitation Method is the same as the Alcoholic Soda Method with the principal exception of the method of extracting the ether-soluble matter from the sample.

The Alcoholic Soda Method, while very rapid, requires a knowledge of its technique for satisfactory results, so it is given below in detail.

[1] Lewkowitsch, "Chem. Technology and Anal of Oils, Fats and Waxes," 5th Ed. Vol. I, p. 458.

[2] Under the general direction of G. S. Fraps, Chemist. Abstracted by the author from Texas Exper. Sta., *Bull.* **169.**

[1] *Pflüger's Arch.*, **72** (1898), 360-366.

[2] *Biochem. Zeit.*, **8**, 212.

[3] *Pflüger's Arch.*, **61**, 341-43.

[4] *Proc. 20th Conv. A. O. A. C.*

[5] Texas Station, *Bull.* **162.**

[6] *Loc. cit.*

[7] U. S. D. A., Bureau Chem., *Bull.* **107** (revised).

[8] Texas Experiment Station, *Bull.* **169.**

EXTRACTION OF ETHER-SOLUBLE MATERIAL—Digest 10 g. of the sample, or 5 g., if it contains more than 4 per cent ether extract, or is bulky, with 50 cc. of approximately 2 *N* alcoholic soda, for one hour under a reflux condenser. Filter with suction through asbestos in a carbon funnel of suitable size and wash 10 times with boiling alcohol (redistilled). Transfer to a dish with water and evaporate to about 10 cc. Transfer with hot water to a pear-shaped separatory funnel. Acidify with 10 cc. acetic acid, and extract the warm solution 5 times with 50 cc. portions of ethyl ether (redistilled).

DETERMINATION OF UNSAPONIFIED MATTER[1]—Transfer the ether extract to a 500 cc. separatory funnel, wash once with 50 cc. water and remove the bulk of the suspended matter in the manner described under Determination of Fatty Acids below. Add to the etheral solution 10 cc. of a warm 1:2 aqueous sodium hydroxide solution, turn the funnel on its side and shake gently. Allow the precipitate to settle, add 25 cc. warm water, hold funnel in vertical position and give rotary motion. Allow the two layers to separate, and draw off the clear aqueous solution into a 500 cc. Erlenmeyer flask, leaving any emulsion in the funnel. Repeat and then shake gently as above with 5 successive 30 cc. portions of cold water, allowing a short time for the two solutions to separate, and add the washings to the soap solution in the flask. Transfer the ethereal solution to a tared 200 cc. flask, evaporate or distil off the ether, and dry to constant weight in a steam oven at 100° C.

CORRECTION FOR FATTY ACIDS IN UNSAPONIFIED MATTER (For material high in fatty acids and low in unsaponified only)—Add 20 cc. of 0.2 *N* hydrochloric acid to the ethereal solution of the unsaponified matter in the separatory funnel before evaporation, stopper and shake vigorously. Draw off the aqueous layer and discard. Evaporate the ethereal solution as above, dry and weigh. Heat to boiling with 20 cc. alcohol, titrate with 0.1 *N* sodium hydroxide and phenolphthalein, running a blank on the alcohol. Multiply the corrected reading by 0.28 (or 0.56 if 5 g. sample is taken). The result is percentage fatty acids in the unsaponified matter. Subtract this figure from the percentage of unsaponified matter and add it to the fatty acids (below). The amount of fatty acids dissolved in the ethereal solution of the unsaponified matter is, on an average, 16 mg. for substances very low in unsaponified matter, and this figure may be used if very accurate results are not desired. No correction for fatty acids in unsaponified matter is necessary for products containing 25 or more per cent unsaponified matter.

DETERMINATION OF THE FATTY ACIDS—Heat the soap solution on a steam bath to remove dissolved ether, shaking gently from time to time. This must be done carefully to avoid frothing of the soap. Cool the soap solution nearly to room temperature under the tap, add 8 cc. of glacial acetic acid or its equivalent in weaker acetic acid, and extract in the separatory funnel with 40 cc. of redistilled petroleum ether, distilling below 75° C., shaking violently. Draw off aqueous layer, hold funnel in a vertical position and give it a rotary motion and let stand a minute. This will cause the suspended matter to settle in a compact mass at the bottom of the funnel. Draw off this portion into the flask containing the aqueous mixture. Extract the aqueous mixture 3 times more in a similar manner. By using a pear-shaped funnel and following the above method, filtration to remove suspended matter may generally be avoided. Shake well with two 50 cc. portions of water to remove suspended matter and traces of inorganic substances, allowing any emulsion to go into aqueous mixture. Extract the latter a fifth time with petroleum ether, and after washing this extract twice with small portions of water, add to other extracts. Evaporate and dry to constant weight. If the evaporation is carried to completeness on a steam bath, the flask being turned on its side to facilitate removal of gasoline fumes, the product may be dried to constant weight in 3 or 4 hrs. This fraction is fatty acids.

DETERMINATION OF SAPONIFIED RESIDUE—Acidify further the aqueous residue from the extraction of the fatty acids, with hydrochloric acid, warm and extract 5 times as above with 40 cc. portions of ethyl ether. Wash the combined extracts twice with 50 cc. portions of water, discard any suspended matter, evaporate and dry to constant weight.

The results are shown in the following table.

PERCENTAGE TOTAL FATTY ACIDS AND OTHER ETHER-SOLUBLE CONSTITUENTS OF SOME FEEDS AND EXCREMENTS

| No. | | Unsaponified in | | Total Fatty Acids in | | Saponified Residue in | |
|---|---|---|---|---|---|---|---|
| | | Ether extr. | Alc. soda extr. | Ether extr. | Alc. soda extr. | Ether extr. | Alc. soda extr. |
| 1 | Wheat shorts | 3.79 | 0.23 | 0.24 | 3.08 | 4.43 | 0.39 | 0.71 |
| 2 | Corn chops | 4.31 | 0.16 | 0.18 | 3.77 | 4.34 | 0.14 | 0.27 |
| 3 | Cottonseed meal | 15.23 | 0.47 | 0.31 | 13.82 | 14.46 | 0.18 | 0.38 |
| 4 | Rice bran | 7.75 | 0.60 | 0.65 | 6.21 | 8.10 | 0.72 | 0.91 |
| 5 | Milo maize chops | 3.22 | 0.21 | 0.21 | 2.05 | 2.92 | 0.64 | 0.19 |
| 6 | Cold pressed cotton seed | 7.26 | 0.29 | 0.23 | 6.49 | 7.32 | 0.24 | 0.26 |
| 7 | Kafir chops | 3.20 | 0.26 | 0.26 | 2.57 | 3.18 | 0.60 | 0.24 |
| 8 | Corn bran | 8.59 | 0.29 | 0.34 | 5.50 | 8.13 | 1.70 | 0.59 |
| 9 | Red rice | 1.64 | 0.15 | 0.21 | 1.04 | 1.81 | 0.25 | 0.34 |
| 10 | Wheat bran | 4.10 | 0.25 | 0.25 | 3.50 | 4.41 | 0.14 | 1.01 |
| 11 | Wheat shorts | 2.65 | 0.17 | 0.23 | 2.22 | 2.84 | 0.12 | 0.31 |
| 12 | Rice polish | 10.38 | 0.51 | 0.70 | 8.53 | 10.29 | 0.55 | 0.50 |
| 13 | Tobosa grass | 0.92 | 0.56 | 0.44 | 0.30 | 0.61 | 0.18 | 1.57 |
| 14 | Excrement from No. 13 | 1.06 | 0.70 | 0.75 | 0.25 | 0.90 | 0.17 | 1.85 |
| 15 | Prairie hay | 2.30 | 0.84 | 0.78 | 0.65 | 1.11 | 0.44 | 2.00 |
| 16 | Sudan grass | 1.46 | 0.55 | 0.49 | 0.63 | 1.03 | 0.23 | 1.71 |
| 17 | Excrement from No. 15 | 2.83 | 1.68 | 1.74 | 0.90 | 1.49 | 0.36 | 3.02 |
| 18 | Excrement from No. 16 | 1.90 | 1.41 | 1.50 | 0.25 | 1.61 | 0.34 | 2.62 |
| 19 | Sudan straw | 1.44 | 0.55 | 0.65 | 0.67 | 1.29 | 0.16 | 1.75 |
| 20 | Sorghum hay | 1.82 | 0.49 | 0.55 | 0.89 | 1.17 | 0.29 | 1.60 |
| 21 | Excrement from No. 19 | 1.71 | 1.09 | 1.29 | 0.39 | 1.64 | 0.20 | 2.44 |
| 22 | Moth bean hay | 1.55 | 0.66 | 1.03 | 0.62 | 1.70 | 0.27 | 1.25 |
| 23 | Excrement from No. 20 | 1.78 | 1.08 | 1.24 | 0.62 | 1.71 | 0.25 | 2.87 |
| 24 | Excrement from No. 22 | 3.03 | 1.99 | 2.20 | 0.62 | 2.28 | 0.46 | 2.53 |
| | Average for concentrates | 6.01 | 0.30 | 0.32 | 4.90 | 6.02 | 0.50 | 0.48 |
| | Average hays and excrements | 1.82 | 0.97 | 1.06 | 0.57 | 1.38 | 0.28 | 2.10 |

THE TOTAL FATTY ACIDS—This heading covers all fatty acids, whether free or combined, that may be saponified, except volatile fatty acids, which are probably not present in appreciable amount.

The fatty acids in the concentrates make up from 64 to 84 per cent of the ether extract. The fatty acids in the alcoholic soda extracts of these samples averaged 19 per cent higher than those of the ether extract, or about the same as the total ether extract of the concentrates.

The fatty acids in the ether extract of the hays and excrements make up from 13 to 49 per cent of the ether extract, with an average of 31 per cent. The results by the Alcoholic Soda Method are higher in

[1] "Precipitation Method," THIS JOURNAL, 7, 34.

every case, averaging 250 per cent as much as by the Ether Extraction Method.

THE UNSAPONIFIED MATTER—The unsaponified matter in the ether-soluble portion of the alcoholic soda extracts of the concentrates varied from 0.21 per cent in red rice to 0.65 per cent in rice bran, and averaged 0.32 per cent. The unsaponified matter in the ether extract of the concentrates is essentially the same in amount as that in the alcoholic soda extract, averaging 0.02 per cent lower than the latter. The unsaponified matter in the alcoholic soda extracts of the hays and excrements from them varied from 0.44 per cent in Tobosa grass to 2.20 per cent in excrement from mothbean hay and averaged 1.06 per cent. The unsaponified matter in the alcoholic soda extract averages 0.07 per cent (in per cent of sample) higher than the corresponding fraction of the ether extract.

THE SAPONIFIED RESIDUE—Under this head we include all ether-soluble, saponifiable material difficultly soluble in petroleum ether. Practically all of the chlorophyll, when present, is found in this fraction.

The saponified residue in the alcoholic soda extract of the concentrates varied from 0.19 per cent in milo maize chops to 1.01 per cent in wheat bran, and average 0.48 per cent. The similar fraction in the ether extract varies considerably, but averages the same.

The saponified residue in the alcoholic soda extract of hays and excrements varied from 1.25 per cent to 3.02 per cent, and averaged 2.10 per cent. This is over twice as much as the average for the ether extracts of the same samples. The saponified residue of the ether extract of the hays and excrements was, in every case, much higher, averaging 0.28 per cent, less than 15 per cent of the average for the saponified residue of the alcoholic soda extract.

The nature of the fatty acids not extracted by ether, and the reasons for considering that the fraction, saponified residue, contains no fatty acids are discussed in another place.[1] It may be stated here, however, that these fatty acids have mean molecular weights of about the same magnitude as several of the most common fatty acids.

The results presented here show that on an average 14 per cent of the ether extract of these concentrates and 68 per cent of the ether extract of hays, and excrements from them, consist of non-fats. If anything more than an approximation of the fat content of a hay is desired, some method must be resorted to which will remove unsaponifiable matter and saponifiable non-fats soluble in ether. We believe that the Precipitation Method described elsewhere[1] is rapid, accurate and simple enough to be used as a routine as well as a research method for this purpose.

The results show that ether is at best a very imperfect medium for the extraction of the total fatty acids of feedstuffs, and that alcoholic soda gives much higher results in most cases.

SUMMARY

A method for the determination and fractionation of the total fatty acids and other ether-soluble constituents of plant products is proposed which gives much higher results than does extraction with ether. Total fatty acids by this process were one-fifth higher in the concentrates and more than twice as high in the hays and excrements, than by extraction with ether.

The ether extract of these concentrated feedingstuffs contained on an average 14 per cent non-fats, and that of the hays and excrements 68 per cent non-fats. Ether extraction is a very imperfect method of determining fats or of total fatty acids in plant products.

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[1] Texas Experiment Station, *Bull* **169**.

## A CHEMICAL STUDY OF TWO DROUGHT-RESISTING FORAGE PLANTS

By S LOMANITZ

Received November 25, 1914

The two plants, the analyses of which are given below, have been introduced into Mexico for experimental purposes by Dr. Mario Calvino, now Chief of the Central Agricultural Experiment Station of Mexico. The first, commonly known as "Rhodes Grass" (*Chloris virgata* or *Ch. Abyssinica* or *Ch. Gayana*), has been grown with great success in the dry arid regions of Australia, Costa Rica and Mexico. The second, *Phalaris nodosa* or *Ph. bulbosa*, called erroneously *Ph. commutata*, has been grown in Italy, Algeria and Mexico. Freezing has very slight effect on the former but none on the latter. Both are practically unaffected by drought and are excellent forage plants since cattle eat them very readily and they exert no harmful effects upon the milk. The plants grow well under a wide range of conditions and give very good yields.

| | Rhodes Grass | | | Phalaris Nodosa | | |
|---|---|---|---|---|---|---|
| Per cent | Air-dry | Dried at 100° C. | Green | Air-dry | Dried at 100° C. | Green |
| Moisture (at 100° C.) | 8.30 | 0.0 | 68.83 | 9.15 | 0.0 | 77.84 |
| Crude protein (N × 6.25) | 6.87 | 7.49 | 2.33 | 10.54 | 11.60 | 2.57 |
| Crude fat | 1.64 | 1.79 | 0.56 | 2.66 | 2.93 | 0.65 |
| Ash | 11.39 | 12.42 | 3.87 | 12.77 | 14.05 | 3.11 |
| Crude fiber | 28.42 | 30.99 | 9.66 | 25.82 | 28.42 | 6.30 |
| Nitrogen-free extract | 43.38 | 47.31 | 14.75 | 39.06 | 43.00 | 9.53 |
| PROTEIN AND CARBOHYDRATE COMPOUNDS | | | | | | |
| Pure protein (Grandeau's method) | 5.00 | 5.45 | 1.70 | 7.81 | 8.59 | 1.90 |
| Digestible protein (Sjollema's pepsin method) | 3.25 | 3.54 | 1.10 | 6.25 | 6.88 | 1.52 |
| Amide, etc., nitrogen | 0.30 | 0.33 | 0.10 | 0.44 | 0.48 | 0.11 |
| Reducing sugars (Allihn's method) | 1.37 | 1.49 | 0.46 | 1.69 | 1.86 | 0.41 |
| Sucrose (Clerget's method) | 1.31 | 1.43 | 0.44 | 2.02 | 2.22 | 0.49 |
| Soluble starch and dextrin | 0.76 | 0.83 | 0.26 | 1.19 | 1.31 | 0.29 |

The analyses given above were made of plants furnished by Dr. Calvino, and grown in the experimental plots of the Division of Horticulture of this Experiment Station. They were of about a meter length, the seeds being already formed but not ripened. For the analyses the whole plant, stalk and ear, were taken.

From the above analyses it can be seen that both these grasses have a comparatively high nutritive value. Especially is this the case with the Phalaris. The proportion of the digestible protein is especially high in this last-named plant. The proportion of ash is rather high but this seems to be a characteristic of quite a number of grasses grown here.

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## THE DETERMINATION OF AMMONIA IN SOILS

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Theoretically, the ideal method for ammonia in soils would give the absolute amount of ammonia present as such and as the ammonium radical, but in the light of our present knowledge, it cannot be said beyond all doubt that any conceivable method would give this ideal result. This is true because a large part of the nitrogen of the soil is present in protein and protein degradation products, the extensive decomposition of which gives large amounts of ammonia. The uncertainty regarding just what products are present does not permit the finding of conditions which we can be certain will expel ammonia already present and not decompose any material to give, among other products, ammonia. The problem is further complicated by the well-known absorptive and adsorptive powers of the soil. Therefore, since this ideal result is not attainable, in our opinion the value of any method will depend upon whether it fulfils the requirements given below.

### REQUIREMENTS OF A METHOD FOR AMMONIA

I—Closely agreeing duplicate results should be given and the same result obtained whether the reagent or reagents act, within reasonable limits, for a longer or shorter period. Of course, the reagent or reagents must not include any which are known to decompose material contained in the soil to give ammonia. For instance, it would not be permissible to use strong, hot hydrochloric acid, for this reagent decomposes proteins to give large amounts of ammonia.

II—Upon the addition of a known amount of ammonia, the method must give this added amount plus that previously found in the soil. Not enough time, of course, should elapse between the addition of the ammonia and the determination for any bacterial action to take place. In soils already containing ammonia, and apparently all soils do, it is difficult to see how any chemical reaction could, in a reasonable length of time, change the added nitrogen to some other combination than the ammonium. Because his method does not recover all added ammonia, Russel assumes the ammonia to be chemically changed. This will be further discussed later.

III—For use in a soils laboratory, the method should permit one to run several determinations within a reasonable length of time.

### DISCUSSION OF METHODS

The seven methods for ammonia are discussed below.

I—Schloesing's first method[1] consists in leaving a mixture of the soil with strong sodium hydroxide solution under a bell jar, together with a vessel containing some standard acid to absorb the ammonia evolved. This method has fallen into complete disuse because of the recognition of the fact that strong sodium hydroxide solution even in the cold would gradually decompose the organic nitrogen compounds to give ammonia.

II—In Schloesing's second method[1] the soil is treated with dilute hydrochloric acid until the liquid remains distinctly acid. The mixture is then well shaken, filtered and an aliquot portion distilled with alkali. Since this method complies with the third requirement named above, and since no evidences in the literature that it does or does not comply with the first two can be found, the method has been given a rather detailed examination by us, the results of which are reported and discussed in the experimental part of this paper.

III—In Boussingault's method,[1] a mixture of about one part of soil to two parts of water, together with a little magnesia, is distilled into standard acid. It is quite generally admitted that this method does not give true results with material containing protein and protein degradation products as does the soil. Yet, because of its ease and simplicity of manipulation, it is often used, it being stated that the results, although not absolute, are comparable with one another. This method has also been examined by us and the results will be taken up in the experimental part of this paper.

IV—The method of Wolf and Knop[2] consists in treating the soil with sodium hypobromite, which reacts with the ammonia to give nitrogen gas which is measured. Baumann[2] has shown that this method does not give accurate results.

V—In Baumann's method[3] a hydrochloric acid extract is made as in Schloesing's second method. To this extract, magnesia is added and ozone is bubbled through the solution, and it is then treated with sodium hypobromite and the nitrogen collected and measured. In view of the facts which are brought out below in regard to the hydrochloric acid extract of soils, together with the fact that the sodium hypobromite used contained an excess of sodium hydroxide which would gradually decompose nitrogenous organic compounds to give ammonia, Methods IV and V may be considered as unreliable.

VI—In Russel's first method,[3] 150 g. of soil are distilled at the pressure obtainable with a water pump with 2 g. of magnesia suspended in 100 cc. of water. The distillation flask is kept at 40° C., and the distillation continued for six hours.

VII—Russel's second method[4] is just like his first method, except that the 2 g. of magnesia are replaced by 0.7 g. potassium hydroxide and the 100 cc. of water by an equal volume of alcohol, and the temperature of the distillation flask is kept at 25° C. instead of 40° C. Russel states that in so far as he has tested his methods, they give practically identical results. He also points out that with the use of magnesia there is some decomposition. Indeed, with the soil upon which he reports he obtained both on the second and the third distillation as much ammonia as was obtained on the first.

Although Russel shows that his potash method gives concordant results and no ammonia is evolved after a reasonable length of time (first requirement), yet upon addition of ammonia to the soil, only from 50 to 84 per cent is recovered by either method. Hence,

[1] *Analyse des Matieres Agricoles*, **1879**.

[1] *Agronomie*, **3** (1864), 206.

[2] *Chem. Centralbl.*, **1860**, pp. 243, 253.

[3] *Landw. Vers. Stat.*, **33** (1886), 247.

[4] *Jour. Agr. Sci.*, **3** (1910), 233.

they do not comply with the second requirement. He explains this by stating that the ammonia enters into a stable combination which is not an ammonium compound. It could be argued with equal force that the ammonia forms a relatively insoluble ammonium compound with the complex organic or inorganic material of the soil, or that it was physically adsorbed. It does not seem surprising that all the ammonia was not expelled when 50 cc. of water were left with the soil after the distillation was stopped, and the high solubility of ammonia[1] and the low solubility of magnesium hydroxide[2] are considered.

## EXPERIMENTAL

In the following work, the ammonia-free water which was used was prepared by boiling ordinary tap water for a few minutes with about two grams of potassium acid sulfate to one liter of water, and then distilling the solution and condensing the vapor in block-tin tubes which had previously been steamed for 12 hours. The distillate in every case was found to be neutral to alizarin red and gave but a slight indication of ammonia when tested with Nessler's solution.

Whenever magnesia was used, it was always freshly calcined.

Alizarin red was the indicator used in all ammonia titrations. It has been found by far the most satisfactory indicator for ammonia titrations, and it is now exclusively used for that purpose in this laboratory.

Blanks were always run and the suitable corrections made.

Duplicates were not run, except as reported.

The following soils were used in this work:

Soil No. 1—Southern Iowa loess
Soil No. 2—Iowa drift
Soil No. 3—Wisconsin drift
Soil No. 4—Mississippi loess
Soil No. 5—Missouri loess
Soil No. 6—Alkali I
Soil No. 7—Alkali II

Soils Nos. 1 to 5 were typical samples from the five principal soil areas of Iowa. Soils Nos. 6 and 7 were from the Wisconsin drift area.

## AMMONIA IN THE HYDROCHLORIC ACID EXTRACT OF SOILS

To find out whether the Schloesing method would give reliable results, it was examined as follows:

1—The strength of the hydrochloric acid used for extraction was varied.

2—The time of extraction was varied.

3—Known amounts of ammonia as sulfate were added to the soil and it was then extracted with different strengths of hydrochloric acid for different lengths of time.

All of the acid extracts were obtained by shaking in a mechanical shaking machine for the indicated length of time a mixture of one part of air-dry soil with two parts of ammonia-free acid. When ammonia was added, it was done by means of standard ammonium sulfate solution immediately before the addition of acid of suitable strength to give the desired normality. Thus, any appreciable bacterial change of the ammonia was precluded. After removing from the shaking machine, the mixture was filtered through a double folded filter, a clear filtrate being obtained in all cases. For the magnesia distillation, 200 cc. of the filtrate, representing 100 g. of soil, were distilled after the addition of about 10 g. of magnesia until 150 cc. of distillate had been collected. In some cases, 0.1 *N* acid and alkali were used in the titrations, and in others 0.02 *N*. The results of the magnesia distillations are given in Table I.

TABLE I

| Soil No. | Lab No. | Normality of acid | Time shaken Min. | Mgs. N as ammonia Added | Found Duplicates | | Average | N recovered Mgs. | Per cent |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1, 2 | 0.2 | 20 | None | 1.26 | 1.19 | 1.23 | | |
| | 3, 4 | 0.3 | 20 | None | 1.26 | 1.26 | 1.26 | | |
| | 5, 6 | 0.2 | 60 | None | 1.26 | 1.23 | 1.25 | | |
| | 7, 8 | 0.3 | 60 | None | 1.26 | 1.26 | 1.26 | .... | .... |
| | 9, 10 | 0.2 | 30 | 2.25 | 2.60 | 2.60 | 2.60 | 1.35(*a*) | 60.0 |
| | 11, 12 | 0.3 | 30 | 2.25 | 2.60 | 2.64 | 2.62 | 1.37(*a*) | 60.9 |
| 3 | 13 | 0.2 | 20 | None | 0.772 | | .. | | |
| | 14 | 0.3 | 20 | None | 0.842 | | | | |
| | 15 | 0.2 | 60 | None | 0.814 | | | | |
| | 16 | 0.3 | 60 | None | 0.482 | | | | |
| | 17 | 0.2 | 20 | 2.25 | 2.32 | ... | .... | 1.55 | 68.0 |
| | 18 | 0.3 | 20 | 2.25 | 2.22 | ... | .... | 1.38 | 61.3 |
| | 19 | 0.2 | 60 | 2.25 | 2.25 | ... | .... | 1.44 | 64.0 |
| | 20 | 0.3 | 60 | 2.25 | 2.36 | ... | .... | 1.32 | 67.6 |

(*a*) In computing these values the average of the averages of Nos. 1 to 8 were used

The results in Table I show that within reasonable limits no ammonia enters into solution after 20 min., and that also within the limits of the experiment the amount of ammonia dissolved is independent of the strength of acid. It is also shown that not nearly all the ammonia which was added was recovered. The rather wide variation of the percentages recovered in the case of Soil 3 is due to the error in the determination of such a small amount of ammonia as was in this soil.

Since the hydrochloric acid extract undoubtedly contains some organic nitrogenous material, it was of some interest to subject the residues in some of the distillation flasks to a second distillation. Accordingly, 150 cc. of ammonia-free water were added to each of the flasks of Nos. 1 to 4 and 150 cc. distilled as before. The results are given in Table II.

TABLE II

| Lab. No. | Residues from | Mgs. N as ammonia found |
|---|---|---|
| 21..... | No. 1 | 0.28 |
| 22..... | No. 2 | 0.27 |
| 23..... | No. 3 | 0.42 |
| 24..... | No. 4 | 0.39 |

It is seen that an appreciable amount of ammonia is given in each instance, and this no doubt comes from a decomposition of organic material. To further test this point and to test the applicability of Folin's[1] method for ammonia to the hydrochloric acid extract of soils, 100 cc. portions of the same filtrates of which 200 cc. were used in experiments Nos. 1 to 4 were aerated for four hours, after the addition of 4 g. of sodium carbonate, in an apparatus which will be described later. The results are given in Table III, and are for 100 g. of soil. For purposes of comparison, the results obtained by distillation with magnesia are repeated here.

TABLE III

| Lab. No. | From same filtrate as was used in | Mgs. N as ammonia found by Aeration | Distillation |
|---|---|---|---|
| 25 | Nos. 1 and 2 | 1.26 | 1.23 |
| 26..... | Nos. 3 and 4 | 1.26 | 1.26 |
| 27..... | Nos. 5 and 6 | 1.26 | 1.25 |
| 28..... | Nos. 7 and 8 | 1.29 | 1.26 |

The aeration was continued for one hour more, but no ammonia was recovered. The results obtained by the

[1] Seidell, "Solubilities of Inorganic and Organic Substances," **1911**, p. 17. 30.7 g. per 100 g. water at 40° C. and 760 mm. pressure. At the pressure Russel used, the ammonia would be soluble to the extent of approximately 1 g. per 100 g. water.

[2] *Ibid.*, p. 181. 0.008–0.009 g. $Mg(OH)_2$ per liter of water at 18° C.

[1] *Z. physiol. Chem.*, **37** (1902), 161.

aeration method do not vary from those found by distillation by more than the experimental error. Owing to the possibility of decomposition with magnesia at 100° C. one would expect the results obtained by aeration to be slightly lower. The results show that this method can be applied to the hydrochloric acid extract and its desirability over the distillation method is recommended both from the standpoint of accuracy and ease of manipulation.

In Table IV are given the results obtained by aerating the acid filtrates from soils Nos. 2, 4 and 5 as outlined above. For purposes of comparison, the results are computed for 100 g. of soil, although as above they were obtained on 100 cc. of filtrate representing 50 g. of soil.

TABLE IV

| Soil No. | Lab. No. | Normality of acid | Shaken Min. | Mgs. N as ammonia Added | Found | Ammonia recovered Mgs. | Per cent |
|---|---|---|---|---|---|---|---|
| 5 | 29 | 0.2 | 20 | None | 1.10(*a*) | .... | .... |
| | 30 | 0.3 | 20 | None | 1.21 | .... | .... |
| | 31 | 0.2 | 60 | None | 1.24 | .... | .... |
| | 32 | 0.3 | 60 | None | 1.24 | .... | .... |
| | 33 | 0.2 | 20 | 2.25 | 2.63 | 1.40 | 62.2(*b*) |
| | 34 | 0.3 | 20 | 2.25 | 2.63 | 1.40 | 62.2(*b*) |
| | 35 | 0.2 | 60 | 2.25 | 2.59 | 1.36 | 60.4(*b*) |
| | 36 | 0.3 | 60 | 2.25 | 2.63 | 1.40 | 52.2(*b*) |
| 2 | 37 | 0.2 | 30 | None | 1.24 | .... | .... |
| | 38 | 0.2 | 30 | 2.25 | 2.80 | 1.56 | 69.3 |
| 4 | 39 | 0.2 | 30 | None | 0.53 | .... | .... |
| | 40 | 0.2 | 30 | 2.25 | 1.93 | 1.40 | 62.2 |

(*a*) Probably an error.
(*b*) In computing these results, the average of the results obtained in xperiments Nos. 30, 31 and 32 was used.

The results recorded in Table IV bring out about the same points as those in Table I: namely, that the amount of ammonia extracted is within the limits of the experiment independent of the strength of acid or the time of extraction and that not all of the added ammonia is recovered. For the soils tested, and these represented quite a range of soil types, we are forced to the conclusion that any method which depends upon an examination of the hydrochloric acid extract is not reliable. It might indeed be contended that treatment with fresh portions of hydrochloric acid would finally recover all the added ammonia. It is doubted if this point could easily be proven, for no doubt long-continued treatment of the soil with even this weak acid would gradually decompose organic matter with the production of ammonia. It was not thought worth while to investigate this point, for even if a method could be elaborated, it probably would not comply with the third requirement, *i. e.*, that of practicability. As to the cause of the failure to recover all the added ammonia, any answer would be purely speculative. In the course of some work which we shall publish later, we have found that the use of too rigorous flocculating agents to clear the solution for the determination of nitrates in the soil causes a decided lowering in the amounts of nitrates found. It is just possible that the phenomenon of the incomplete recovery of ammonia is due to the flocculating action of the acid.

## DISTILLATION OF SOIL AT ORDINARY PRESSURE WITH MAGNESIA

It has been shown[1] that successive distillation with magnesia of such substances as beef, eggs, dried blood and cottonseed meal gives for several distillations small but appreciable amounts of ammonia, but so far as we know, this method has never been critically examined with regard to soil. We have accordingly carried out the following tests:

100 g. of soil were placed in a copper flask, together with 200 cc. of ammonia-free water, a small piece of paraffin and about 10 g. of magnesia and distilled until 150 cc. of distillate had been collected in standard acid. The receiving flask was removed and another one with a suitable quantity of standard acid was put in its place: 150 cc. of ammonia-free water were then put in the copper flask and 150 cc. of distillate were again collected. This was repeated a third, and in the case of one soil, a fourth time. The results are given in Table V.

TABLE V—MGS. N AS AMMONIA

| Soil No. | Lab. No | Distillation 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| 1 | 41 | 3.51 | 1.54 | 0.91 | .... |
| | 42 | 3.16 | 1.54 | 0.91 | .... |
| 2 | 43 | 3.79 | 1.26 | 0.84 | .... |
| | 44 | 3.89 | 1.26 | 0.84 | .... |
| 3 | 45 | 2.67 | 1.12 | 0.81 | .... |
| | 46 | 2.67 | 1.12 | 0.84 | .... |
| 4 | 47 | 2.46 | 0.98 | 0.70 | 0.70 |
| | 48 | 2.53 | 0.84 | 0.70 | 0.63 |
| 5 | 49 | 3.16 | 0.77 | 0.98 | .... |
| | 50 | 3.26 | 0.77 | 0.91 | .... |

From the results recorded in Table V, it is apparent that the amount of ammonia obtained by distillation is dependent upon the duration of the distillation which is, of course, dependent upon the amount of water and soil used and upon the magnitude of the heat applied. The results of the following experiments emphasize the later point in a striking way. For each experiment, 100 g. of soil, 200 cc. of ammonia-free water, a small piece of paraffin and 10 g. of magnesia were used. The full flame of a large burner was used on each of the flasks of Nos. 51, 52, 55 and 56. The flames played directly upon the flasks, while in Nos. 53, 54, 57 and 58, a low flame was used, and each flask was protected with a wire gauze. The results are given in Table VI.

TABLE VI

| Soil No. | Lab. No. | Time, Min. | Mgs. N as ammonia |
|---|---|---|---|
| 1 | 51 | 40 | 2.80 |
| | 52 | 40 | 2.67 |
| | 53 | 150 | 4.63 |
| | 54 | 150 | 4.63 |
| 2 | 55 | 45 | 3.37 |
| | 56 | 40 | 3.09 |
| | 57 | 140 | 4.49 |
| | 58 | 160 | 5.34 |

From a consideration of the results in Table VI, although the conditions have been made extreme, there seems to be room for doubt as to whether even comparable results can be obtained by distillation with magnesia. Although one might regulate the gas flame during the distillation of a single series so that each gave about the same heat, yet the results obtained on different days or at a different time on the same day might be appreciably variable.

It is, therefore, seen from the data presented above and from the work of others which has been mentioned that there is no very reliable method available for the determination of ammonia in soils. That it is highly desirable to have such a method is apparent from the general importance of the soil nitrogen problem, and particularly in the study[1] of the influence

[1] Trescott, U. S. Dept. of Ag., Bur. of Chem., *Bull.* **132**, p. 20.

[1] Ehrenburg, *Landw. Ztg.*, **60** (1911), 441 and 479. Von Wlodeck, *Jour. Chem. Soc.* (Eng.), **102**, 2, 85; O. Lemmermann and L. Fresenius, *Landw. Jahrb.*, **45** (1913), 127.

of lime and various other substances added to soil upon its ammonia content; in the study of the ammonia evaporation from soils; in the study[1] of the direct assimilation of ammonia by higher plants and in the study of the ammonia problem in many other practical and theoretical phases. We have, therefore, attempted to find a method for the determination of ammonia in the soil which would comply with the three requirements named in the introduction to this paper. Our results as given below will show to what extent we have succeeded.

### AMMONIA IN THE SOIL BY AERATION

In 1902, Folin[2] outlined the method which, with some modifications, is largely used for the determination of ammonia in urine and various other physiological products. Originally, the method involved drawing air at the rate of 600 to 700 liters per hr., for 1 to 1½ hrs. through 25 cc. of urine containing 1 g. of sodium carbonate and 8 to 10 g. of sodium chloride. From the cylinder containing the urine the air passed through standard acid, which absorbed the ammonia. Steel and Gies[3] found that with urines containing magnesium ammonium phosphate crystals, low results were given because this salt was but slowly decomposed by sodium carbonate. It was later shown[4] that all urines upon the addition of sodium carbonate gave copious deposits of magnesium ammonium phosphate and, therefore, low results for ammonia. Steel,[5] therefore, recommends the use of 0.5 g. sodium hydroxide in place of the one gram of sodium carbonate. He found that with the use of these reagents (sodium hydroxide and sodium chloride) all the ammonia was readily driven off from triple phosphate crystals, and that apparently they did not decompose any organic materials, as no ammonia was obtained after four hours aeration. He also found that aeration of solutions of each of the following substances gave no ammonia: glycine, urea, uric acid, leucine, tyrosine, hippuric acid, guanine, allantoin, creatine and creatinine. Of these compounds, creatinine[6] and guanine[7] have been isolated from the soil by such methods as would make it appear that they were present as such and not in combination. Tyrosine[8] and leucine[9] have been isolated from the solution obtained by long-continued boiling of the soil with hydrochloric acid.

Since the aeration methods have been so successfully used in connection with ammonia determinations in urine, which contains a wide variety of organic nitrogenous products, we decided to make an attempt to modify it for use with soil. Since ammonia has been shown by Russel[10] and ourselves to be rather tenaciously held by the soil, the stronger reagent used in Steel's modification was first tried. In the course of some preliminary investigations, various forms of aeration apparatus were tried, but the form which was found most satisfactory was similar to the apparatus used by Kober[1] in his "Ammonia Distillation by Aeration" method. We use a 16 oz. bottle for the absorption bottle, and a 500 cc. round-bottomed Kjeldahl flask for the aeration flask. The air and ammonia enter the absorption bottle through a specially made absorption tube. The directions for making this tube are given by Folin.[2]

For any further details as to the setting up of the apparatus, the accompanying illustration should be consulted. The titration flask must always be set perpendicular to the table, and the long tube in the aeration flask should reach to within not more than 1/8 of an in. of the bottom of the flask. Both of these last precautions are necessary to secure adequate stirring of the mixture. Only four units are shown in the cut, but as many as fourteen determinations in series on one pump have been run. For all the work reported in this paper, a current of air of about 250 liters per hour was used.

In our trial of the Steel method, the following technique has been used: The "Alkali" was prepared by saturating ammonia-free water with sodium chloride. In order to be always sure that a saturated solution

was obtained, the calculated amount of the salt was added to a known volume of water. Sodium hydroxide was added at the rate of 2 g. per 100 cc. of water: 25 g. of soil were placed in a Kjeldahl flask. The absorption bottle was half-filled with ammonia-free water[3] and 10 cc. of 0.02 *N* sulfuric acid added. The apparatus was then connected up, the stopper in the Kjeldahl flask raised, 50 cc. of "Alkali" added, the stopper replaced and the flask shaken and the suction started.

The results are tabulated in Table VII, and are given for 100 g. of air-dry soil. For purposes of comparison the results obtained for the corresponding soils on the first distillation with magnesia are given.

TABLE VII

| Soil No. | Lab. No | Aeration Hrs. | Mgs. N as $NH_3$ by aeration | Soil No. | Lab No. | Aeration Hrs. | Mgs. N as $NH_3$ by Aeration | $NH_3$ by MgO |
|---|---|---|---|---|---|---|---|---|
| 1 | 59 | 4½ | 3.87 | 1 | 68 | 19 | 8.99 | 3.33 |
| | 60 | 4½ | 3.93 | 3 | 69 | 15 | 4.21 | .... |
| | 61 | 6 | 4.49 | | 70 | 15 | 4.49 | .... |
| | 62 | 6 | 4.63 | | 71 | 19 | 6.60 | .... |
| | 63 | 8 | 5.61 | | 72 | 19 | 6.46 | 2.67 |
| | 64 | 8 | 5.56 | 5 | 73 | 15 | 7.58 | .... |
| | 65 | 15 | 7.02 | | 74 | 15 | 7.86 | .... |
| | 66 | 15 | 7.30 | | 75 | 19 | 9.13 | 3.21 |
| | 67 | 19 | 8.70 | | 76 | 19 | 9.41 | .... |

Since after aerating fifteen hours ammonia was being given off in relatively large amounts, and because the

[1] Hutchinson and Miller, *Jour. Agr. Sci.*, **3**, 179.
[2] *Z. physiol. Chem.*, **37** (1902), 161.
[3] *Jour. Biol. Chem.*, **5** (1909), 71.
[4] Benedict and Osterburg, *Biochem. Bull.*, **3** (1913), 41.
[5] *Jour. Biol. Chem.*, **8** (1910), 365.
[6] Shorey, U. S. Dept. of Agr., Bur. of Soils, *Bull.* **83** (1911).
[7] Lathrop, *Jour. Am. Chem. Soc.*, **34** (1912), 1260.
[8] Suzuki, *Bull. Coll. Tokyo*, **7** (1908), 513.
[9] Robinson, *Mich. Tech. Bull.*, **7** (1911).
[10] *Loc. cit.*

[1] *Jour. Am. Chem. Soc.*, **35** (1913), 1594.
[2] *Loc. cit.*
[3] The reason for using ammonia free water here was that a sharper end point was obtained with it than when ordinary distilled water was used in the titration. This was, no doubt, due to a slight trace of amphoteric organic matter in the distilled water.

amounts evolved are far in excess of those obtained by distillation with magnesia, there is no other conclusion but that there is a decided decomposition of organic nitrogenous matter to give ammonia. The work of Steel[1] shows that probably this excess ammonia is not due to a decomposition of amino acids. Another class of nitrogenous compounds less stable in the presence of alkalies than the amino acids is the acid amides. Kelly and Thompson[2] in analyses of the alkali extract of nine soils found an average of 14.3 per cent amide nitrogen. Jodidi,[3] Robinson[4] and others have found from 20 to 30 per cent of amide nitrogen in the solution obtained by boiling the soil for several hours with strong acid. But because of their inherent instability, it seems highly improbable that acid amides are present in soils in much larger, if as large, percentages as ammonia. Many acid amides would slowly decompose in the presence of the Steel reagent. For instance, we found that 0.1 g. acetamide, purified by recrystallization from ether, in two hours aeration with the Steel reagent gave 1.54 mg. ammonia and in four hours 2.56 mg. It seems quite probable, therefore, that at least part of the excess ammonia is due to the decomposition of acid amides.

It was next decided to try the use of sodium carbonate as the alkali. Accordingly, as a preliminary test, 0.1 g. of acetamide was dissolved in 50 cc. of water, 2 g. of sodium carbonate added and the solution aerated. At the end of two hours, 0.08 mg., and at the end of twenty hours 0.02 mg. ammonia was given. No doubt the production of even the 0.08 mg. during the first two hours was from a trace of ammonium salts in the acetamide.

As is stated above, it has been found that all urines upon the addition of sodium carbonate give triple phosphate crystals, and on aeration low results are given for ammonia. Since magnesium, ammonium and phosphate ions are present in the soil solution, it would seem that the same thing would take place as with urines, namely, low results with sodium carbonate. In 1908, Folin[5] found that this objection in the case of urine could be overcome by the addition of potassium oxalate to the solution before the addition of sodium carbonate. If the magnesium ammonium phosphate was already there as a precipitate, the solution should first be made acid, which would dissolve the crystals and then the potassium oxalate added. This same procedure could, of course, be applied directly to any solution besides urine. We have, therefore, tried the use of sodium carbonate with and without the use of potassium oxalate on seven soils, and in the case of one soil, we have tried sodium chloride and sodium carbonate. The results are all grouped together in Table VIII, and are for 100 g. of soil.

In all cases, 25 g. of soil, 50 cc. of ammonia-free water and about 2 g. of sodium carbonate, and where indicated 8 to 10 g. of potassium oxalate and 15 to 17 g. of sodium chloride were used. Also when potassium oxalate was used, the mixture was always made slightly acid before the addition of the sodium carbonate.

An examination of Table VIII brings out many interesting points. For the soils tested, sodium carbonate used alone causes no appreciable decomposition of organic matter. It is possible that with a soil high in organic matter, it might be advantageous to use sodium chloride, which, of course, acts to weaken

TABLE VIII—AERATION METHOD WITH VARIOUS ALKALI REAGENTS

| Soil No. | Lab. Nos. | Aeration Hrs. | Milligrams N as ammonia Found: Added | Duplicates | | Av. | $NH_3$ recovered: Mgs. | Per cent |
|---|---|---|---|---|---|---|---|---|
| 1—$Na_2CO_3$ and NaCl: | | | | | | | | |
| | 78 & 79 | 15 | None | 2.08 | 2.08 | 2.08 | .... | .... |
| | 80 & 81 | 15 | 2.25 | 4.29 | Lost | 4.29 | 2.21 | 98.2 |
| | 82 & 83 | 19 | None | 1.97 | 2.08 | 2.03 | .... | .... |
| | 84 & 85 | 19 | 2.25 | 4.29 | 4.27 | 4.28 | 2.25 | 100 |
| $Na_2CO_3$: | | | | | | | | |
| | 86 & 87 | 19 | None | 2.08 | 1.97 | 2.03 | .... | .... |
| | 88 & 89 | 19 | 2.25 | 4.27 | 4.32 | 4.30 | 2.27 | 100.9 |
| $K_2C_2O_4$ and $Na_2CO_3$: | | | | | | | | |
| | 90 & 91 | 15 | None | 2.08 | 2.08 | 2.08 | .... | .... |
| | 92 & 93 | 15 | 2.25 | 4.32 | 4.27 | 4.30 | 2.22 | 98.7 |
| | 94 & 95 | 19 | 2.25 | 4.32 | 4.32 | 4.32 | 2.24 | 99.5 |
| 2—$Na_2CO_3$: | | | | | | | | |
| | 96 & 97 | 15 | None | 2.59 | 2.53 | 2.56 | .... | .... |
| | 100 & 1 | 15 | 2.25 | 4.84 | 4.78 | 4.81 | 2.25 | 100 |
| | 102 & 3 | 19 | None | 2.53 | 2.55 | 2.54 | .... | .... |
| | 104 & 5 | 19 | 2.25 | 4.60 | 4.78 | 4.69 | 2.15 | 95.6 |
| $K_2C_2O_4$ and $Na_2CO_3$: | | | | | | | | |
| | 106 & 7 | 15 | None | 2.59 | 2.59 | 2.59 | .... | .... |
| | 108 & 9 | 15 | 2.25 | 4.84 | 4.78 | 4.81 | 2.22 | 98.7 |
| | 110 & 1 | 19 | 2.25 | 4.71 | 7.84 | 4.78 | 2.19 | 97.3 |
| 3—$Na_2CO_3$: | | | | | | | | |
| | 112 & 3 | 15 | None | 1.23 | 1.23 | 1.23 | .... | .... |
| | 114 & 5 | 15 | 2.25 | 3.48 | 3.54 | 3.51 | 2.28 | 101.3 |
| | 116 & 7 | 19 | None | 1.23 | 1.18 | 1.21 | .... | .... |
| | 118 & 9 | 19 | 2.25 | 3.48 | 3.48 | 3.48 | 2.27 | 100.9 |
| $K_2C_2O_4$ and $Na_2CO_3$: | | | | | | | | |
| | 120 & 1 | 15 | None | 1.23 | 1.18 | 1.21 | .... | .... |
| | 122 & 3 | 15 | 2.25 | 3.48 | 3.54 | 3.51 | 2.30 | 102.1 |
| | 124 & 5 | 19 | 2.25 | 3.48 | 3.48 | 3.48 | 2.27 | 100.9 |
| 4—$Na_2CO_3$: | | | | | | | | |
| | 126 & 7 | 15 | None | 1.39 | 1.39 | 1.39 | .... | .... |
| | 128 & 9 | 15 | 2.25 | 3.59 | 3.65 | 3.62 | 2.23 | 99.1 |
| | 130 & 1 | 19 | None | 1.29 | 1.34 | 1.32 | .... | .... |
| | 132 & 3 | 19 | 2.25 | 3.59 | 3.59 | 3.59 | 2.27 | 100.9 |
| $K_2C_2O_4$ and $Na_2CO_3$: | | | | | | | | |
| | 134 & 5 | 15 | None | 1.34 | 1.34 | 1.34 | .... | .... |
| | 136 & 7 | 15 | 2.25 | 3.59 | 3.59 | 3.59 | 2.25 | 100 |
| | 138 & 9 | 19 | 2.25 | 3.54 | 3.59 | 3.57 | 2.23 | 99.1 |
| 5—$Na_2CO_3$: | | | | | | | | |
| | 140 & 1 | 15 | None | 2.35 | 2.19 | 2.27 | .... | .... |
| | 142 & 3 | 15 | 2.25 | 4.44 | 4.49 | 4.47 | 2.20 | 97.8 |
| | 144 & 5 | 19 | None | 2.25 | 2.25 | 2.25 | .... | .... |
| | 146 & 7 | 19 | 2.25 | 4.44 | 4.44 | 4.44 | 2.19 | 97.3 |
| $K_2C_2O_4$ and $Na_2CO_3$: | | | | | | | | |
| | 148 & 9 | 15 | None | 2.19 | 2.25 | 2.23 | .... | .... |
| | 150 & 1 | 15 | 2.25 | 4.44 | 4.49 | 4.47 | 2.24 | 99.5 |
| | 152 & 3 | 19 | 2.25 | 4.49 | 4.49 | 4.49 | 2.26 | 100.5 |
| 6—$Na_2CO_3$: | | | | | | | | |
| | 154 & 5 | 15 | None | 0.79 | 0.79 | 0.79 | .... | .... |
| | 156 & 7 | 15 | 2.25 | 3.03 | 3.03 | 3.03 | 2.24 | 99.5 |
| | 158 & 9 | 19 | None | 0.79 | 0.84 | 0.82 | .... | .... |
| | 160 & 1 | 19 | 2.25 | 3.03 | 3.14 | 3.09 | 2.25 | 100 |
| $K_2C_2O_4$ and $Na_2CO_3$: | | | | | | | | |
| | 162 & 3 | 15 | None | 0.90 | 0.79 | 0.85 | .... | .... |
| | 164 & 5 | 15 | 2.25 | 3.03 | 3.09 | 3.06 | 2.21 | 98.2 |
| | 166 & 7 | 19 | 2.25 | 3.09 | 3.09 | 3.09 | 2.24 | 99.5 |
| 7—$Na_2CO_3$: | | | | | | | | |
| | 168 & 9 | 15 | None | 1.12 | 1.12 | 1.12 | .... | .... |
| | 170 & 1 | 15 | 2.25 | 3.37 | 3.26 | 3.32 | 2.20 | 97.8 |
| | 172 & 3 | 19 | None | 1.23 | 1.18 | 1.21 | .... | .... |
| | 174 & 5 | 19 | 2.25 | 3.48 | 3.37 | 3.43 | 2.22 | 98.7 |
| $K_2C_2O_4$ and $Na_2CO_3$: | | | | | | | | |
| | 176 & 7 | 15 | None | 1.12 | 1.23 | 1.18 | .... | .... |
| | 178 & 9 | 15 | 2.25 | 3.37 | 3.37 | 3.37 | 2.19 | 97.3 |
| | 180 & 1 | 19 | 2.25 | 3.37 | 3.48 | 3.43 | 2.25 | 100 |

the base. The use of potassium oxalate, it is seen, gives no more ammonia than sodium carbonate alone. This is at first thought somewhat surprising, but no doubt the reason for this is that the phosphate and ammonia are present in such high dilution in the soil solution that the magnesium ammonium phosphate does not precipitate. In urine[1] the phosphate content averages about 2000 parts per million, and the ammonia[2] 1000 parts per million, while in the soil King[3] found as a maximum amount of water-soluble phosphate about 20 parts per million, and we have found as a maxi-

[1] *Loc. cit.*
[2] *Jour. Am. Chem. Soc.*, **36** (1914), 438.
[3] *Mich. Tech. Bull.*, **4** (1909); *Iowa Research Bull.*, **1** and **3** (1911).
[4] *Mich. Tech. Bull.*, **7** (1911).
[5] *Jour. Biol. Chem.*, **8** (1910), 497.

[1] Hammarsten, "Text Book of Physiological Chemistry," 6th English Ed., p. 646.
[2] Hawk's "Practical Physiological Chemistry," 4th Ed., p. 313.
[3] King, U. S. Dept. of Agr., Bur. of Soils, *Bull.* **26**.

mum amount of ammonia about 30 parts per million. Since by our method two parts of water to one part of soil are used, these values should be halved. It is, therefore, apparent why there is no interference of the triple phosphate.

From the data presented in Table VIII we feel safe in recommending the aeration method with sodium carbonate as the alkali for ammonia determinations in normal and Iowa alkali soils. The method complies with the three requirements laid down as fundamental. Excellent duplicates are given; no appreciable amount of ammonia is given off after fifteen hours aeration, and within the experimental error 100 per cent of any added ammonia was always recovered; also the method is eminently practical.

For purposes of comparison the results obtained by the three methods are assembled in Table IX.

TABLE IX—MGS. NITROGEN AS AMMONIA

| Soil No. | HCl extraction | MgO distillation | $Na_2CO_3$ aeration |
|---|---|---|---|
| 1 | 1.25 | 3.33 | 2.03 |
| 2 | 1.24 | 3.84 | 2.56 |
| 3 | 0.80 | 2.67 | 1.23 |
| 4 | 0.53 | 2.50 | 1.39 |
| 5 | 1.23 | 3.21 | 2.27 |

It is seen that there is very little co-relation in the amounts of ammonia found by the three methods, except that extraction with the hydrochloric acid gives lower results, while distillation with magnesia gives higher results than the aeration method. This is to be expected as we have shown that hydrochloric acid holds back ammonia, while distillation with magnesia effects some decomposition. Contrary to our findings, Kelley and McGeorge[1] report in speaking on the ammonia determinations in the hydrochloric acid extract, that the "results were very similar to those obtained by direct [magnesia] distillation." Table IX emphasizes the fact that in reporting ammonia determinations in soil, the method used should in all cases be given.

For the convenience of those who wish to use the aeration method for ammonia in soils, we will give the technique in detail which we have used. After all the apparatus is at hand, the procedure is as follows: Prepare the absorption bottles as was described above for the Steel method. Weigh 25 g. of soil into the 500 cc. Kjeldahl flasks, add 50 cc. of ammonia-free water and a few drops of a heavy oil to prevent foaming, and then put in the rubber stopper bearing the tube for the entrance and exit of the air. Have the end of the long glass tube come within not more than $^1/_8$ of an inch of the bottom of the flask. See that no water is between the rubber stopper and the mouth of the flask to collect ammonia. The best way to eliminate this danger is to have the rubber stopper fit very tightly. Now, connect up the whole series, but do not start the pump. As many as fourteen determinations can be run in series. The air before entering the system must, of course, be passed through a wash bottle containing dilute sulfuric acid. Now loosen all the rubber stoppers in all the Kjeldahl flasks, start the pump, add about two grams of sodium carbonate to the flask closest to the pump, shake the flask and then insert the rubber stopper and then take the flasks in succession in just the same way. After a series is once started, the pump should not be stopped. If anything happens to a determination, do not try to remove it. After the aeration has run as long as desired, with the pump still going, remove the flasks one by one, starting with the one farthest removed from the pump.

This same apparatus has been used by us for the determination of total nitrogen in soil. The digestion is carried out in the usual way, and the aeration carried out in much the same way as Kober recommends. A water bath as he advises was not used, but instead, add about one-third of the required amount of alkali; shake and allow the mixture to cool and then add the remainder of the alkali by the same procedure he uses, except the absence of the water bath. To prevent spattering, the Kjeldahl flask is tilted in a plane perpendicular to the line joining the absorption bottles. As to accuracy and ease of manipulation, Kober's[1] statements have been confirmed.

As has been stated, all aeration work reported in this paper is for a current of air of about 250 liters per hour. If a pump is available which moves more air than this, no doubt the time of aeration could be correspondingly lessened.

## CONCLUSION

1—The amount of ammonia extracted by hydrochloric acid is within the limits of the experiment independent of the strength of the acid and the period of extraction.

2—In the five soils tested, hydrochloric acid removes approximately from 60 to 70 per cent of the ammonia added.

3—The Folin aeration method can be advantageously applied directly to the hydrochloric acid extract.

4—The amount of ammonia obtained by distillation of the soil directly with magnesia is dependent upon the duration of the distillation.

5—The Steel method of aeration is not suitable for the determination of ammonia in soils.

6—The Steel reagents slowly decompose acetamide.

7—The Folin method of aeration is suitable for the determination of ammonia in soils, for the same result is obtained whether the reagent acts for a shorter or longer period; all added ammonia is recovered and the method is practicable.

8—In the soils tested, there is no interference through formation of triple phosphate.

9—For the soils tested, there is no need of using sodium chloride with the sodium carbonate.

10—Acetamide is not decomposed by 4 per cent sodium carbonate.

11—The results for ammonia obtained by examination of the hydrochloric acid extract are lower than those obtained by the aeration method. This is due to an occlusion of the ammonia by the soil, the nature of which is not clear.

12—The ammonia results from the direct distillation of the soil with magnesia are higher than those obtained by the aeration method. The difference is due to a partial decomposition of the organic material by the magnesia, which gives ammonia.

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[1] Hawaiian Sta., *Bull.* **30** (1913), 31.

[1] *Loc. cit.*

## THE DETERMINATION OF SOIL CARBONATES A MODIFICATION

By W. H. MacIntire and L. G. Willis

Received January 8, 1915

In *Bulletin* **100** of the Tennessee Station, September, 1913, the writers reported certain studies and advanced a new method for the determination of carbonate $CO_2$ in soils. The method was predicated upon results which showed that phosphoric acid was less active than sulfuric or hydrochloric acid upon soil organic matter at boiling temperature, when an equal volume and dilution of the concentrated acid was used; and upon data which showed that theoretical evolutions of $CO_2$ were obtained from precipitated calcium and magnesium carbonates, 100-mesh limestone, and finely ground dolomite, both with and without soil, by agitation and aspiration for 30 minutes with 4 inches of vacuum at room temperature.

At the time of the publication of the above-mentioned bulletin the gravimetric procedure was in use in this laboratory, and the substitution of phosphoric acid for hydrochloric acid afforded a compacted multi-unit apparatus as a result of the elimination of the silver sulfate absorption tubes. Since publishing the method cited, the authors have done a large amount of work with the method, in its adaptation to the Amos double titration procedure[1] for the collection of $CO_2$, and this method of absorption has supplemented the gravimetric one in this laboratory. Careful studies with the Folin absorption tube, in comparison with Camp's bead tower, have convinced the writers that for $CO_2$ work the latter apparatus is preferable to the former because of more nearly theoretical efficiency. It was found that in the rapid passage of heavy evolutions of $CO_2$ through the Folin tubes, some of the gas was not absorbed. The writers have also simplified the apparatus, as previously described by them, by the substitution of a small fan motor for manual agitation. The motor can be obtained of chemical supply houses at a cost of but $7.50. A four-unit modified apparatus is shown in Fig. I. The motor may be advantageously attached to a wall or other perpendicular face. This affords a simple knock-down apparatus, without permanent occupancy of bench space by the motor, and at the same time furnishes a gravity belt-tightening arrangement which is secured by one end of the gearing axle being free from rigid support.

### MODIFICATION IN THE PROCEDURE

In making $CO_2$ determinations by the use of 1/15 phosphoric acid upon one of three soils sent out by Mr. J. W. Ames, the Referee on Soils for the A. O. A. C., we found that we were unable to secure a complete decomposition of all carbonates within the usual aspiration period of 30 minutes, although long-continued aspiration effected complete recovery as judged by a comparison with the Marr method.[2] We found, however, that we were able to secure complete decomposition by the use of 1/15 HCl, with 30 minutes agitation and aspiration. The soil sent out by Mr. Ames was a very unusual one, and it contained about 5.2 per cent carbonates, calculated as a $CaCO_3$. The soil was taken to a depth of 18 inches, and examinations by Mr. Ames and by the writers tended to show that $MgCO_3$ was present. This occurrence would probably be exceptionally rare, as has been shown recently.[1] However, the writers wish to have their method applicable without exceptions, and for that reason they have recommended that for miscellaneous soils 1/10 HCl be used with the Camp absorption tower. The use of the volumetric method of absorption eliminates, of course, the objection to the passing over of traces of HCl, and the necessity for silver sulfate tubes. We have found that the action of 1/10 HCl on soil organic matter at room temperature is altogether negligible upon 5-, 10- and 20-gram charges of the average soil.

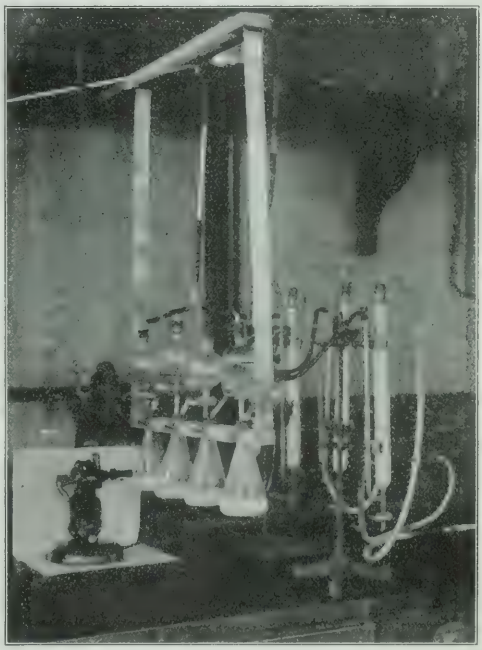

Fig. I.—A Four-Unit $CO_2$ Apparatus

Where analyses are to be made of soils treated with CaO, MgO, precipitated carbonates of calcium and magnesium, or limestone such as we have used, 1/15 phosphoric acid may be used with assurance of complete decomposition. A soil treated with limestone chemically equivalent to 200,000 pounds of CaO per two million pounds of soil gave 14.15 per cent $CaCO_3$ by the Marr method and 14.16 per cent by the Tennessee Station method, when run in the Ohio Station laboratory under the direction of Mr. Ames, and in this laboratory 14.29 per cent of $CaCO_3$ was found by the Tennessee Station method. This is

[1] *Jour. Agr. Sci.*, **1**, 322.

[2] *Ibid.*, **3**, 155.

[1] Tenn. Sta., *Bull.* **107**

probably a much higher occurrence of carbonate than would be found in virgin or cultivated calçareous soils adapted to plant growth. In cases of soils running over 15 per cent $CaCO_3$, it would be well, probably, to increase the strength of acid to 1/5.

Two soils treated with an exceedingly insoluble dolomite to the amount of chemical equivalence of 200,000 pounds of CaO per two million pounds of soil gave the following results:

| PER CENT $CaCO_3$ in | Soil A | Soil B | Av. |
|---|---|---|---|
| Boiled, minus boiling blank on original soil | 13.69 | 14.21 | 13.95 |
| 1/5 HCl, room temp., 30 min. agitation and aspiration | 13.80 | 14.10 | 13.95 |

As emphasized by italics in *Bulletin* **100,** we were able to secure by the use of 1/15 phosphoric acid complete decomposition of a very insoluble dolomite, when it was EXCEEDINGLY FINE. It would not be feasible, however, to grind all miscellaneous and unknown soils to such fineness as would be essential, in order to insure complete decomposition by 1/15 $H_3PO_4$ of a possible exceptional occurrence of dolomite. For this reason, together with the substitution of the absorption tower for the gravimetric procedure, we modify the method by the suggestion that 1/10 HCl be used for miscellaneous work.

Instances where considerable residual magnesite might be expected to occur in soils would be exceedingly rare. We should probably note, however, that we have found that in such cases neither the old procedure of boiling for one minute or several minutes, nor the Marr method, nor the Tennessee Station method will effect the complete decomposition of the mineral magnesium carbonate. In soils treated excessively with magnesite at this Station, we found it essential that boiling be continued during the 30-minute period of aspiration in order to decompose completely all of the magnesite.

### MANIPULATION OF MODIFIED PROCEDURE

Twenty-five cc. of approximately 4 per cent NaOH solution are placed in each absorption tower, and $CO_2$-free distilled water added to cover the beads. The suction, which is applied before running the acid from the bulb of the inlet tube into the 300 cc. Erlenmeyer soil-container flask, is controlled by screw corks on the rubber tubing to better advantage than by use of the metal stopcocks of the suction system. After agitation and aspiration for 30 minutes, the caustic is drawn out of the towers into glass tumblers and the towers are completely filled with $CO_2$-free water. After this washing has been drawn the tower should be rinsed several times. The NaOH solution is then titrated almost to a disappearance of the color given by one cc. of phenolphthalein, by the use of approximately normal sulfuric or nitric acid and the red color is then completely removed with the standardized weaker acids, $N/2$ and $N/20$. Two drops of methyl orange are then added and the $CO_2$ is determined by titration to the end point of methyl orange. For the average soil the entire methyl orange titration is carried out by the use of $N/20$ acid, but with excessive $CO_2$ occurrences, it is convenient to use $N/2$ acid to the near end point, and the titration is then completed with $N/20$ acid, which has a $CO_2$ value of 0.0022 g. per cc. In determining the blank on the NaOH we also include the atmosphere blank of the apparatus. This atmosphere blank is usually exceedingly small and constant, and its use eliminates the necessity of sweeping the apparatus free of $CO_2$ before making determinations. For the average soil 20-gram charges should be used and 60 to 75 cc. of 1/10 acid added for decomposition of the carbonates. A nitrogen bulb should be inserted as a trap between the bottle containing NaOH for purification of incoming air and the acid bulbs of the apparatus.

### A CORRECTION

As above stated, it was found that it is necessary to have dolomite in the form of a floury powder in order to insure its complete disintegration by 1/15 phosphoric acid and in the original $CO_2$ determinations upon the dolomite used for treatments, the analyses of which were given in Table V, Tennessee Station, *Bull.* **107,** the analyzed samples were so conditioned. However, in the supplementary determination for residual $CO_2$ in the field samples reported in Table VI of that bulletin the soil samples were ground to pass a 100 mesh sieve.

Upon recently submitting the composites of these two sets of eight soils each to boiling and applying the boiling blank of the untreated soil, 0.441 per cent of $CO_2$ was found in the limestone residues while 0.450 per cent was obtained from residual dolomite. The same composite soils, when analyzed by the use of 1/10 HCl at room temperature, gave 0.481 and 0.490 per cent of residual $CO_2$ for limestone and dolomite treatments, respectively. This means that the results for residual carbonates of dolomite treatment given in Table VI of *Bulletin* **107** are erroneous, in that they are too low as a result of insufficient fineness of samples. All of the other tables of the residual carbonates, however, were verified by boiling and applying the boiling blank prior to the publication of the data.

The writers would qualify their previous conclusions, then, as to the complete disappearance of the magnesium carbonate of the COARSELY GROUND dolomite in the short length of time given. The general principle, however, is unaltered, as relating to the unusual affinity of magnesium carbonate for siliceous substances. And the corrected results for the residual carbonates indicated that the greater affinity between magnesium carbonate and silicates has offset to an extent the lesser solubility of the dolomite in carbonated water, as compared to the greater solubility of limestone.

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## THE CHEMISTRY OF BASE GOODS FERTILIZER

By ELBERT C. LATHROP

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### INTRODUCTION

Although it has been long recognized that organic matter is a necessity for soil fertility, it is but lately that the deeper significance of soil organic matter in

relation to the complex problems of the soil and of the crop production has become apparent. Investigations have shown that the organic compounds in soils not only affect the physical conditions and chemical reactions of the soil but that they are also directly connected with fertility or infertility, some of them being essentially beneficial to the growth of plants while others are distinctly harmful. Of the organic compounds thus far isolated from soils, a large number contain nitrogen, and of these nitrogenous substances, some have been found rather widely distributed in soils varying as to location, climate, methods of cropping, etc. These nitrogenous compounds either occur as plant constituents or arise from the decomposition of plant or animal protein, brought about by the various biological and biochemical agents in the soil. Not only compounds of this class found in soils but also many other protein decomposition products have been studied, both alone and in conjunction with the three fertilizer elements, in respect to their action on plant growth, and they have been shown in a number of cases to exert a beneficial influence; furthermore, these complex compounds are available for use by the plant without first being changed by chemical or biochemical means into ammonia and then to nitrates.[1]

That these facts have an immense practical bearing on fertilizers and the fertilizer industry, both from the standpoint of the producer and of the consumer, is at once obvious. The consumer of commercial organic fertilizers should be concerned not alone with the availability of the nitrogen in fertilizer but also in knowing the nature of the organic compounds he is adding to his soil and in understanding the physiological effect of these on plant growth, whether their action will be harmful or beneficial or a balance of these two effects. A chemical investigation of some of the types of commercial organic fertilizers with the view of determining the kinds and nature of the organic compounds in the fertilizer is therefore of interest to the agriculturist. The old high-grade nitrogenous fertilizers, such as cottonseed meal, dried blood, fish scrap, etc., are being used more and more for feed purposes, and the time cannot be far distant when their use as fertilizers will cease to be economic; thus a necessity for other and cheaper fertilizers of this type arises. On the market are a large number of fertilizers which may be characterized as "processed," *i. e.*, the crude materials, not in themselves permissible as fertilizers, are made to undergo some decided chemical change to render them suitable as plant nutrients. It has been found that the "availability" of the crude substances is nearly always greatly increased by such processing and that a much larger percentage of the nitrogen in the finished product is soluble in water, although the actual chemical changes produced seem to have received little attention. The chemical compounds in process fertilizers which are here shown to have direct fertilizer significance have not been determined, other than to show that ammonia is formed during processing and that ammonia is more readily produced from the processed goods.

Since the wastes from which this type of fertilizer is made contain more or less protein, or protein-like substances, it seemed quite obvious that the finished fertilizers must contain more or less of the chemical compounds which would arise from pure proteins by similar treatment in the laboratory. As the action on plants of many of this class of compounds has been determined it is evident that the finding of such compounds in the fertilizers would throw much light on the question of the "availability" of the nitrogen in the fertilizer itself.

### BASE GOODS A TYPE OF PROCESSED FERTILIZER

For a chemical study of processed fertilizers a sample of "wet-mixed" or "base goods" fertilizer was chosen as a representative of this type of fertilizer material. The base goods was obtained directly from the factory for use in this investigation. This fertilizer is made by the treatment of various trade wastes and refuse, such as hair, garbage tankage, leather scraps, etc., with rock phosphate and the requisite amount of sulfuric acid. These materials are mixed together in a "den" and the resulting mass is allowed to stand for several days, or until it is cool enough to be conveniently handled. In the course of the reaction the mass reaches a temperature approximating 100° C., and the identities of the original substances are almost or entirely lost. Under these conditions it is certain that more or less hydrolysis of the proteins in the crude materials takes place, with the formation of proteoses, peptones, polypeptides, or the simple amino acids, the kinds and number of products formed necessarily depending on the proportion of the different proteins in the original materials, on the amount and strength of the acid, the length of time of the reaction, and the temperature reached during the treatment.

Hartwell and Pember[1] have recently made a study of base goods in order to determine the availability

TABLE I—PERCENTAGE TOTAL NITROGEN IN CRUDE MATERIALS AND FINISHED PRODUCT (HARTWELL AND PEMBER)

| | | | |
|---|---|---|---|
| Hair tankage | 6.28 | Base goods, including the above | 1.68 |
| Roasted leather | 6.49 | Water-soluble nitrogen in base goods | 1.28 |
| Garbage tankage | 2.87 | Water-insoluble nitrogen in base goods | 0.40 |

TABLE II—PERCENTAGE OF THE TOTAL NITROGEN PRESENT IN DIFFERENT FORMS (HARTWELL AND PEMBER)

| | Before put into den | After removing from den |
|---|---|---|
| In ammonia | 6.5 | 14.3 |
| In water-soluble organic matter | 7.8 | 57.7 |
| In water-insoluble organic matter | 85.7 | 28.0 |

of the nitrogen contained compared with that of the high-grade nitrogenous fertilizers. The product they used was made from hair tankage, garbage tankage, and roasted leather, together with rock phosphate and sulfuric acid. Tables I and II give their figures for the analysis of the crude materials used in producing the fertilizer and of the finished product.

The experimental work of the present investigation was along two separate lines:

[1] "A Beneficial Organic Constituent of Soils Creatinine," Oswald Schreiner, E. C. Shorey, M. X. Sullivan and J. J. Skinner, *Bull.* **83**, Bur. Soils, U. S. Dept. Agr., 1911. "Nitrogenous Soil Constituents and their Bearing on Soil Fertility," Oswald Schreiner and J. J. Skinner, *Bull.* **87**, Bureau of Soils, U. S. Dept. Agr., 1912.

[1] THIS JOURNAL, **4** (1912), 441.

I—Analytical, involving total nitrogen determinations and the separate estimation of the various forms in which nitrogen may occur.

II—A determination of the definite chemical compounds present in the fertilizer by suitable methods of isolation and identification.

THE CHEMICAL CHANGES INVOLVED IN PROCESSING

It is not the purpose of the present paper to enter in detail into the methods used in the chemical examination of the base goods. For the analytical study of the forms of nitrogen in the base goods the method of Van Slyke[1] was used in its essential details, omitting the determination of cystine, since the method for its determination is not applicable in this case.

It should also be stated that, although the results from the Van Slyke analysis are expressed in the usual way, arginine nitrogen, histidine nitrogen, etc., it is not intended to convey the impression that these fractions contain pure arginine, histidine, etc., since, as will be shown later, other compounds are included under these analytical terms. However, the nitrogen so expressed is that contained in compounds which give the various reactions upon which the Van Slyke method depends.

The analytical figures obtained by this method appear in Table IV and will be discussed after the isolation of certain of the constituents has been presented.

The method used for isolating and identifying the various organic compounds are such as have been used in this laboratory in separating these compounds from soils and are described in various publications from this laboratory.[2]

Since this investigation aims only at an explanation and exposition of the general chemical principles involved in the treatment of trade wastes and other organic material to render the nitrogen contained therein more available for agricultural purposes, it does not aim to present the research methods here employed as general methods for analyzing such fertilizers. Nor can the quantitative figures obtained be expected to apply to all products of similar manufacture, for the reason that the different kinds of nitrogen compounds will necessarily show different proportions according to the nature of the materials which enter into the mixture.

The compounds which were isolated from the base goods are tabulated in Table III according to the sources from which they have been derived and the chemical groups to which they belong.

TABLE III—ORGANIC COMPOUNDS ISOLATED FROM SAMPLE OF BASE GOODS

| | | |
|---|---|---|
| Arginine, Histidine, Lysine | Diamino acids or hexone bases | Products of protein hydrolysis by acid treatment of raw materials. |
| Leucine, Tyrosine | Monoamino acids | |
| Guanine | Purine base | Plant constituent, or product of hydrolysis of nucleoprotein. |
| Hypoxanthine | Purine base | Plant constituent, or product of conversion of nucleoprotein-base. |

Establishing the presence of these products of acid hydrolysis of proteins, namely, the diamino acids, arginine, lysine, and histidine, and the two monoamino acids, leucine and tyrosine, in the amounts in which they were found is of itself sufficient evidence to demonstrate that by the acid treatment of the crude materials used in the manufacture of the base goods the proteins contained therein have been changed. The change is shown to be a deep-seated one, since five of the compounds known to be final products of protein hydrolysis by acids are found. This, however, cannot be taken to mean that the proteins have been completely hydrolyzed by the acid treatment since it is possible to have present in the product of partial hydrolysis of proteins, not only the diamino and monoamino acids, but also such intermediate compounds as polypeptids, peptones, proteoses, etc.

In this connection the results obtained by use of the Van Slyke method, and given in Table IV, are of particular interest. For the nitrogen partition two samples of base goods were extracted: (1) with boiling water and (2) with boiling acid. In the former case only slight further hydrolysis of the materials in the base goods is to be expected since the free acid in the fertilizer is extremely weak, and the boiling temperature, 100° C., is that which was reached in the process of manufacture. In the case of the second extract complete hydrolysis of all the proteins or protein-like materials is certainly to be expected, since in addition to the original hydrolysis the material was boiled with strong hydrochloric acid for 24 hours, a treatment sufficient for the complete hydrolysis of most proteins. The differences in the results obtained from the analyses of the two extracts may, therefore, be expected to throw some light on the question of the completeness of hydrolysis of the original proteins by the acid processing.

TABLE IV—NITROGEN FORMS AS DETERMINED BY THE VAN SLYKE METHOD

| Results expressed in per cent of | Base goods | | Total N in base goods | |
|---|---|---|---|---|
| EXTRACT | $H_2O$ | HCl | $H_2O$ | HCl |
| Total nitrogen | 1.610 | 1.610 | | |
| Total soluble nitrogen | 1.372(*a*) | 1.435 | 85.24(*a*) | 88.64 |
| Total insoluble nitrogen | 0.238(*a*) | 0.175(*a*) | 14.76(*a*) | 11.36(*a*) |
| Amide nitrogen | 0.374 | 0.382 | 23.23 | 23.70 |
| Humin nitrogen | 0.031 | 0.074 | 1.95 | 4.61 |
| Diamino acid fraction — Arginine N. | 0.111 | 0.104 | 6.89 | 6.46 |
| Diamino acid fraction — Histidine N. | 0.117 | 0.070 | 7.26 | 4.38 |
| Diamino acid fraction — Lysine N. | 0.081 | 0.117 | 5.06 | 7.26 |
| Monoamino acid fraction — Amino N. | 0.543 | 0.546 | 33.75 | 33.92 |
| Monoamino acid fraction — Nonamino N. | 0.114 | 0.133 | 7.10 | 8.27 |

(*a*) Obtained indirectly.

Without discussing the significance of all the figures obtained by the use of this method it is interesting to note that the differences between the water extract and hydrochloric acid extract indicate the presence in the base goods of a nitrogenous compound not yet completely hydrolyzed.

In order to prove the presence of some intermediate product of protein hydrolysis, which is thus indicated by analytical methods, an aqueous solution of about 2.5 lbs. of base goods was made and the diamino acids were precipitated with phosphotungstic acid in the presence of 5 per cent sulfuric acid. The precipitate which formed was allowed to stand over night and after filtering off it was washed well with 5 per cent sulfuric acid and dissolved in sodium hydroxide. The phosphotungstic acid was then precipitated by adding barium hydroxide solution, and after filtering, the excess of barium was removed by adding sulfuric

[1] *J. Biol. Chem.*, **10** (1911), 15–55.

[2] Oswald Schreiner and E. C. Shorey, Bur. Soils, U. S. Dept. Agr., 1910; Oswald Schreiner and E. C. Lathrop, *Bull.* **80**, Bur. of Soils, U. S. Dept. Agr., 1911; E. C. Shorey, *Bull.* **88**, Bur. Soils, U. S. Dept. Agr., 1913; Oswald Schreiner and E. C. Lathrop, *Bull.* **89**, Bur. Soils, U. S. Dept. Agr., 1912; E. C. Lathrop, *Bull.* **168**, U. S. Dept. Agr., 1914.

acid until a neutral reaction was obtained. Portions of this solution were tested for peptones, proteoses, etc., with the following results: (1) The biuret test was positive; (2) a precipitate was obtained on saturation of the solution with ammonium sulfate, or with sodium chloride; (3) when the filtrate from the latter solution was treated with acetic acid a cloudy precipitate developed; (4) precipitates were also obtained with sulfuric acid, hydrochloric acid, phosphomolybdic acid and with phosphotungstic acid; (5) a precipitate was formed in the addition of alcohol to the solution. This precipitate was filtered off, dissolved in dilute alkali, and on addition of very dilute copper sulfate solution the biuret reaction was again obtained. These reactions are those which are given by proteoses and by the proteins and confirm the conclusions arrived at from the results with the Van Slyke method. The Millon reaction and the Hopkins-Cole reaction were both negative, showing the absence from this protein-like compound of the tyrosine and the tryptophane radicals.

A very large number of compounds intermediary between the protein and its primary hydrolysis products may occur, depending on a great variety of conditions, so that the actual identification of the compounds under discussion would be a difficult matter. However, the nature of this compound may be approximately determined by the results obtained in the study of the two extracts by the Van Slyke method. These results indicate the presence in the base goods of a compound of a proteose nature, which, since it gives a biuret test, must be composed of at least three amino acids. The results indicate still further that the compound is composed of acid amide radicals, diamino acids—particularly lysine, and monoamino acids—those containing amino nitrogen and especially those containing non-amino nitrogen. Since the figures obtained by the nitrogen partition method are subject to a certain amount of error when applied to such a mixture the figures can be taken as only approximate for the various forms of nitrogen which make up this compound.

In Table V are given the primary hydrolysis products of a number of proteins which may be present in the base goods. These results were obtained by the esterification method and show how the different proteins vary in the nature and amount of the units composing them. Many monoamino acids, besides leucine and tyrosine, occur in these proteins, and there must consequently be present in the base goods amino acids other than the two isolated. This is apparent from the composition of the various proteins shown in the table. Owing to the large amount of amide nitrogen present in the fertilizer, which was split off by the acidulation of the original proteins of the trade wastes, it may be concluded that considerable quantities of aspartic or glutamic acids are present in this sample of base goods.

The conclusion to be drawn from the results obtained by the examination of this fertilizer by means of the analytical and isolation methods are as follows: The process by which the nitrogen of certain trade wastes, such as hair, lather, garbage, etc., is made more available, is recognized as a process of partial hydrolysis of the complex protein contained in such materials, resulting in ammonia, amino acids, etc., all of which are more available than the original protein material; this hydrolysis is almost complete, the nitrogenous compounds formed being principally the primary products of protein hydrolysis, together with a small amount of proteose-like compound which has not been fully decomposed.

TABLE V—PRODUCTS OF ACID HYDROLYSIS OF VARIOUS PROTEINS

| COMPOUND | "Synotin" from cattle flesh (a) | "Keratin" from sheep's horn (b) | "Keratin" from sheep's wool (b) | "Keratin" from horse's hair (c) | "Keratin" from Hali- but muscle (d) | Ox muscle (e) | "Leguмin" from pea (f) |
|---|---|---|---|---|---|---|---|
| Glycine (g) | 0.5 | 0.5 | 0.6 | 4.7 | 0.0 | 2.1 | 0.4 |
| Alanine(g) | 4.0 | 1.6 | 4.4 | 1.5 | (?) | 3.7 | 2.1 |
| Valine | 0.9 | 4.5 | 2.8 | 0.9 | 0.8 | 0.8 | .. |
| Leucine(g) | 7.8 | 15.3 | 11.5 | 7.1 | 10.4 | 11.7 | 8.0 |
| Isoleucine | .. | .. | .. | .. | .. | .. | .. |
| Phenylalanine(g) | 2.5 | 1.9 | .. | 0.0 | 3.1 | 3.2 | 3.8 |
| Tyrosine(g) | 2.2 | 3.6 | 2.9 | 3.2 | 2.4 | 2.2 | 1.6 |
| Serine | .. | 1.1 | 0.1 | 0.6 | (?) | (?) | 0.5 |
| Cystine | .. | 7.5 | 7.3 | 8.0 | .. | .. | .. |
| Proline | 3.3 | 3.7 | 4.4 | 3.4 | 3.2 | 5.8 | 3.2 |
| Oxyproline | .. | .. | .. | .. | .. | .. | .. |
| Aspartic acid(g) | 0.5 | 2.5 | 2.3 | 0.3 | 2.8 | 4.52 | 5.3 |
| Glutamic acid(g) | 13.6 | 17.2 | 12.9 | 3.7 | 10.1 | 15.5 | 17.0 |
| Tryptophane | .. | .. | .. | .. | (+) | (+) | (+) |
| Arginine(g) | 5.1 | 2.7 | .. | 4.5 | 6.4 | 7.5 | 11.7 |
| Lysine(g) | 3.3 | 0.2 | .. | 1.1 | 7.5 | 7.6 | 5.0 |
| Histidine(g) | 2.7 | .. | .. | 0.6 | 2.6 | 1.8 | 1.7 |
| Ammonia(g) | 0.9 | .. | .. | .. | 1.4 | 1.1 | 2.1 |
| | 47.3 | 62.3 | 49.2 | 39.6 | 50.7 | 67.5 | 62.4 |

(a) Abderhalden and T. Saski, *Z. physiol. Chem.*, **51** (1907), 404.
(b) E. Abderhalden and A. Voitinovici, *Ibid.*, **52** (1907), 348.
(c) E. Abderhalden and H. G. Wells, *Ibid.*, **46** (1905), 31; A. Argiris, *Ibid.*, **54** (1905), 86.
(d) T. B. Osborne and F. W. Heyl, *Am. J. Physiol.*, **22** (1908), 433.
(e) T. B. Osborne and D. B. Jones, *Ibid.*, **24** (1909), 437.
(f) T. B. Osborne and F. W. Heyl, *J. Biol. Chem.*, **6** (1908), 197.
(g) Physiological action on plant growth has been determined and reported in *Bull.* **87**, Bureau of Soils, U. S. Dept. Agr.

## AVAILABILITY OF THE NITROGEN OF ORGANIC FERTILIZERS

The question of the availability of the different kinds of nitrogen contained in organic fertilizers is one that has caused considerable discussion. A number of methods have been proposed for determining this factor, and while some of them give helpful results, all except the plant method are open to more or less objection, since the methods are empirical and the nature of the complicated compounds in which the nitrogen is linked in the fertilizer is unknown or only guessed. When these nitrogen compounds are known and their action on plants, as well as the action of the compounds formed from them during their decomposition in the soil, have been determined, then the question of the availability of the nitrogen of organic fertilizers can be understood. Originally it was held that plants were able to use nitrogen only when it was offered to them in the form of nitrates; this idea, however, was modified when it was discovered that under certain conditions plants used ammonia or ammonium salts without their conversion into nitrates quite as well as they used the nitrates themselves. During the past few years it has been clearly demonstrated that plants use nitrogen not only in the form of nitrates and ammonia but in the form of complex organic compounds.[1] The action of a number of these nitrogenous compounds has been tested in this laboratory in conjunction with the three fertilizer elements and it has been found that in some cases

[1] Hutchinson and Miller, *Centr. Bakt. Parasitenk*, **30** (1911), 513; Schreiner and Skinner, *Bull.* **87**, Bureau of Soils, U. S. Dept. Agr., 1912.

the nitrogen compounds are not only used as a source of nitrogen for the growing plant, without any change in the compound, but that they are apparently nitrate sparers, *i. e.*, the plant uses them in preference to the nitrates. Instead, then, of only one kind of nitrogen compound, *nitrate*, or at most two, *nitrate* and *ammonia*, there appear to be a very large number of nitrogenous compounds which have properties of physiological importance to plant growth. The question of the availability of nitrogen compounds can therefore be answered only when the nitrogen compounds contained in the fertilizer can be determined in amount and at the same time classified according to their physiological action on plant growth. It is hardly necessary to state that such a method does not exist at present and that the physiological action of only a part of the total number of nitrogenous compounds present in fertilizers is known.

The physiological action on plants of all of the nitrogenous compounds isolated from base goods has been determined by means of water cultures[1] and the results obtained may be stated briefly, as follows: Both of the purine bases are used by the plant as a source of nitrogen and are beneficial to plant growth; furthermore, the hypoxanthine acts as a nitrate sparer, there being less nitrate used by the plant in the presence of hypoxanthine than when the hypoxanthine is absent. Histidine, arginine, and lysine[2] are all beneficial to plant growth, causing nitrogen increases in the plant, and the two first diamino acids act as nitrate sparers; this may also be true of lysine, although this property of lysine has not been studied. Leucine is also beneficial to plant growth, but tyrosine, in the light of later investigations, is somewhat doubtful in action. Of the other monoamino acids which may be present in base goods, aspartic acid, glutamic acid, and glycocoll have been found to be beneficial. The action of alanine is somewhat doubtful, it apparently being beneficial in low concentrations, while phenylalanine is reported as harmful. Thus six of the seven compounds isolated from the base goods are actually available to plants as such and have a beneficial action. Of the monoamino acids, other than the two isolated from base goods, which have been studied in regard to their action on plant growth, three have been found to be beneficial, one doubtful, and one is reported as being harmful.

The high-grade nitrogenous fertilizers, such as dried blood, are considered to have a high availability owing to the fact that the nitrogenous materials when placed in the soil quickly undergo the process of ammonification and nitrification, the nitrogen thus being changed into a form which can be immediately used by the plant. In fact, Lipman[3] has proposed a method for the determination of the availability of the nitrogen of organic fertilizers, depending on the amount of ammonia produced under certain conditions in a given length of time. It is evident from the above consideration that such a method does not tell the whole story, since, in the decomposition of protein materials, such as dried blood, intermediate compounds are formed which are undoubtedly in themselves beneficial to plant growth. In order, therefore, to understand the complete action of the nitrogenous materials in the base goods it is necessary to know how the compounds contained in it are acted upon by ammonifying bacteria. Jodidi[1] has shown that the amino acids and acid amides are quite readily ammonified when placed in the soil, the rate of ammonia formation and the amount of ammonia formed depending apparently upon the chemical structure of the particular compound under consideration. In general, he found that the simpler the chemical structure of the nitrogen compound the more quickly and readily it was ammonified. In the light of these facts it appears that polypeptides, peptones, proteoses, and proteins would be ammonified still more slowly than the amino acids since their structure is increasingly more complex.

Hartwell and Pember[2] in their study on the availability of the nitrogen of base goods, by means of plant tests found that it had apparently as high an availability as dried blood, the water-soluble nitrogen having even a higher availability. From the nature and amounts of the compounds present in the base goods this might be predicted. In the case of the dried blood, the nitrogen is practically all in the form of complex protein material which must be broken down into simpler compounds by bacterial action, with the formation of ammonia and other nitrogenous compounds, some or all of which may be of physiological importance to plants. With the base goods the case is a little different; the greater part of the nitrogen is at once available for plant use, and at the same time these available compounds may be changed more easily and quickly by bacteria of the soil into ammonia and nitrate, which in turn are used by the plant. The soluble nitrogen of base goods should therefore be in a more readily available form than the nitrogen of dried blood or other nitrogenous fertilizers which are entirely of a protein nature.

### THE CHEMICAL PRINCIPLES UNDERLYING THE UTILIZATION OF NITROGENOUS TRADE WASTES

It has already been stated that in order that the plant may make use of the nitrogen of even high-grade organic fertilizers, it is necessary for the proteins therein to be at least partially decomposable by the biological and biochemical agencies of the soil. The low-grade organic nitrogenous fertilizers resist decomposition by these biological and biochemical soil agencies, and their nitrogen is therefore considered to be less available for plant use. The guiding idea behind the processes proposed for the treatment of trade wastes, which will not decompose easily in the soil as such, is to change the nitrogen compounds contained in them in such a way that ammonia is formed and that their decay in the soil is more rapid.

Much of the nitrogenous materials in trade wastes is of a protein nature, since the products from which

[1] *Bull.* **87**, Bureau of Soils.

[2] Unpublished data.

[3] Lipman, Brown and Owen, *Centr. Bakt. Parasitenk.*, **31**, *II Abt.* (1911–1912), 49–85.

[1] Research Bull. No. **9**, Iowa Expt. Sta.

[2] *Loc. cit.*

these wastes are derived are either of animal or vegetable origin. Such is the case with the wastes used in the manufacture of base goods. It has been shown that by the process used in the case of this fertilizer the nonavailable nitrogenous materials have been made highly available, not only because the nitrogen compounds can be ammonified quickly in the soil, but also because these compounds are directly utilizable by plants. This change in the nature of the nitrogen compounds has been brought about by the partial hydrolysis of the proteins contained in the various trade wastes used in the manufacture of the fertilizer. When proteins decompose through natural conditions, be they in the soil or out of it, a certain amount of hydrolysis of the proteins takes place and if the decomposition is allowed to proceed long enough under proper conditions complete hydrolysis will result.

The principle involved in making the nitrogenous material in the soil available and in increasing the availability of low-grade nitrogenous materials by factory treatment is therefore the same. In other words, the general chemical principle to be applied in making available the nitrogen of low-grade fertilizers, trade wastes, etc., is that of complete or partial hydrolysis by any suitable means of the proteins contained in the wastes. Partial hydrolysis of proteins may be accomplished by means of heat, boiling, steaming, heating under pressure; both partial and complete hydrolysis may be obtained by treating with strong acids or alkalis, either in the cold for a long time or heating to a high temperature, the extent of hydrolysis depending on the several conditions. An examination of the patent literature shows that all of these means have been proposed for the treatment of waste materials, although the actual chemical principle of hydrolysis involved in the treatment is not considered. Also, in a number of processes in actual use, various of these treatments are practiced, resulting in different degrees of hydrolysis of the original proteins. While the availability of the nitrogen of a fertilizer depends on the substances in which the nitrogen is contained, it also depends on the extent of hydrolysis of the proteins used in the manufacture. It may be stated that in general the more extended and final the hydrolysis the more available the nitrogen of the compounds formed, since, as has been shown, the final products of hydrolysis are utilized by the plants as such and are at the same time more readily changed into ammonia by bacteria, etc., than are the intermediate compounds produced by partial hydrolysis.

SUMMARY

The base goods used as a type of processed fertilizer is an organic nitrogenous fertilizer which contains acid phosphate. This product is produced by the action of hot sulfuric acid on certain trade wastes; the heat is generated by the interaction of the acid with the organic wastes and rock phosphates in the course of the manufacture of acid phosphate. It is here shown that the hydrolysis of the protein is almost complete, the nitrogenous compounds in the finished fertilizer being principally the products of primary protein decomposition, together with a small amount of a proteose-like compound which has persisted.

From the sample of base goods were isolated the following nitrogenous compounds: two purine bases, guanine and hypoxanthine; the three diamino acids, arginine, histidine, and lysine; and two monoamino acids, leucine and tyrosine. A proteose-like compound was also obtained and its general nature established.

By means of the Van Slyke Method the approximate proportions of the different forms of nitrogen contained in the fertilizer were estimated, and the extent of the hydrolysis of the original proteins was determined. It was also shown by this method that the proteose-like compound was composed of acid amide radicals, diamino acid radicals, especially lysine, and monoamino acid radicals, particularly the monoamino acids which contain non-amino nitrogen.

The question of the availability of nitrogen is discussed, and from a consideration of the amount and the physiological action on plants of the different forms of nitrogen present in the fertilizer it is concluded that the water-soluble nitrogen of this fertilizer should have an availability equal to or greater than the nitrogen of dried blood, or other high-grade fertilizers. These results are in accord with the results obtained by the plant method of determining availability.

The general chemical principle which underlies the method for rendering available the nitrogen contained in most trade wastes, which are to be used as fertilizing materials, is shown to be either partial or complete hydrolysis of the protein of the wastes by any suitable means.

The more complete the hydrolysis the more available the nitrogen in the fertilizer becomes, since the products of complete hydrolysis of proteins are not only utilized by the plants themselves as nutrients but they are more easily ammonified when placed in the soil than are the more complex compounds, such as peptones, proteoses, and the proteins themselves.

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# LABORATORY AND PLANT

## PURIFICATION AND STERILIZATION OF AIR[1]

By S. BORN AND WM. F. CARTHAUS

Received November 16, 1914

In considering the question of air, we have taken it up mainly from the standpoint of the fermentation industry, but the methods employed here could easily be extended to other fields such as the ventilation of hospitals, schools, public buildings and factories.

Air is one of the most important factors in the brewing process, and as sterile air can be obtained by none of the ordinary methods employed for purifying

[1] Presented before the St. Louis Section of the American Chemical Society, June 8, 1914.

air, we have developed several new processes for accomplishing this purpose.

Bacteria, moulds and wild yeast are the undesirable factors in air used for brewing purposes, although

FIG. I—TANKS USED FOR STEEPING BARLEY SHOWING AIR LINES

offensive or disagreeable odors must also be avoided. The species of bacteria, moulds and wild yeast encountered in air are very many, but fortunately only five species of bacteria are dangerous in a brewery, *i. e.*, acetic, lactic, butyric, sarcinae or pediocci, and *Bacillus viscosus*. Practically all others, including all the common pathogenic bacteria, will not survive fermentation. This is very important from a sanitary standpoint.

In our plant we use air of different degrees of sterility,

FIG. II PERMANGANATE TANKS

depending upon the use to which the air is to be applied. All air used is drawn through a pipe line from the top of our highest building by means of a pump which compresses it and conveys it to the various points where it is needed.

The first place that air is used in the brewery is in the steeping of the barley. After the barley is cleaned in the grain elevator it is sent to the malthouse and poured into large tanks filled with water; air is then bubbled through these tanks. The air serves the purpose of agitating the grains before they can settle to the bottom; thus the grains are thoroughly scoured and cleaned; the dust, chaff and undeveloped barley grains are carried to the surface of the tank and removed by an overflow device. The air used in this process is purified by passing it through a series of large drums filled with a solution of potassium permanganate. As the air is sprayed through these tanks of permanganate in a very fine spray the permanganate not only washes the air but oxidizes or removes any objectionable odors and also removes the greater part of the dust, dirt, and bacteria.

After being steeped for a certain length of time, the wet barley is conveyed to a series of compartments kept at a uniform temperature in order to allow the barley to grow. During this growth certain changes take place in the barley kernel, various enzymes, such as amylase and peptase, develop, and during the growing process large amounts of carbon dioxide and other gases are evolved. It is necessary to remove these gases and at the same time provide the barley with a fresh supply of oxygen. This is accomplished by means of air. This air is purified by passing it through a series of galleries constructed of perforated metal plates. Through the center and running the entire length of these galleries there is a water pipe equipped with a large number of very fine sprays. The air must pass through this fine spray of moisture. After the growing process is complete the barley or as it is now called, "green malt," is transported to kilns and dried. It is then cleaned and this represents the finished malt.

The third and perhaps the most important place that air is used is in the fermenting department. The green malt is mixed with water and an infusion made; this is finally boiled with hops and the resulting wort must then be cooled to the proper temperature at which the yeast is to be added for the fermentation by a series of coolers very similar in construction to the ordinary condensers used in the laboratory for distillation purposes. Air is passed through the wort when it is still hot. This air functions mainly as an oxidizing agent. The specific nature of this oxidation has not been very thoroughly investigated but it plays a very important rôle in the brewing process and serves to render certain constituents of the hop, commonly termed hop resins, insoluble; it also has some action on the proteins and carbohydrates at this high temperature.

After the temperature of the wort has been considerably reduced, more air is added, not as an oxidizing agent, but for solution by the cold wort. This dissolved air is necessary for the respiration and growth of the yeast.

When the wort has been cooled and the yeast added, more air serves merely to mechanically agitate the yeast and wort and secure a more or less uniform mixture.

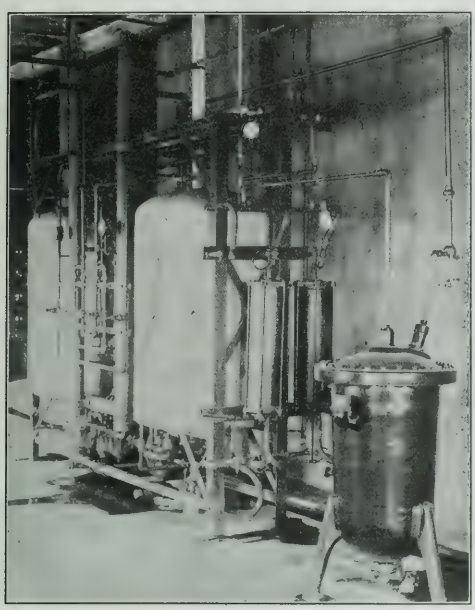


FIG. III—STERILIZER FOR AIR IN FERMENTATION DEPARTMENT PERMANGANATE TANK AND HIGH PRESSURE STEAM BOILER

This object can be accomplished more easily and with a greater degree of sterility with air than by any mechanical device. All the above air used in the fermenting department must, as it comes in direct contact with the beer, necessarily be of a high degree of purity, and we resort to the following method of obtaining it in a sterile condition.

It is a common statement in the literature that all that is necessary in order to obtain sterile air, is to pass it through a cotton filter. We have never been able to obtain sterile air by such a simple method although we have made quite a few experiments along this line.

The air is first passed through a series of drums tightly packed with cotton, which are sterilized at regular intervals in the laboratory. After passage through the cotton, it is then sprayed through a tank filled with a solution of potassium permanganate and from there it is passed through a sterilizing apparatus which consists of a high pressure boiler filled with a series of baffle plates and kept at a temperature of about 265° F. Here the air is intimately mixed with steam at a pressure of 125 pounds, and it remains in contact with this steam at this temperature for about fifteen minutes. It then goes through a series of condensers for cooling it and condensing the moisture, through a small cylinder filled with potassium permanganate (a sight glass, not a sterilizing apparatus) and is then passed into the beer.[1]

The advantages of this method of sterilizing over any washing method can readily be seen when we consider that no matter how small a bubble may be, the volume of the interior is considerable compared to its surface area so that only a small part of the bubble comes in actual contact with the washing or disinfecting liquid. However, in the very intimate mixture of air and steam all parts of the air are reached.

The air for the fermenting cellar and storage cellars (which does not come in direct contact with the beer) is purified as follows: As the temperature of the fermenting and storage departments is generally far below that of the outside air, we use a unique and very simple system of ventilation. Cold air is heavier than warm air and hence sinks, especially if the air contains large quantities of carbon dioxide such as are normally present in a fermenting department; so, at the upper part of the fermenting department we have installed a series of cotton filters and a number of galleries filled with ammonia coils, which cool the air and precipitate any moisture which may be in it. At the lowest floor we open a window or door. The result is that the cold air rushes through the open door and the suction created draws in the outside air through the filter and coils mentioned above. The actual draught at the lower level is strong enough to blow out a candle. The following method is used for testing air: Sterile Petri dishes are provided with a layer of sterile meat gelatine agar or wort gelatine agar; the former is a suitable medium for bacterial growth and the latter for moulds and yeast. If we desire to test the air in a room or cellar we simply expose a plate for a definite length of time, *e. g.*, one minute, and examine the contents developed after 72 hours.

However, testing the air in pipe lines, such as we use throughout the plant, offers more difficulty. We have placed small stopcocks at various points in our air lines but we found that by opening these and exposing a Petri dish near them we never could get a sterile plate. Investigation showed that a siphon was

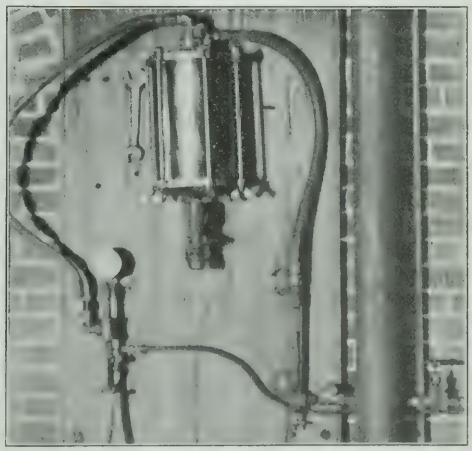


FIG. IV—SIGHT GLASS USED TO INDICATE AMOUNT OF AIR BEING PUMPED INTO WORT

[1] This apparatus was designed and built in our shops in 1913.

created by the outrushing air which dragged micro-organisms from the surrounding air onto the plate. In order to eliminate this undesirable effect we tried fastening funnels of various sizes by means of a rubber attachment to the cock. We found that a funnel whose circumference was exactly that of our dish gave us the best results so this method has been adopted for taking air samples rapidly throughout the plant.

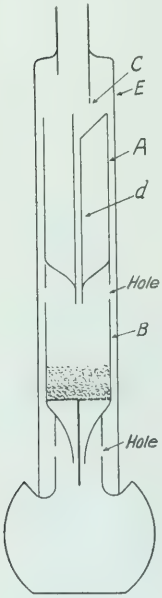
LABORATORY OF THE WM. J. LEMP BREWING COMPANY
ST. LOUIS

## AN ETHER RECOVERY TUBE

By J. M. PICKEL

Received December 17, 1914

In fat extractions with the Knorr flask, it is customary to recover the ether by removing the extraction tube and putting in its place a test tube. The accompanying sketch shows an arrangement by which this exchange of tubes and attendant loss of time and ether are obviated. During the extraction the ether drops from the point C into the funnel *d*, which conveys it into the extraction tube B. When the extraction is finished, the other side of the tube A is brought under the point C; this is accomplished without interrupting the distillation, by merely turning the Knorr flask. The funnel, which is made of either glass or metal, has the peculiarity of being a half funnel, covering but one-half the mouth of the tube A to which it is fused at its lower end only.




The extraction tube B need not be over 4 or 5 cm. long to accommodate an ordinary charge (2 g. substance) and instead of two holes near its top for the circulation of vapor, two V-shaped notches filed in its edge are equally efficient. The inside diameter of the standard cylinder E is about 3.2 cm. (1.25 inches); the outside diameter of A should therefore be not less than 2.7 cm. ($1^1/_8$ inches). The length of A should be the greatest possible without touching the point C when it is revolved.

The inside diameter of the necks of the Knorr flasks need not, and should not, be less than 22 or 23 mm. In that case, the extraction tube can be dispensed with, and in its stead a standard paper thimble, 19 mm. diameter, used. The thimble is placed inside the neck of the Knorr, its lower end reaching down to within 1 cm. of the surface of the ether; it may be conveniently supported in that position by a small copper wire permanently wound around it, ends of the wire on opposite sides resting on top of the neck of the Knorr. The space gained in the cylinder E by thus sinking the extraction thimble into the Knorr, makes it possible to give added length and capacity to the recovery tube A. Moreover, the extraction takes place in ether vapor, at practically the boiling point of ether, and it is claimed that an extraction in that case is complete in about 4 hours instead of the usual sixteen.

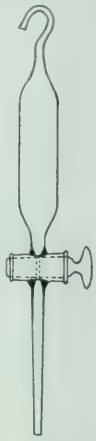
NORTH CAROLINA DEPARTMENT OF AGRICULTURE
RALEIGH

## A CONVENIENT FORM OF WEIGHING PIPETTE

By A. T. MERTES

Received January 27, 1915

For conveniently and accurately weighing out quantities of glycerine such as are used in the determination of glycerol by the acetine method, the writer devised the form of apparatus shown. It is convenient and useful for weighing out oils for the determination of the Iodine Number, especially those oils having a high iodine absorption, and which require an accurate weight. For Koettstorfer and Reichert-Meissl Numbers, the pipette may be calibrated so as to assist in delivery of the proper amount of fat or oil.



The pipette can be made by any one having a little skill in glass working. The writer uses an old 10 cc. pipette and fuses a glass stopcock to one end. The other end of the bulb is drawn out and bent into a hook as shown in the sketch.

In order to fill the pipette, a rubber tube is attached to the upper end and the desired amount of the fat or other substance sucked up into it. The stopcock is then closed, the delivery tube wiped off and the pipette suspended by the hook from a balance and weighed.

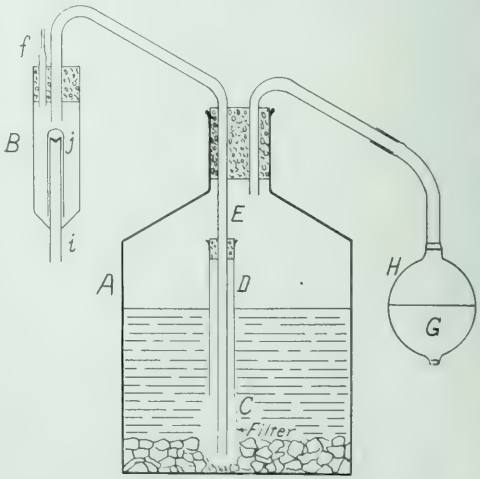
6537 WOODLAWN AVENUE, CHICAGO

## A FILTER-PIPETTE FOR ETHER

By J. M. PICKEL

Received December 17, 1914

The accompanying illustration shows a device for filtering ether without waste and simultaneously delivering it in requisite measure into fat extraction flasks.



The ether is forced by the rubber bulb G, through the filter C, up the tube E, into the pipette B, which delivers it into the flasks. The bulb has only one valve; the small hole H in its side is to be closed by the thumb during compression and to be uncovered the instant the ether begins to overflow into the tube *i*.

The filter is an ordinary paper thimble for fat extraction, fitting snug and tight over the tube D, which is attached by fusion or by cork to the tube E. A thimble 19 mm. in diameter and extending 2 or 3 cm. below the end of the tube D furnishes ample filtering surface. A few wrappings of thread will make it fast to D.

The pipette is what is known as the engineers' siphon. It consists of the cylinder B, inside diameter about 27 mm. and length 10 or 15 cm., as may be required; the fused-in tube *i*, about 3 or 4 mm. inside diameter and about 57 mm. long above its union with the cylinder; the cap *j*, about 8 mm. inside diameter by about 53 mm. long; the vent tube *f*. A pipette of these dimensions will deliver about 25 cc., ample in the Raleigh climate for an ordinary extraction (2 g. of substance), but it is well to give the pipette greater capacity than that and reduce it to any desired volume by placing inside the cylinder glass beads, or better, glass rods. The cap *j* is supported on the end of *i*, which end should be ground slanting on opposite sides, V-shaped, permitting the passage of the liquid.

This method of filtering ether was devised and used by the writer six or eight years ago but it had fallen into disuse until the past winter since which time he has again had occasion to make numerous fat extractions.

North Carolina Department of Agriculture
Raleigh

# ADDRESSES

## THE DYESTUFF SITUATION AND ITS LESSON[1]

By Arthur D. Little

Manufacturers of American flags are in no immediate danger of having to rely upon Cape Cod cranberries for their red or California skies for their blue. Nor is it probable that our textile manufacturers generally will be forced to adopt the suggestion that we utilize our native rainbows to supply the tinctorial requirements of their industry. Six months ago the situation was different. You could have sold rainbows by the foot. The people generally and even the consumers of dyestuffs awoke at the first declaration of war to the long patent fact that the industries of these United States are dependent upon Germany for their supplies of coloring matters, synthetic drugs and many other highly necessary products derived from coal tar. A situation which had been eminently satisfactory to consumers for many years suddenly appeared humiliating and intolerable when the embargo first threatened to cut off supplies. There were insistent demands for the immediate inauguration of an American coal-tar color industry to relieve the situation and render impossible its recurrence. It was to be established by changing the tariff and the patent laws and letting somebody else find the money. Government ownership of dyestuff plants was not considered seriously because there were no German plants interned.

With the lifting of the embargo and the resumption of shipments by way of Rotterdam most of the humiliation disappeared while now there is even a growing disinclination upon the part of textile manufacturers to let the other fellow find the money—and make those essential changes in the tariff. The situation nevertheless remains one to cause concern and involves many factors which are worthy of your serious consideration.

All the world knows that during the last fifty years a sweeping revolution has been effected in the art of dyeing. The vegetable dyes like logwood, fustic, sumac, madder, indigo and many others, the few animal dyes like cochineal and the relatively crude mineral pigments have all been displaced completely or in greater part by the products of synthetic chemistry after a record of tinctorial service extending back to the days of Genesis. The coal-tar color industry, which began in 1856 with the discovery of mauve by an English boy of eighteen, known later as Sir William Henry Perkin, soon took root in Germany where it has attained its present great development and delicately adjusted organization mainly through the genius of a few and the plodding industry of many German chemists, the far-sighted courage of German financiers and the technical and business sagacity of German managers. It is in a very real sense a created industry brought into being by the reaction of intellect upon the black chaos of coal tar. It is peculiarly a German industry and its products for the most part may justly and proudly bear the legend, "Made in Germany."

Contrary to popular belief the products of this industry have displaced the old vegetable dyes because they are better, brighter, faster, easier of application, cheaper and incomparably wider in color range.

With our textile and paper mills, paint and varnish manufacturers, makers of printing inks, and many minor industries thus definitely committed to the use of coal-tar dyes it is not surprising that the sudden prospect of a dyestuff famine should have occasioned grave concern. At the outbreak of the war the textile mills were generally credited with having not more than five months' supply on hand. The other industries concerned were probably less fortunate. For a time the German embargo on dyestuffs prevented shipments, and stocks were rapidly depleted. Through the persistent, earnest and capable efforts of American representatives of the German manufacturers shipments have been resumed under some restrictions but with reasonable regularity. The German plants are running at about 60 per cent capacity and distribution of their product is regulated by the government through the Society of Dyestuff Manufacturers. The basis of allotment is said to be 75 per cent of the 1913 consumption distributed over monthly shipments which must go forward in American boats. There is little doubt that to prevent reshipment to the allies it is the German policy to keep our own mills in a chronic state of dyestuff hunger. As a result many mills are now running from hand to mouth, others claim to be provided for three months and a few for a somewhat longer period on certain lines of colors.

As a result of the close interdependence of the coal-tar dyes and coal-tar explosives industries there has been a practically complete cessation of receipts of such dyes and developers as require for their manufacture nitric acid or raw materials derived from coal tar and available for the production of explosives. Such materials for example are toluol and carbolic acid.

The acid blues and acid blacks largely used in dyeing woolens are already scarce as are also most yellows and oranges and a wide variety of blues and greens. Paranitraniline, used in connection with pigment red in poster work, is practically out of

[1] Address before the United States Chamber of Commerce, Washington, February 5, 1915.

the market and it may be said that pigment workers generally find themselves in an especially precarious condition as to dyes.

Nitro developers are cut off entirely and beta-naphthol is obtainable only at prices which are almost prohibitive. Within a fortnight a large gingham mill has purchased 1200 pounds at $1.50 a pound, as against a normal price of 9 to 9½ cents.

In this connection it is only just to point out that the German manufacturers and the agents and importers here have handled the difficult and abnormal situation created by the war in a spirit of great fairness. They have prevented stocking up by greedy consumers, they have apportioned supplies impartially on the basis of past consumption and they have shown remarkable restraint in the matter of prices. The present average advance on obtainable colors is about 25 per cent based on a 10 per cent increase in factory price and higher insurance and freights. In some cases the advance is 35 to 40 per cent. There is every prospect that with the diminution in the supply of raw materials prices will go much higher in the near future. There is a compensating, though somewhat remote, possibility that the manufacture of nitro dyes and developers may be resumed as the German government has subsidized the construction of two large plants for the manufacture of nitric acid from the air and these are expected to come into operation during the present month.

In the face of the present emergency the textile mills are resorting wherever possible to the old vegetable dyes and are already making free use of logwood and fustic. As a result these woods and their extracts have experienced a marked advance amounting in case of fustic to 100 per cent. Paper mills are endeavoring to confine their product to natural and white papers or those which are tinted rather than deeply colored and all consumers are husbanding their color resources with the utmost care and adopting makeshifts wherever possible. It is gratifying to note that in these efforts they have the cordial and effective coöperation of the laboratories and technical staffs of the great importing agents.

In 1913 the average dividend paid by German dyestuff factories was 21.74 per cent. The actual earnings were much greater and have sufficed in the past to provide sinking funds to cover the entire costs of development and plant. Few industries in the United States can make so good a showing. It seems reasonable, therefore, to inquire why we should endure indefinitely the present hardships and why we should not have a coal-tar color industry of our own which should supply our wants without let or hindrance from Germany. There is but one answer to these questions and but one consideration to restrain us. We can have such an industry whenever we are prepared to pay the price but is it worth that price?

The coal-tar color and explosives industry as developed by Germany is probably the most highly organized of any industry in the world. Starting with less than a dozen crude raw materials such as benzol, toluol, anthracene, naphthalene, carbolic acid, etc., derived from coal tar, it builds up by complex chemical processes which often involve elaborate and expensive plant and the most rigid scientific control of operating conditions more than nine hundred separate ultimate products and over three hundred intermediates, so called, or over twelve hundred products in all, some of which cannot be turned out commercially in quantities much over 100 pounds. The whole system of production depends for its commercial efficiency upon the close correlation and interdependence of these many products. The industry is self-contained. It makes its own crudes and converts its own wastes into raw materials for new processes to be applied to them by itself. The adjustment of the economic balance is so close that a slight change in the value of some one product may disarrange whole series of processes and affect disastrously many products. Obviously, therefore, at this stage of its development the industry must be considered as a whole if any effective competitive development in this country is to be attained. The situation is not unlike that now existing in our packing industry, where, by rougher methods indeed, but on a far greater scale, the entire raw material is utilized in a complex series of related products which are individually profitable only because of their relations to the others.

Twenty-two factories are involved in the German dyestuff industry but by far the larger portion of the business is in the hands of four great companies. The industry as a whole is bound together by trade agreements and coöperative arrangements which add greatly to the efficiency of production.

A few figures regarding one of these companies are instructive. For transportation within the plant it utilizes 42 miles of railroad. Its water works supply 10 billion gallons yearly and its ice factory 12,000 tons of ice. It has four hundred steam engines, five hundred electric motors, nearly as many telephone stations, and 25 steam fire engines. It has a frontage on the Rhine of one and a half miles and handles sulfuric acid in tank steamers. Seven years ago it employed 217 chemists, 142 civil engineers, 8,000 workmen and a commercial staff of 918. Perhaps even more important from the present point of view of the American business man is this significant statement published by this company:

"On looking back upon the successes which the Badische Anilin und Soda Fabrik has achieved since its foundation the management feel it to be their pleasant duty to remember gratefully the benevolent and appreciative support which their efforts have always met at the hands of the State authorities."

Within the last few weeks, Dr. B. C. Hesse, of New York, who combines in a remarkable manner the functions of the chemist and statistician, has brought together many figures which bear upon our present problem and which give some indication of the price which we would have to pay for an American coal-tar color industry.

The world's production of all coal-tar dyes is substantially $100,000,000. The annual turnover of the German plants is about $80,000,000; the plant value on various estimates is not far from $400,000,000. It will be noted that the relation of plant investment to output is extremely high, being $5 to $1. There is one works chemist to every $80,000 of output and about 50,000 employees in all. The total export value of the German product was about $55,000,000, which was distributed among 33 countries. China takes four times as much German indigo as the United States consumes. The average wage in the industry was 4.80 marks inclusive of boys, common labor and skilled labor. The average men's wage was 5.85 marks or $1.40, which is brought by bonuses and social service to the equivalent of $1.84. The gross average export value of the 912 dyes produced is $61,405 each, or, excepting a very few of the most important, the corresponding figure for the remaining 900 or more is $40,811. Dr. Hesse has characterized the German coal-tar color industry as "just about a one-nation business" and on this showing I would ask you if Dr. Hesse is not right.

It is nevertheless an industry which has been replete with romance and with great achievement. The synthesis of alizarine for example gave a death blow to the cultivation of madder, the annual production of which 45 years ago was about 500,000 tons. Synthetic indigo upset the social economy of whole regions in India, and made available for raising food great tracts of land before devoted to the cultivation of natural indigo. These triumphs of organic chemistry unquestionably reacted throughout the entire range of German industry and did much to convert the nation to the cult of science upon which its extraordinary efficiency in material affairs is based. These considerations, coupled with the industrial miracle of the genesis of the rainbow from so unpromising a material as coal tar, enable the coal-tar color industry to make a peculiarly powerful appeal to the imagination. We would be justly proud had we developed it ourselves.

We have in a sense had a coal-tar color industry in this country for thirty years but it has failed to take deep root or flourish even under the protection of a 30 per cent tariff and during the very period when the German industry, under the far greater stimulus of organized and persistent research, achieved its greatest technical and commercial triumphs. There are today four plants in the country and they make perhaps 15 per cent of the total American consumption but confine themselves to less than 100 products. They hold out no promise of extensive increase in production without government assistance to the extent of a 30 per cent *ad valorem* duty plus $7\frac{1}{2}$ cents per pound specific and an effective anti-dumping clause. In this connection it might be pointed out that from 1880 to 1883 the *ad valorem* duty was 35 per cent with 50 cents specific. The present duty is 30 per cent on colors and 10 per cent on intermediates with synthetic indigo and alizarine colors free. Under it, probably not more than 17 of the 912 German dyes are completely fabricated in this country; the remaining 83 of the 100 types claimed as American products are merely developed or "assembled" here from intermediates obtained from Germany. Were our own manufacturers to secure the entire American business it would amount to only about $10,000,000 annually—a little more than the value of the candy sold by the Woolworth stores.

Since the United States now produces 125,000,000 gallons of coal tar annually it may here be pointed out that the country already possesses a coal-tar industry as distinguished from a coal-tar color and explosives industry, and that the coal-tar industry as such has been developed here to an extent unthought of in Germany. An average tar yields 70 per cent of pitch and only 6 per cent of materials useful to the color industry. In Europe the pitch is commonly used for fuel. In the United States upon the other hand over 90 per cent of the pitch is utilized in roofing, waterproofing and roadmaking, while the creosote oil and naphthalene find other profitable and well known applications.

The plain underlying reason why we have been unable during thirty years of tariff protection to develop in this country an independent and self-contained coal-tar color industry while during the same period the Germans have magnificently succeeded is to be found in the failure of our manufacturers and capitalists to realize the creative power and earning capacity of industrial research. This power and this capacity have been recognized by Germany and on them as corner-stones her industries are based. As a result the German color plants are now quite capable of meeting the demands of the whole world when peace is once restored. Why, then, should we duplicate them only to plunge into an industrial warfare against the most strongly fortified industrial position in the world. Let us rather console ourselves with a few reflections and then see how otherwise we might spend our money to our better advantage.

The gross business of the Woolworth 5 and 10 cent stores in 1913 exceeded the entire export business of the whole German coal-tar color industry by $11,000,000. The sales of one mail order house, Sears Roebuck & Co., in the same year were far greater than the total output of all these German color plants and its last special dividend is about twice the amount of their total dividend payment in 1913. The Eastman Kodak Company, with about twice the capital of the largest German color company, the Badische, and with a government suit on its hands, earned during 1913 net profits of over $14,000,000, or 230 per cent on its preferred stock and over 70 per cent on its common, while the Badische with "the benevolent and appreciative support" of the German government earned 45 per cent. In that year the entire German industry paid $11,000,000 in dividends. The Ford Motor Company with one standardized product does a greater annual business than all the German color plants with their 1200 products and earns four times their combined dividend while paying three times their wages.

Now that our perspective is adjusted let us consider for a moment some of the things which might be done with the vast expenditure of effort, money and research required to establish in this country this "one-nation" industry.

We should first of all review our own almost boundless natural resources and especially should we consider our gigantic and shameful wastes. They offer opportunity for the ultimate development of a score of industries, each of a magnitude comparable to the color industry of Germany, and for the almost immediate upbuilding of hundreds of smaller enterprises relatively no less profitable. We waste for instance 150,000,000 tons of wood a year, a billion feet of natural gas a day, millions of tons of flax straw at every harvest, untouched peat deposits fringe our entire Atlantic seaboard, beehive coke ovens flame for miles in Pennsylvania, wasting precious ammonia and exciting no comment while the burning of a $1,000 house would draw a mob. The whole South is a reservoir of industrial wealth untapped in any proper sense. We have heard these things so often that we can go to sleep while hearing them. We need to really sense them, to get before our consciousness a clear conception of what they actually mean in terms of wasted wealth and present opportunity. When we do this, and there is no better time than now, let us apply the lesson of the German coal-tar color industry to these far greater problems and solve them by the compelling agency of sustained, intensive research.

To take one illustration only, the application to the lumber industry of the South of one-tenth the research energy and skill which were required to bring the coal-tar chemical industries to their present proud preëminence would unquestionably result in the creation of a whole series of great interlocking industries, each more profitable than that of lumbering. The South would be in position to dominate the paper market of the world, it would transport denatured alcohol by pipe line and tank steamer, make thousands of tons a day of carbohydrate cattle feeds, reorganize and develop along new lines and to far better purpose its languishing naval stores industry, and find new opportunity at every hand. To do these things in one industry and many things as good in other industries requires only a little faith, sustained, courageous effort, and the appreciation by American financiers of the earning power of research.

93 Broad Street, Boston

## THE NEW KNOWLEDGE OF COAL AND ITS PRACTICAL APPLICATION[1]

By Horace C. Porter

### THE INDUSTRIAL IMPORTANCE OF COAL

The question may be asked: Why should a chemical-engineering course begin with a lecture on coal? Is the efficient use of coal a fundamental thing in engineering?

Unquestionably power production stands as one of the foundation stones in the structure of any industry, and of the total power which operates modern industries at least 80 per cent is derived from the combustion of fuel, a chemical process. Coal and the coke and gas made from it constitute 85 per cent of the industrial fuel of America.

Proportionate cost of power varies widely in the different industries, but taking them as a whole, census reports show that fuel constitutes about 8 per cent of the operating costs (exclusive of the cost of materials) in manufacturing industries. The importance of efficiency in the use of fuel becomes at once apparent. Over 150,000,000 tons of coal are used for industrial power. If the percentage utilization of the energy of this coal were everywhere increased by 8 per cent, an increase entirely

[1] Lecture delivered by permission of the Director of the U. S. Bureau of Mines, before the Department of Chemical Engineering, University of Pittsburgh, November 9, 1914.

possible through the use of modern, improved, steam engineering appliances and of the gas producer and gas engine, the cost of the industrial fuel used in the United States would be cut in two, and at least $150,000,000 saved. If all the coke produced in the United States in 1913 had been made in by-product ovens, $80,000,000 worth of by-products might have been saved and $10,000,000 in higher yield of coke.

Coal is by far the biggest mineral product of the United States. The production in 1913 was about 570,000,000 tons and the bulk of this was consumed in our own land. The nation's coal bill was, therefore, in the neighborhood of $1^1/_2$ billions of dollars or $60 for each wage-earner per annum. The United States is far ahead of other nations in coal production, having passed Great Britain, the nearest competitor, in 1899, and now surpassing her by nearly 100 per cent. Since we export very little coal and other nations export a great deal, our home consumption surpasses that of other countries by even a much greater margin. Our industries are greater, to be sure, but we must face the fact also that an abundance of fuel resources has made us careless of efficiency in their use.

The coal reserves of this country are immense, the most recent estimates of the United States Geological Survey (for the XII International Congress of Geology, Canada, 1913) showing 1500 billions of tons easily available, not including the sub-bituminous and lignitic coals, these being not widely used now. If production should increase in the future at the rate it has in recent years, the exhaustion of our high-grade reserves may come at no very distant day. But unquestionably there will be a tendency toward a lesser rate of increase in consumption as the present movement toward greater efficiency in the mining and use of coal gains headway and brings results.

We may inquire somewhat analytically: What are the uses of coal and in what ways can they be made more efficient? The 570,000,000 tons produced in 1913 in the United States were used approximately as follows:

| | Tons |
|---|---|
| Domestic | 120,000,000 |
| Other heating of buildings | 85,000,000 |
| Coke and gas | 75,000,000 |
| Locomotives and steamboats | 110,000,000 |
| Industrial power (including central power plants) | 180,000,000 |

Scientifically the methods of utilizing coal may be classified into (1) combustion, (2) carbonization, and (3) gasification by partial combustion. Probably 80 per cent of the coal consumption in America comes under class (1), *i. e.*, it is burned in air directly, and we see therefore, the great importance of improving practical methods and appliances for combustion.

### COMBUSTION

When we analyze combustion as ordinarily carried out in practice we find all three of the fundamental processes going on. Coal does not burn as a whole on the furnace grate. The upper layers of the fuel bed undergo decomposition by destructive distillation, liberating 15 to 40 per cent of the coal as volatile gases and vapors, while combustion of the residual material is going on in the lower portions of the bed. Gasification of the carbon to carbon monoxide also constitutes an important part of the burning process, the fuel bed acting as a gas-producer.

Smoke prevention is essentially a problem of proper handling and thorough combustion of the volatile products of the coal; in fact, furnace efficiency is to an important degree dependent on the same factor. The successful and efficient operation of a coal-burning furnace requires an understanding of the nature and behavior of the volatile matter of coal, and especially of that of the particular coal that is used in each case. Something as to the new knowledge of the volatile matter of coal will be presented later, after other methods of utilizing coal have been considered briefly.

### CARBONIZATION

Carbonization, from the point of view of fuel efficiency, deserves a much greater industrial application than is now given it. It enters as a factor to be sure, into all the applications of coal, and in coke and gas manufacture it constitutes the essential factor. But only a small percentage of the coal produced goes into coke and gas manufacture.

In carbonization the coal is decomposed under the influence of heat, without access of air, and the entire substance other than the mineral constituents breaks down into volatile products and a fixed residue, principally carbon and ash. The volatile matter of the coal here again comes into play as an exceedingly important phase of the process. The manner of the first breaking down of the coal substance as it begins to be heated probably determines in large measure what quality of coke any coal will form. The early or primary volatile products and the kind of heat treatment they receive as they issue from the retort determine the gas and by-product yields of the coal.

Instead of carbonizing and burning in a single operation as is done in a combustion furnace using coal, whereby all of the coal and the intermediate products evolved from it are burned for their heating value only, the coke oven or gas retort utilizes the coal more scientifically by converting it into two improved forms of fuel—coke and gas—with a combined heating value about 85 per cent of that of the coal, and in addition thereto saving the intermediate by-products—tar, benzol, and ammonia—which have a chemical value far exceeding their fuel value. The coke and gas can be burned as fuels without smoke and with greater efficiency than the raw coal. A portion of the coke or of the gas, to be sure, must be used to supply the heat for carbonizing, this item amounting usually to from 10 to 14 per cent of the original heat units in the coal.

It is not an idle dream to look forward to the time when there will be many central power and heating stations in the form of large by-product coke-oven plants, placed at the mines or near large cities. As influences leading to this end, we may mention the following: modern advances in long-distance transmission of electric power, the increasing demand for and value of coal by-products for chemical purposes, the successful use of coke as a domestic and industrial fuel, the development of the gas engine, and the growth of public opposition to the smoke nuisance.

Low-temperature or medium-temperature carbonization of coal has lately been introduced in Europe on an industrial scale. Coal is heated at 500–700° C. either under reduced pressure or in a current of auxiliary gas which passes directly through the coal, producing high yields of tars or oils and rich gas in small quantity. These processes depend for their commercial success on the quality of and the demand for the oils and the solid residues produced. Because of their adaptability to the recovery of oils, possibly motor fuels, from coals not heretofore commonly used for by-products, they offer an interesting field for industrial experiment in the United States. In the present commercial situation brought on by the European war the lack of an adequate supply of creosote oil, largely a coal-tar product, is a big incentive to the increase of coal-carbonizing operations in this country. Sufficient coal tar and benzol can be produced from existing by-product coke ovens and gas retorts to supply the present American demand for all other coal-tar products, creosote oil being excepted. But in view of the increasing use of benzol for many purposes and of the growing demand for coal-tar products of all kinds, there is an opportunity for a large expansion of the coal-carbonizing industry in the near future.

### GASIFICATION BY PARTIAL COMBUSTION

The third general method by which coal is used industrially is exemplified in the gas-producer, comparatively a very efficient method of recovering the potential energy of the fuel. Carbonization enters into this process also, since at the top of the fuel bed the coal is destructively distilled before passing down to be gasified by the air and steam from below. The gas producer

will be treated thoroughly in one of the succeeding lectures of this series.

Having considered the industrial uses of coal in a general way, we may, to advantage, take up now some of the scientific aspects of the problems and allude to some of the more recent findings in this field.

## NATURE OF COAL

It is of interest to inquire first: What is coal? What is its chemical nature and constitution? A knowledge of this would surely be of great value in promoting an understanding of its behavior; in determining, for example, the explanation of the coking property, the cause of spontaneous combustion, or the difference between coals in liability to dust explosions in mines. Unfortunately, however, the problem has proven a most difficult one, and as a result of the work of many investigators during the last 20 years or more, little of a definite nature has been determined. We may say without hesitation that coal is a mixture of complex organic substances which are degradation products of cellulose, resins and gums, and vegetable fats and waxes. Free carbon has never been proven to exist in coal, and hydrocarbons are probably not present in an amount greater than one per cent.

The problem of the constitution of coal has been attacked chiefly by two methods: (1) Extraction with solvents, and (2) destructive distillation at low temperatures. Extraction, while it has resulted, by use of pyridine, in dissolving and removing 15 to 18 per cent of the coal substance, has not separated any single definite identifiable compound in more than mere traces.

Destructive distillation also has led to no exact results, but it has given, on the other hand, certain well-defined indications of the nature of the substances present. These indications are mainly that coal is made up of a great many complex substances, which have resulted from degradation or decay of plant cellulose, lignose, resins and waxes. These substances in coal are closely graded into one another in chemical nature and composition, except that the cellulose and lignose group is probably more or less sharply distinguished from the resinous group. Within each group are substances in many different stages of alteration by aging. Chemically the cellulosic bodies are distinguished by their higher content of oxygen, by their tendency to combine with or absorb oxygen, and by their thermal decomposition into $CO_2$ and CO, water of constitution, and paraffin hydrocarbons. The resinous constituents, on the other hand, have a higher content of hydrogen, less of oxygen, and decompose by heat into hydrocarbons and hydrogen with small quantities of $CO_2$ and water. The resinous bodies are contained most abundantly in the coking and mature coals of the Appalachian region.

## THE VOLATILE MATTER OF COAL

The term "volatile matter of coal" is more or less of a misnomer, but serves as well as any other. There is probably little or no material in coal which is volatile without decomposition. What we call "volatile matter" is the mixture of vapors and gases resulting from decomposition of the coal substance by heat. Its composition depends on the kind of coal and also very much on the temperature to which the coal is heated and to which the primary products are subjected. By "primary products" are meant those which form first as the coal slowly rises in temperature. These are, in order of their formation: water, hydrogen sulfide, carbon dioxide, various saturated and unsaturated paraffin hydrocarbons and hydrogen. Many, in fact most, of the commonly known constituents of coal gas, coal tar and gas liquor, such as benzene, naphthalene, pitch and ammonia, are the products of secondary decomposition of these primary products.

The volatile products of coal are not all combustible. From some bituminous coals, completely dried, we obtain by decomposition as much as 10 per cent of noncombustible volatile matter, and from some lower-grade coals even as much as 15 or 18 per cent. So there can be no question that the term "volatile combustible matter" as frequently used is decidedly a misnomer, since from one-eighth to one-half of the volatile matter of coal is non-combustible. It is important to bear this in mind when comparing coals, since those coals having rich, smoky volatile matter are more difficult to burn efficiently than others having a volatile matter possibly greater in amount but containing a larger proportion of inert matter.

An organic substance, of the nature of cellulose, produces water and $CO_2$ (with CO also) on decomposition by heat. When cellulose itself decomposes at temperatures below 500° C., 43 per cent of its weight appears as water and $CO_2$ in the volatilized products. So also coal produces these things by decomposition, and the more abundantly the less matured and metamorphosed is the coal. We must expect to find an aqueous liquor distilled from coal during its decomposition, and in fact at gas works and coke ovens such is the case, a much greater volume of aqueous ammonia liquor being obtained, especially in the hydraulic mains (the first condensing point), than corresponds to the volume of the wash water added.

These facts enable us to draw inferences, at least, as to the chemical character of some of the substances in coal. The younger coals, like the lignites and sub-bituminous coals, must contain large proportions of bodies with —OH or —CHO groupings, like the celluloses, since they produce water and $CO_2$ so readily; in the more mature coals, like the coking and high-grade steaming coals, there are not as many of these oxygen-bearing groups, but, probably, more of certain highly complex long-chain or many-ringed bodies having side-groups of readily separable hydrogen atoms or of alkyls corresponding to the paraffin and possibly the aromatic hydrocarbons. These hydrocarbon groups are set free by heat, and then easily undergo further decomposition into the simple, commonly known products like methane and hydrogen.

The theory of Wheeler (of the British Coal-Dust Experiment Station) and others, that coal contains considerable quantities of certain substances which decompose only above 700° C. and yield principally thus hydrogen and the oxides of carbon, is hardly justified by the experimental data at hand. More reasonably is it to be supposed that the large amount of hydrogen produced above 700° C. comes from secondary breaking down of the hydrocarbons first liberated, and of the partially carbonized solid material left behind, these things not having been present, either of them, as such in the original coal. It is likely that all the organic substance in coal decomposes early by heat, below 500° C.

The nature of the substances liberated or volatilized from coal by moderate heat throws some light on the coking properties of the coal. If by prolonged heating at 400° C. the coal shows little or no tendency to soften or sinter together, and liberates water and gas but only a small quantity of heavy, viscid tar or pitch, it has not good coking properties. Laboratory tests to show coking quality of coals have never been satisfactory. Several are used which give more or less indication but are not definite. Among these may be mentioned (1) heating to a red heat a small sample enclosed in a covered, well-filled platinum box, and examining the coke bar produced; (2) rubbing or grinding the coal in a mortar and noting the tendency to cake or adhere to the pestle and mortar; (3) analyzing for C, H and O and comparing ratios of O to H.

In recent laboratory experiments in Germany cellulose has been converted into coal by subjecting it to very great pressure with moderate heating.

Investigations are in progress at several places to determine methods of increasing yields of some of the by-products of coal carbonization, *e. g.*, the commercially desirable

benzol and light oils, through carbonization under carefully controlled conditions, of the tars thus produced.

RATE OF EVOLUTION OF VOLATILE MATTER—In the utilization of coal, particularly in burning on furnace grates, the rate at which the volatile matter is set free is frequently of greater importance than the total quantity produced. Coals vary greatly in this respect. The following results obtained in the laboratory on three different coals similarly treated (0.4 gram powdered, air-dry coal heated at 1000° C.) bring out this variation:

| Time | 5 seconds | | 80 seconds | |
|---|---|---|---|---|
| Per cent volatile matter | Total | Combustible | Total | Combustible |
| New River, W. Va., coal... | 5.8 | 4.8 | 20.0 | 17.5 |
| Pittsburgh, Pa., coal..... | 9.0 | 7.5 | 34.0 | 28.1 |
| Sheridan, Wyo., coal..... | 36.0 | 12.4 | 49.0 | 21.6 |

It may be seen from these data that while the Pittsburgh coal produces finally more combustible volatile matter than the Wyoming, the latter on the other hand liberates considerably the more in the first few seconds of heating.

The rate at which a given coal liberates volatile matter depends (1) on its chemical character, *i. e.*, its ease of decomposition; (2) on the rate at which heat is supplied to it. The ratio between the quantity of coal heated and the quantity of heat supplied in unit time determines the rate at which any given coal becomes heated. It is, therefore, not a question of temperature as much as of quantity of heat and quantity of coal. When each particle of coal has attained a temperature of 900° C. its decomposition into coke and volatile matter is practically complete.

SUMMARY—Three points stand out as of importance in connection with the volatile matter—the element which is so vital in all processes of coal utilization:

1—The composition as well as the quantity of volatile matter varies greatly among coals.

2—The first products volatilized in the early stages of a coal's rise in temperature are essentially different from the total product as usually obtained. These first primary products are largely tarry liquids, with some water vapor and heavy complex gases. Heating conditions determine the degree of secondary thermal decomposition of these products and the composition of the final gas and tar.

3—The rate of evolution of the volatile matter from coal is of practical importance and varies considerably with the kind of coal. For a given coal it is dependent upon the relation between the quantity of coal heated and the quantity of heat supplied—not the temperature.

## OXIDATION, IGNITION, SPONTANEOUS COMBUSTION OF COAL

Next to thermal decomposition or the evolution of volatile matter perhaps the most fundamental process involved in the practical utilization of coal is that of oxidation or burning of the substance as a whole.

Slow oxidation at ordinary temperatures gives rise to spontaneous combustion and deterioration in storage; rapid oxidation has much to do with the initiation and propagation of coal-dust explosions in mines, and with the relative ease of ignition of fuels in general. The process of igniting a combustible substance is not as simple as it may seem on first thought, and just why some fuels ignite more easily than others requires careful analysis.

At temperatures above that of the first appreciable decomposition of the substance (say 250–300° C. in case of coal), the process of combustion is complicated by the distillation of combustible gases and vapors and the alteration of the solid material. The gases and vapors of decomposition are not, however, all combustible and in fact those produced from the most readily ignited materials, such as wood, are largely non-combustible. A splinter of wood held in a flame ignites quickly, it is true, because the gases of decomposition are heated to their ignition temperatures quickly. But we can also ignite the wood easily in a glass tube at 250° C. by passing a current of oxygen over it. Here the ignition cannot be a matter of distilled gases since the temperature used is much below the ignition points of those gases.

Relative ease of ignition is unquestionably dependent to some extent on ease of oxidation, *i. e.*, the rapidity of the reaction of the substance with oxygen. Recent laboratory studies have shown a wide variation among different coals and other combustible substances in their rates of oxidation, and the variation in this property follows the known variation in ease of ignition, in susceptibility to spontaneous combustion, and in rate of deterioration in storage.

The action of oxygen on coal at ordinary temperatures has been shown by recent investigation to consist not in a burning of the carbon to $CO_2$ nor probably of a burning of the hydrogen to water, but largely of an addition of oxygen to the coal substance. This action develops heat. English investigators have shown that the calorific effect of this oxidizing action at 40° C. amounts to between 2 and 3 calories per cc. of oxygen consumed—only a little less than that produced per cc. of oxygen when coal is completely burned (3.0 to 3.5 calories). The rate of oxidation increases rapidly with rise of temperature. A coal which at 30° C. consumes 10 cc. of oxygen per 100 grams in an hour, multiplies this rate so rapidly from the effect of its own production of heat that the temperature would rise to 180° C. in a little over two days if no heat were lost. This would result speedily in ignition if an adequate oxygen supply were at hand.

Spontaneous combustion in stored coal results from this slow oxidation by the air at ordinary temperatures. It is not, in any important degree, a matter of bacterial action, or fermentation. When conditions as to the size of coal and manner of piling are such that the rate of heat production by oxidation is greater than the rate of heat loss by convection currents and radiation, the temperature rises. One of the most important practical considerations is whether an adequate air supply can penetrate to an inner section of the pile where the heat loss is slow. Fine slack coal does not heat seriously in the interior of a pile, if no lump is present. If, however, the interior of a pile consist largely of fine coal and the outer and lower sections consist of lump with very little fine, one of the worst possible conditions is maintained, and spontaneous fires commonly result therefrom.

Deterioration of coal in storage is due to slow oxidation, not to loss of volatile matter. The deterioration in heating value is not as great as has been commonly supposed. With high-grade bituminous and semi-bituminous coals, careful determination has recently shown that this loss amounts to less than 1 per cent in one year's exposure to the weather, and less than 3 per cent in 5 years. With our middle-western and western coals or lignites the loss is greater but probably does not exceed 4 or 5 per cent in one year in any case. Deterioration in size or physical character may be somewhat more serious, and spontaneous heating even though moderate in degree causes very serious loss. Deterioration of any kind may be quite largely prevented by submergence storage under water.

Much more might be said of the new knowledge of coal, if time permitted; of the different ways in which water is held in the coal substance, of occluded gases, of the fusibility or softening of the mineral constituents at high temperatures, of the forms in which nitrogen and sulfur are combined in the coal and how they behave on heating, etc., etc.

From what has been told, however, it is hoped that some understanding may have been given of the importance of scientific knowledge of coal and its behavior and of the practical bearing of this knowledge on every-day industrial problems.

BUREAU OF MINES, PITTSBURGH

# PERKIN MEDAL AWARD

The Perkin Medal for 1915 was conferred on Edward Weston, Sc.D., LL.D., for his distinguished services in the field of Chemical Engineering and Metallurgy, at the regular meeting of the New York Section of the Society of Chemical Industry held at The Chemists' Club, January 22, 1915.

Dr. Weston's pioneer work in the fields of nickel plating, dynamos, arc lights, incandescent lamps and filaments and his remarkable success in the invention and manufacture of standard electrical measuring apparatus, based on his alloy researches, were reviewed in addresses by Prof. Chandler, Dr. Leo H. Baekeland, Mr. Carl Hering, and by the medalist himself. Owing to illness, Dr. Weston had been unable to prepare a manuscript copy of his address and the version printed below was abstracted by the editors from their stenographic notes. The other addresses are presented in full herewith. [EDITOR.]

EDWARD WESTON, PERKIN MEDALIST, 1915

## INTRODUCTORY ADDRESS

By G. W. THOMPSON

LADIES AND GENTLEMEN:

This is the annual gathering when the Perkin Medal Committee makes its presentation of the Perkin Medal. It is hardly necessary or even advisable that your Chairman tonight should do more than preside at this meeting. The speakers that will come after will go into detail concerning the work which leads up to this presentation. There is only one thing which has come to me which I am taking the liberty of presenting, hoping that in doing so I shall not anticipate anything that may be said later on. It would seem as though in the last fifteen or twenty years, during which great progress has been made in our electrochemical industries, that much of that progress has been dependent upon the proper measurement of currents and voltage, and the recipient of the medal tonight is one who has contributed particularly in laying the foundation for precision in electrochemical industry. Efficiency in this means a great deal. Efficiency in labor, efficiency in the utilization of materials, and especially efficiency in the utilization of power, and this final efficiency in the utilization of power would hardly have been possible at all without the development of precision testing instruments, with which we mostly know Dr. Weston and his connections.

The presentation of the medal, however, does not rest upon this, and while it is the thing which we are most apt to think of, and for that reason I mention it at this time, his work in the chemical industry itself warrants us in the presenting of this medal.

The first speaker on our program is the senior American Past President of the Society of Chemical Industry, and I take much pleasure in asking Dr. Chandler, whom we all love and revere, to begin the speeches of the evening.

129 YORK STREET
BROOKLYN

## PRESENTATION ADDRESS

By C. F. CHANDLER

MR. CHAIRMAN AND BROTHER CHEMISTS:

It is my privilege and very pleasant duty, as the senior Past-President of the Society of Chemical Industry, residing in this country, to present to Edward Weston, LL.D. and D.Sc., the ninth impression of the Perkin Medal, in recognition of his most valuable work in applied chemistry.

Dr. Weston has worked upon a great variety of subjects—chemical, electrical and mechanical—and in each of these fields he has been led to most important discoveries which have been promptly recognized and as promptly applied in their respective uses. Prominent among these are his improvements in nickel plating, in the application of dynamos as substitutes for galvanic batteries in electroplating, electrotyping, etc., the Weston standard cell, the flaming arc, the structureless carbon filaments for incandescent electrical lighting, and resistance alloys for electrical measuring instruments.

It is not my purpose to give the details of the varied discoveries and inventions of Dr. Weston, as Dr. Baekeland will follow me and set forth more particularly their nature.

Dr. Weston was born on May 9, 1850, at Brynn Castle, near Oswestry, Shropshire, England. While he was still a lad, his father moved to Wolverhampton in Staffordshire. There he was educated under private tutors. He received his first in-

struction in physics and chemistry from Henry A. Horton, B.Sc. Later he was associated with William H. Harrison, and still later with Thomas Sherlock, both fellows of the London Chemical Society. By this time even, he had already manifested a great taste for science and also for experimenting and occupying himself in the use of mechanical tools. His parents desired him to select some well-established profession for his life work, and they first placed him with a dentist, but this did not suit his tastes. Then they tried him with two physicians, Drs. E. H. and J. M. Colman. He decided that he could stand surgery, but he did not like medicine. However, these physicians exercised a most beneficial influence upon him because they were broad-minded scientific men, both of them in the habit of lecturing on scientific subjects and illustrating them by experiments. So Weston's interest in chemical, metallurgical and electrical subjects, which he had developed while still a boy, was greatly increased by his association with these men. When only sixteen years of age, he delivered an illustrated lecture on electricity, performing the experiments with apparatus which he had himself constructed. The fact soon became apparent to him that he had no taste for the practice of medicine, so he determined to leave home and strike out for himself. Armed with some letters of introduction, he prepared to go to London, but on thinking the matter over, he finally concluded to go to America and make a career there, which he certainly has done. He arrived in New York in May, 1870, with his modest library and outfit of chemical and physical apparatus, a very limited amount of cash and a very simple wardrobe.

He began at once to look for employment, tramping daily through New York, Long Island and wherever he thought chemical operations were carried on. Finally he ran across the small concern of William H. Mardock & Co., manufacturers of photographic chemicals and dealers in photographic supplies and apparatus. Here he made his beginning, manufacturing pyroxyline, and a general line of photographic chemicals, staying about a year. During this period and later, for about three years, he assisted Professor Charles S. Stone, Professor of Chemistry at the Cooper Union. He watched the daily papers and one day saw an advertisement for a man having some chemical and electrical knowledge, especially of electroplating. He answered this advertisement and the next morning a man came to the store and inquired for Weston. This man was a representative of William H. Belden, President of the American Nickel Plating Company. After a short interview, Mr. Belden proposed to engage him at once, but he felt that he could not leave his employers so suddenly, and arranged to continue his position with Mardock & Co. for a fortnight, and to work nights in Belden's establishment. He found that the nickel plating works were in very poor shape, especially the galvanic batteries employed as a source of electricity. He went to work immediately, put the batteries and other things in order and at the end of two weeks everything was working satisfactorily.

When Dr. Weston took his position with the American Nickel Plating Company, he made a most careful investigation into all the details of the art, and made many improvements in these details, by which he improved the quality of the coating, secured great economy in nickel, greatly reduced the time required for plating, and particularly he succeeded in the preparation of the surface to which the nickel was to be applied and in the polishing of the nickel coating. He also discovered a dip which could be conveniently used for removing nickel from damaged goods in order to coat them again. With these improvements the business of the company increased very rapidly and they nickel-plated the greatest variety of articles from a bunch of keys to a fire engine.

Owing to dissentions among the stockholders of the company, the business was finally given up. Weston then went to the Silver Nickel Plating Company about the middle of 1872. He found the process they were carrying on was entirely unsatisfactory and turned the place into a nickel plating business. He soon left the company, however, and was appointed consulting expert by the Commercial Printing Telegraph Company, operating the patents of Foot and Randall. The company was soon bought out by the Gold and Stock Telegraph Company.

Dr. Weston then formed a partnership with a Mr. Harris under the firm name of Harris & Weston for general plating business: copper, brass, nickel, silver and gold. Here he built, in the latter part of 1872, a dynamo as a substitute for batteries in electroplating. This greatly increased his business, so he enlarged the plant and finally moved to Center Street. Here he built another dynamo, larger and somewhat different. Then he built a third dynamo for a manufacturing firm in Newark. At this time he withdrew from the plating business and made an arrangement with the Newark firm to build dynamos for electroplating; he made about twenty of them. They were so expensive, however, that they could be used only by large concerns. He started to design a simpler and cheaper machine, but the firm decided to give up the business. A new firm, Stevens, Robbins & Hayville, bought them out and Weston went into the partnership in order to develop a new nickel anode which he had invented and for which he obtained his first patent in 1875.

Born in 1850, Weston was twenty years of age when he came to America in 1870, and he took out his first patent in 1875 at the age of twenty-five. The record of his varied experience, his efforts and successes for the first five years of his working life is certainly very remarkable, and gave promise of all that he has accomplished since. He has taken out over 350 patents for his various inventions, and has made radical improvements in several arts. Besides that, a great deal of his work has involved the most patient and careful scientific investigations, often of microscopic accuracy, and has contributed largely to the advance of scientific knowledge and theory.

It would give me a great deal of pleasure to explain to you in detail the great variety of subjects which Dr. Weston has investigated and developed during the forty years since he took out his first patent, but as I am to be followed by Dr. Baekeland and by Dr. Weston himself, I must deny myself the pleasure.

In 1903 McGill University conferred upon Mr. Weston the degree of LL.D.; in 1904 the Stevens Institute of Technology bestowed upon him the degree of D.Sc., and in June, 1910, Princeton University conferred the same degree.

To Dr. Weston:

Edward Weston, Doctor of Laws and Doctor of Science, My Dear Friend: It gives me the greatest pleasure, as the representative of the affiliated chemical and electrochemical societies, to place in your hands this beautiful token of appreciation and affection of your fellow chemists.

Columbia University, New York City

## EDWARD WESTON'S INVENTIONS

By L. H. Baekeland

The pioneer work of Dr. Edward Weston is not easy to describe in a few words. His restless inventive activity has been spread over so many subjects, has intertwined so many interlocking problems, that in order to understand its full value it would be necessary to enter into the intimate study of the various obstacles which opposed themselves to the development of several leading industries which he helped to create: the electro-deposition of metals, the electrolytic refining of copper, the construction of electric generators and motors, the development of electric illumination by arc and by incandescent light,

and the manufacture of electrical measuring instruments. An impressive list of subjects; but in every one of these branches of industry Weston was a leader, and it was only after he had shown the way, in an unmistakable manner, that the art was able to make further progress and develop to its present-day magnitude.

But why was Weston able to overcome difficulties which seemed almost unsurmountable to his predecessors and co-workers in the art?

The answer is simple: He introduced into most of his physical problems a chemical point of view—a chemical point of view of his own; a point of view which was not satisfied with general statements, but which went to the bottom of things. He did not get his chemistry wholesale, as it is dispensed in some of our hot-bed-method-educational institutions. He had to get at his facts piece-meal, one by one, adjust them, ponder over them—collect his facts with much effort and discrimination; he did not acquire his knowledge merely to pass examinations, but to use it for accumulating further knowledge.

It seems rather fortunate for him that one of the first employments he got in New York was with a chemical concern which made photographic chemicals. This was the time of the wet-plate, when photographers made their own collodion, their own silver bath, their own paper. Whoever has gone through those delicate operations, knows the difficulties and the uncertainties caused by small variations in the composition of chemicals or in the way of using them. Photochemistry is excellent experience for any young chemist who is too much disposed to generalize all chemical reactions by mere chemical equations. Whoever has to deal with those delicate chemical phenomena which occur in the photographic image, knows that many unforeseen facts cannot be easily accounted for by the self-satisfying but often superficial generalizations of the text-books.

Weston's tendency to observe small details in chemical or physical phenomena led him to improve the art of nickel plating and electrolytic deposition of metals to a point where it entered a new era. When he undertook the study of the difficulties in this art, he took nothing for granted, but, by close observation, succeeded in devising methods not only of improving the physical texture of the deposit, but for increasing enormously the speed and regularity with which the operations could be carried out; all these improvements are now embodied in the art of electrotyping, nickel-, gold-, and silver-plating.

At this time, attempts had already been made for the commercial refining of copper by means of the electric current. But this subject was then in its first clumsy period, far removed from the importance it has attained now among modern American industries. Here again, Weston brought order and method where chaos had reigned. His careful laboratory observations, harnessed by his keen reasoning intellect, established the true principles on which economic, industrial, electrolytic-copper-refining could be carried out. Professor James Douglas[1] referred to this fact in a recent address: "I suppose I may claim the merit of making in this country the first electrolytic copper by the ton, but the merit is really due him (Weston) who in this and innumerable other instances has concealed his interested work for his favorite science and pursuits under a thick veil of modesty and generosity."

The whole problem of electrolytic refining, when Weston took it up, was hampered by many wrong conceptions. One of them was that a given horse power could deposit only a maximum weight of copper, regardless of cathode- or anode-surface. This fallacious opinion was considered almost an axiom until Weston showed clearly the way of increasing the amount of copper deposited per electrical horse power, by increasing the number and size of vats and their electrodes, connecting his vats in a combination of series and multiple, the only limit to this arrangement being the added interest of capital and depreciation on the increased cost of more vats and electrodes, in relation to the cost of horse power for driving the dynamos.

The electro-deposition of metals forced Weston into the study of the construction of dynamos. Until then, the electric current used for nickel-, silver- and gold-plating, as well as for electrotyping, was obtained from chemical batteries. Weston says that it was almost a hopeless task to wean electroplaters from these cells to which they had become tied by long experience and on the more or less skilful use of which they based many of the secrets of their trade.

If the dynamo as a cheap and reliable source of electric current was advantageous for nickel plating, it became an absolutely indispensable factor for electrolytic copper refining. At that time, the dynamo was still at its very beginning—some sort of an electrical curiosity. It had been invented many years before by a Norwegian, Soren Hyjorth, who filed his first British patent as far back as 1855. Similar machines had been built both in Europe and America, but little or no improvement was made until Weston, in his own thorough way, undertook the careful study of the various factors relating to dynamo efficiency.

In 1876, Weston filed his first United States patent on rational dynamo construction, which was soon followed by many others, and before long, he had inaugurated such profound ameliorations in the design of dynamos, that he increased their efficiency in the most astonishing manner. The dynamos which had been constructed heretofore showed an efficiency not reaching over from 15–40 per cent gross electrical efficiency, but the new dynamos constructed after Weston's principles, increased this to the unexpected efficiency of 95 per cent, and a commercial efficiency of 85–90 per cent. He thus marked an epoch in physical science by constructing the first industrial machine which was able to change one form of energy, motion, into another, electricity, with a hitherto unparalleled small loss. As the improvements in dynamos depend almost exclusively on physical considerations, and have little relation to the field of chemistry, I shall dispense with further discussion of this matter. But I should be permitted to point out that the first practical application of electrical power transmission for factory purposes in this country was first utilized in Weston's factory; the success of this installation induced the Clark Thread Works, also located in Newark, to adopt for some special work this method of power transmission which has now become so universal. For this purpose, Weston had to invent new devices for starting, and for controlling, as well as for preventing injuries to motors by overload. In Weston's factory also the electric arc was used for the first time in the United States for general illumination.

In fact, from 1875 to 1886, Weston was very energetically engaged with the development of both systems of arc- and incandescent-illumination by electricity. We see him start the manufacture of arc-light-carbons according to methods invented by him, so that he thus became the founder of another new industry in America. He continued this branch of manufacture until 1884, at which epoch this part of the business was transferred to another company, which has made a specialty of this class of products, and has developed it into a very important industry. Here, again, Weston introduced chemical methods and chemical points of view. Among the many objections which the public had against the electrical arc, was the bluish color of its light. Women especially complained that the blue-violet light did not bring out their complexions to the best advantage. Weston first tried to use shorter arcs which gave a whiter light, but this was only a partial remedy. He soon found a more radical and more complete cure by the introduction of vapors of metals or metallic salts or oxide in the

[1] Commencement address, Colorado School of Mines, *Met. Chem. Eng.*, **11** (1913), 377.

arc itself, so as to modify at will the color of the light; thus he became the inventor of the so-called "flaming arc." It is noteworthy that it took about twenty years before electricians and illuminating engineers became so convinced of the advantages of the flaming arc, that it had to be "reinvented" during these late years, and now it is considered the most efficient system of arc-illumination.

In relation to this invention, it is interesting to quote the following extract of the specifications from his United States Patent 210,380, filed November 4, 1878:

"This rod or stick may be made of various materials—as, for example, of so-called "lime glass," or of compounds of infusible earths and metallic salts, silicates, double silicates, mixtures of the silicates with other salts of metals, fluorides, double fluorides, mixtures of the double fluorides, fusible oxides, or combinations of the fusible oxides with the silicates—the requirements, so far as the material is concerned, being that it shall be capable of volatilization when placed on the outer side of the electrode to which it is attached, and that its vapor shall be of greater conductivity than the vapor or particles of carbon disengaged from the carbon electrodes. The foreign material added to the carbon may be incorporated into the electrode by being mixed with the carbon of which the electrode is composed, or it may be introduced into a tubular carbon; but I have found it best to place it in a groove formed longitudinally in the side of the electrode, as shown."

In his endeavors to make the electric incandescent lamp an economic possibility, we see him introduce over and over again chemical methods and chemical considerations. He first tried to utilize platinum and iridium, and their alloys, which he fused in a specially constructed electric furnace, devised by him, antedating the furnace described by Siemens. This is probably the first electrical furnace if you except the furnace which Hare used in his laboratory in Philadelphia.

But these platinum metals showed serious defects aside from their high cost, and by that time Weston had become so familiar with the properties of good carbon that, like other inventors, he became convinced that the ultimate success lay in that direction.

And now we see him join in that race of rivalry among inventors who all engaged their efforts in search of the really practical incandescent lamp. Among this group of men, the names of Edison here in the United States and of Swan in England, have been best known. To go into the details of this struggle for improvement is entirely outside of the scope of this short review.

Edison succeeded in making incandescent lamp filaments by carbonizing selected strips of bamboo. But even a carbon made of this unusually compact and uniform material was far from being sufficiently regular and homogeneous. Indeed, all the then known forms of carbon conductors had the fatal defect of a structural lack of homogeneity. On account of this, the resistance varied at certain sections of the filament, and at these very spots the temperature rose to such an extent that it caused rapid destruction of the filament; this is somewhat similar to the chain which is just as strong as its weakest link.

These irregularities in the filament reduced enormously the term of service of any incandescent lamp. Weston tried to solve this difficulty by means of his chemical knowledge. He remembered that as a boy, when he went to visit the gas works to obtain some hard carbon for his Bunsen cell, this carbon was collected from those parts of the gas retort which had been the hottest, and where the hydrocarbon gas had undergone dissociation leaving a dense deposit of coherent carbon.

In this chemical phenomenon of dissociation at high temperature, he perceived a chemical means for "self-curing" any weak spots in the filament of his lamp. The remedy was as ingenious as simple. In preparing his filament, he passed the current through it while the filament was placed in an atmosphere of hydocarbon gas, so that in every spot where the temperature rose highest on account of greater resistance, brought about by the irregular structure of the material, the hydrocarbon gas was dissociated and carbon was deposited automatically until the defect was cured, with the result that the filament acquired the same electric resistance over its whole length. But this invention, however brilliant, did not limit his efforts. He had become imbued with the idea that the ideal filament would be an absolutely structureless, homogeneous filament, with exactly the same composition and the same sections throughout its whole length. He reasoned that such a filament could not be obtained from any natural products, neither from paper nor bamboo, but that it had to be produced artificially in the laboratory from an absolutely uniform, structureless chemical substance. After various unsuccessful attempts, he finally secured this result by applying his old knowledge of the days when he used to make collodion. He produced a homogeneous, structureless transparent film of nitrocellulose by evaporating a solution of this material in suitable solvents. As he could not carbonize this film on account of the well-known explosive properties of so-called "gun-cotton," he obviated this difficulty by eliminating the nitrate group of the molecule of cellulose-nitrate by means of ammonium sulfhydrate. This gave him a flexible, transparent sheet, very similar in appearance to gelatine; this material he called "Tamidine." Such films could be cut automatically with utmost exactitude, producing filaments of uniform section, which then could be submitted to carbonization, before fastening them to the inside of the glass bulb of the incandescent lamp.

It is interesting to note here that the modern Tungsten lamp, in all its perfection, made of ductile tungsten, is, after all, the fullest development of the principle of an entirely structureless homogeneous chemical filament. The Tungsten-filament can stand much higher temperatures than carbon and this property gives it higher lighting efficiency, but the former tungsten filaments of a few years ago, which had a granular structure, had the same defect as the earlier carbon lamps, namely, a non-homogeneous texture and corresponding short life.

While Weston was wrestling with all his electrical problems, and more particularly with the construction of dynamos and motors, he was handicapped continuously by the clumsy and time-consuming methods of electrical measurements which were the best existing at that period. Up till then, these methods had been found good enough for physical laboratories, where the lack of accuracy did not result disastrously in hitting the pocket of the manufacturer, or where time—abundant time for observations and calculations—was always available. But progress in the electrical industries lagged behind the delay and uncertainties caused by electrical measurements. So Weston was compelled to invent for his own use a set of practical electrical measuring instruments. It was not long before some of his friends wanted duplicates of his instruments very much; before he knew it, he was giving considerable attention to the construction and further development of these instruments. Just about this time, the electric light and dynamo construction enterprise entered into a new period, where they began to develop into large unwieldy commercial organizations, requiring public franchises and which had to be backed by vast amounts of new capital. In its boards of directors, business men, or financial men and corporation lawyers, became paramount factors and eclipsed in importance the technical or scientific men, who, in earlier days, had almost exclusively contributed to the development of the art.

Following his natural inclinations, Weston soon abandoned his former business connections in order to entrench himself in a field where individuality, science and technology were of almost unique importance, and which he could develop without

the necessity of incurring financial obligations beyond what he could master personally. Thus he dropped his connections with the electric-light and dynamo enterprises, and we see him now, heart and soul, in another new industry which he created—the art of making accurate, trustworthy and easy-to-use electrical measuring instruments. Did he foresee at that time that this art would attain the magnitude to which he has brought it today? Did he dream that his early modest shop was to develop into one of the most remarkably equipped factories in the world; an institution which seems the embodiment of what industrial enterprises may look like in future days, when scientific and liberal-minded management will have become the rule instead of the exception?

In his factory in Newark, Weston seems to have instilled some of his own reliability and accuracy in the minds of the men and women he employs.

In fact, has it occurred to you that even a man with the widest knowledge and the highest intelligence, who is not scrupulously reliable and careful, who is not the soul of honesty personified, could not make honest and trustworthy measuring instruments nor create reliable measuring methods?

What Stas did in chemistry for atomic weights, Weston did for electrical measuring; he created radically new methods of measurement, and introduced an accuracy undreamt of heretofore. Do not forget that his problems were not easy ones. When the British government offered a prize of $100,000 for the nearest perfect chronometer, the problem of a reliable chronometer involved considerably less difficulties and fewer disturbing factors than many of those encountered in devising and making electrical measuring instruments. But here again, even at the risk of monotonous repeating, I want to impress you with the fact that the success of the methods of Weston was found in almost every case in the application of chemical means by which he tried to solve his difficulties.

When he took up this subject, the scientists, as far back as 1884, accepted implicitly the belief that the definition of a metal and a non-metal resides in a physical distinction; that for metals the electrical resistance increased with temperature, while for non-metals, their resistance decreased with temperature. This was another one of those readily accepted axioms which nobody dared to refute or contest because they were repeated in respectable text-books. And yet, this unfortunate behavior of metals was the greatest drawback in the construction of accurate measuring instruments. Indeed, on account of the so-called temperature coefficient, all measurements had to be corrected by calculation to the temperature at which the observation was made. This seems easy enough, but it was time-consuming and often it is more difficult to make rapid accurate observation of the temperature of the instrument itself. First of all, the thermometers are not accurate, and have to be corrected periodically, and, furthermore, it is not an easy matter to determine rapidly the temperature of a coil or an instrument. Moreover, by the very passage of the electric current, fluctuating changes in temperature are liable to occur, which would make the observations totally incorrect. All this led to hesitation and slowness in measurements. Weston wanted to correct this defect, but he was told that the very laws of physics were against his attempts. Before he was through with his work, he had to correct some of our conceptions of the laws of physics; now let us see how he did it:

Weston knew that the favorite metal for resistances was so-called German-silver. Strange to say, he was the first one to point out to the Germans themselves that "German-silver" is a word which covers a multitude of sins, and that the composition of German-silver varies considerably according to its source of supply. The result was that he soon proposed a standard copper- and nickel- and zinc-alloy containing about 30 per cent of nickel, and which had a resistance of almost twice that of ordinary German-silver and a much smaller temperature-coefficient. Not satisfied with this, he took up the systematic study of a large number of alloys. The first series which he undertook to study included more than three hundred different alloys. Since that time, he has considerably increased this number, and is still busy at it. Everyone of these alloys he made himself in his laboratory, starting from pure materials, and controlling the whole operation from the making of the alloy to the drawing of wires of determined size. By long and repeated observations, in which many years have been consumed, he has been able to determine the electrical behavior of each one of these alloys at different temperatures. After awhile, he began to observe remarkable properties in some manganese alloys he compounded. He managed to produce an alloy which had sixty-five times the resistance of copper. But getting bolder and bolder, he strove to obtain an alloy which had no temperature-coefficient whatever. He not only succeeded in doing this, but finally produced several alloys which had a *negative* temperature-coefficient. In other terms, their resistance, instead of increasing with rise of temperature, decreased with increasing temperature. He also showed that the resistance of these alloys depends not only on their composition, but on certain treatments which they undergo, for instance, preliminary heating. And since that day, the physicists have had to bury their favorite definition of metals and non-metals. The present generation can hardly realize what this discovery meant at that time. I could not better illustrate this than by reminding you of the fact that in 1892, at the meeting of the British Association for the Advancement of Science, where it was urged to found an institution similar to the Deutsche Reichsanstalt, Lord Kelvin said in his speech:

"The grand success of the Physikalishe-Reichsanstalt may be judged to some extent here by the record put before us by Prof. von Helmholtz. Such a proved success may be followed by a country like England with very great profit indeed. One thing Prof. von Helmholtz did not mention was the discovery by the Anstalt of a metal whose temperature-coefficient with respect to electrical resistance is practically nil; that is to say, a metal whose electrical resistance does not change with temperature. This is just the thing we have been waiting for for twenty or thirty years. It is of the greatest importance in scientific experiments, and also in connection with the measuring instruments of practical electric lighting, to have a metal whose electrical resistance does not vary with temperature; and after what has been done, what is now wanted is to find a metal of good quality and substance whose resistance shall diminish as temperature is increased. We want something to produce the opposite effect to that with which we are familiar. The resistance of carbon diminishes as temperature increases; but its behavior is not very constant. Until within the last year or so nothing different was known of metals from the fact that elevation of temperature had the effect of increasing resistance. The Physikalische Anstalt had not been in existence two years before this valuable metal was discovered."

Then followed this colloquy:

Prof. von Helmholtz: "The discovery of a metal whose resistance diminishes with temperature was made by an American Engineer."

Prof. Ayrton: "By an Englishman—Weston."

Lord Kelvin: "That serves but to intensify the position I wished to take, whether the discovery was made by an Anglo-American, an American Englishman, or an Englishman in America. It is not gratifying to national pride to know that these discoveries were not made in this country."

The misinformation of Kelvin was due to the fact that after the Weston patents had been published, his alloy was called *manganin* in Germany, and quite some publicity had been given to its properties with scant reference to its real inventor,

an occurrence which, unfortunately, is not infrequent not only among commercial interests but in technical or scientific circles as well.

No less important was the invention of the Weston cell, which in 1908, by the international commission for the establishment of standards of electrical measurements, became the accepted universal practical standard for electromotive force. Here again, this physical standard was obtained by chemical means.

Until Weston's researches on Standard Cells, the Clark cell had been the standby of the electricians and electrochemists of the world, as the standard of electromotive force. It required the keen analysis of a Weston to ascertain all the defects of this cell and to indicate the cause of them. Later, he drew from his careful chemical observations the means to construct a cell which was free from the defects of its predecessors—a cell that had no temperature-coefficient and had no "lag."

He detected that the choice of a saturated solution of sulfate of zinc in which was suspended an excess of crystals of this salt, was an unsuitable electrolyte and one of the principal causes why the indications of the Clark cell varied considerably with the temperature. It is true that this could be obviated by placing the cell in a bath of constant temperature. But this involves new difficulties due to the proper determination of the real temperature. Furthermore, there is always a "lag" in the indications due to the fact that, at varying temperatures, it requires a certain time before the solution of the salt has adjusted itself to the coefficient of saturation for each newly acquired temperature. By studying the comparative behavior of various salts at different temperatures, he came to the conclusion that cadmium sulfate is more appropriate and this was one of the several important improvements he introduced in the construction of a new standard of electromotive force.

Dr. Weston assures me that he has succeeded in making his alloys to show a change of only one-millionth for a variation of 1° C. The metallic alloys he discovered are used in practically nearly all kinds of electrical measuring instruments throughout the world. Weston instruments and Weston methods are now found in all properly equipped laboratories and electrochemical establishments of the world. On a recent trip to Japan, I saw them in the University of Tokio, as well as in the Japanese war museum, where their battered remains attested that the Russians used them on their captured battleships. I have worked in several laboratories in Europe equipped with instruments said to be "just as good" as those of Weston, but in most instances they were imitations of Weston instruments and it was significant that they kept at least one Weston instrument to use to correct and compare with their national product.

Like many inventors, Weston has been engaged extensively in patent litigation. To uphold some of his rights, he had to spend on one set of patents nearly $400,000, a large amount of money for anybody, but, as he told me, he begrudges less the money it cost him than all his valuable time it required—a greater loss to an inventor thus distracted from his work. What is worse, most of this litigation was so long-winded that when finally he established his rights, his patents had aged so much that they had lost, in the meantime, most, if not all, of their seventeen years' term of limited existence. And here I want to point out something very significant. In the early periods of his work, between 1873 and 1886, Weston took out over three hundred patents. Since then, he has taken considerably less, and of late, he has taken out very few patents, after he became wiser to the tricks of patent infringers. Formerly, as soon as he published his discoveries or his inventions, in his patent specifications, he was so much troubled with patent pirates that instead of being able to attend to the development of his inventions, he was occupied in patent litigation. As an act of self-preservation, he has had to adopt new tactics. He now keeps his work secret as long as possible, and in the meantime spends his money for tools and equipment for manufacturing his inventions. In some instances, this preparation takes several years. Then by the time he sends any new type of instruments into the world, and others start copying, he has already in preparation so many further improvements that pretty soon the next instrument comes out which supersedes the prior edition. He had to utilize these tactics since he found how impractical it was to rely on his patent rights for protection. That inventors should have to proceed in this way is certainly not a recommendation for our patent system; it kills the very purpose for which our patent laws were created, namely, *the prompt publication of new and useful inventions.*

YONKERS, NEW YORK

## ADDRESS OF ACCEPTANCE

By Edward Weston

Dr. Chandler, it is nearly 45 years since I first met you. You were then Professor of Chemistry at the School of Mines in the old Columbia College Building. I was then just out of my teens and, only a short time before, I had left the land of my birth in order to escape from parental coercion intended to compel me to continue to follow a profession which I intensely disliked and which I felt was utterly unsuited to my nature, and also to endeavor to carve out here, in my own way, a career in directions which I had previously diligently pursued and really loved. Tonight you have most kindly and appreciatingly referred to my career and work and you have presented me with this beautiful Perkin Medal. I thank you most sincerely for both. But I wish also to now publicly express to you my thanks and my deep sense of gratitude for the gracious manner in which you received and treated me when, in the year 1870, I was a solitary stranger in a strange land. On that occasion, Sir, I was greatly discouraged and distressed: for such money as I had when I came here was nearly all gone, and the prospects of obtaining employment seemed as far away as ever. Hence, I was then in imminent danger of being forced to write home for financial assistance, and this was a thing that I had previously resolved not to do, because I felt that it would be an admission that I had failed and would conclusively demonstrate that I could not get along alone. Your kind words on that occasion, and the letters you gave me to Chas. Pfizer & Co., and other manufacturing chemists, greatly encouraged me and stimulated me to make greater exertions. Soon thereafter I obtained employment, at a very modest salary, it is true, but it was what I needed—a start. In your long, useful and honorable professional career, I know you have frequently done for others what you then did for me, and I assure you that I have never forgotten, but always have cherished the memory of the kindness and real service you did me then

Through you, Sir, I also desire to express my sincere thanks to the representatives of the Society of Chemical Industry, the American Chemical Society, the American Electrochemical Society, the American Institute of Chemical Engineers, Verein Deutscher Chemiker, the Society of Brewers' Chemists of the United States and the Chemists' Club for the manner in which they have honored me by conferring on me the great distinction of being awarded the medal bearing the name and image of that great chemist, Sir William Henry Perkin—a man whose researches, discoveries and labors in chemical science and industry resulted in conferring on mankind such vast and everlasting benefits as to place us all under a deep obligation to forever cherish, respect and revere his name and preserve his memory.

But you, Gentlemen and Ladies, Representatives and Members of the affiliated chemical societies, have also greatly honored me by your presence here tonight; and thus, in all these ways, you have all joined to give me the best possible proofs of your

friendship, of your esteem and of your kind interest in the ways and doings of a fellow traveler in the paths of chemical, electrochemical and other closely related fields of science and industry. Gentlemen and Ladies, I sincerely thank you all for all these great and most touching evidences and tokens of your esteem, your interest in and good will toward me.

I feel considerable diffidence and also much embarrassment in addressing you tonight, and especially is this so in respect to whatever effort I may make to re-traverse a part of my paths in those fields of activity in which you, as chemists and electrochemists, are most directly interested. Dr. Chandler and Dr. Baekeland have each generously and graciously referred to my work and to some of my rather numerous wanderings into ways which at first sight seem to be but little, if at all related to those usually traversed by members of the chemical profession. But, let me say to you that, in none of these frequent, and often apparently long-continued excursions from the domains of chemical science, have I ever been a real deserter from your ranks; and at no time in my career have I entered any field of work when I have not found abundant scope for the employment, to great advantage, of that kind of knowledge, caution, extreme care and regard for exactness and scientific truth, which, in my opinion, can be obtained only by the study of chemistry, and by that kind of experience which is gained in conscientious efforts to apply chemical facts and chemical principles to the development of new arts or new industrial enterprises, or to the advancement or proper conduct of long-established ones.

In addressing you tonight I am laboring under a number of rather serious disadvantages: on account of urgent new work and the nearly constant demands of somewhat pressing daily duties, so that I have been unable to prepare a properly arranged address or the experiments and specimens necessary to adequately and satisfactorily place before you the entire range of my work. Furthermore, it will not take you long to discover that I am not a trained and accomplished public speaker, and it could scarcely be otherwise in view of the fact that I have addressed an audience only twice in nearly twenty years. Therefore, I bespeak your forbearance and consideration if some things are not well described and if what is said lacks somewhat in coherence and logical order.

I received my first employment as a chemist by the firm of W. H. Maduck Company, which then carried on business in Broome St. I left that concern because it was dangerous to continue the manufacture of pyroxylin in such quantities as we were then doing, and with such appliances as we then had. As is usual in such cases an accident occurred. Fortunately only one person was injured, and he not very seriously. After that experience I determined to give up the situation, and soon thereafter found employment with the American Nickel Plating Co., located at 17 Howard Street, this city.

## NICKEL PLATING

At that time the art of nickel plating had just begun, and very little was known about the chemical, electrochemical or even the mechanical conditions necessary to carry it on successfully. Moreover, the public knew practically nothing about the properties of the metal nickel, or the advantages to be derived from coating articles with it. In other words, the public had to be educated to use nickel-plated articles, and those who undertook to practice the art had to learn much about the conditions which had to be complied with in order to successfully prepare, plate and finish the various metals and combinations of metals to which nickel might be advantageously applied for protective or for ornamental purposes.

In general, there was no difficulty with the nickel solutions. The solutions when properly used gave good results. The trouble was mainly due to using methods that were similar to those employed in depositing silver, but silver, as you know, is a very soft metal, whereas deposited nickel is very hard. Electrodeposited silver is *burnished* with a burnishing tool, which, with the aid of a little lubricant, is worked backwards and forwards until a lustrous finish is obtained. The last operation is just to touch the surface lightly on a very soft canton-flannel buff covered with a little rouge and water. A nickel deposit, however, cannot be burnished. It is too hard; consequently it must be polished. The processes then employed in preparing the articles for nickel plating were mechanical. The articles, after they came from the buffs, were dipped in a hot or boiling solution of caustic potash, in order to saponify whatever grease might remain on the surface. The article was kept in the potash bath until not only the fat was saponified, but a rather dark coating of oxide was formed on its surface. It was withdrawn from the hot potash solution and was scoured with a common plater's brush, dipped in rather fine pumice stone. You can imagine exactly what would take place in these circumstances with a soft metal like brass. Of course, it would be scratched very badly. The article was then washed in water and placed either directly in the bath or immersed in a solution intended to remove the last faint trace of oxide which might have been formed on the surface of the metal during the operation of scouring. In the processes then employed the standard voltage recommended was two volts, that is, two Snee cells, which gave very closely approaching two volts under ordinary conditions of their use. That recommendation was fundamentally wrong because, as chemists, you can readily see that what was necessary was to cover the inferior metal as quickly as possible after it was placed in the solution, because if this was not done, secondary reactions were apt to take place between the inferior metal and the nickel in solution, and then the adhesive characteristics of the coating were lost. Hence, in reality one of the most important things was to increase the voltage and quickly coat the whole article with a film of nickel, transfer it to a bath in which the voltage was lower, and let the deposit go on until it reached the required thickness. If the article was very large or irregular in shape or was a long distance from the operation, parts of the surface would get covered with secondary compounds and any attempt at polishing would cause flaking. Now, when we plated that relatively rough surface we were, of course, compelled to put on a sufficient coat to cover up those scratches. We lost a very large percentage of the nickel in this way and also a very great deal of time in carefully polishing the nickel coat. The remedy would seem to be obvious—chemical cleaning and putting on the soft metal before placing it in the bath just as good a finish as was wanted on the nickel after polishing. However, I was told that chemical cleaning would spoil the plating solutions, since the claim in the patent was that potash or soda would ruin the solutions. That induced me to take up the question of what the influences of these substances were, and, of course, I found that really they did no harm. The chemical method of cleaning was adopted entirely and is still in use except that the cleansing of iron or steel articles or other metals not readily acted upon by caustic potash or soda is done by the aid of electrolysis.

It then occurred to me that we ought to be able to get softer nickel, but at first the only way I could do it was by reducing the rate of deposition, keeping down the tendency of the evolution of hydrogen at the cathode. Some years later I was rewarded by finding a solution which yielded a nickel deposit with characteristics closely approaching those of good copper. It could be rolled and drawn and I called it "malleable nickel." I think that was the first time malleable nickel had been produced by the electrolytic cathode. It was done by using a *single* salt of nickel, at that time a subject for considerable disagreement among chemists. Beckold actually produced and exhibited before the French Academy of Sciences samples produced by deposition from a sulfate of nickel solution, and later from a solution of a double sulfate of nickel and potassium; he then

stated that it was perfectly easy to get from either of these solutions the required amount of metal. Now it is a rather strange thing that he did not continue his investigation a little longer and discover that his solutions were limited to one or possibly three sheets.

No single salt of nickel that I know can be used for depositing nickel commercially, and no double sulfate of nickel and potassium or any other alkali can be used for depositing nickel, and for a time the cause of it was quite a mystery to me. The supposition was that electrolysis of the double salt would deposit the potassium together with the nickel at the cathode. However, that is not possible, for the potassium would attack the water and cause the formation of caustic potash, which would, in turn, take the acid radical and precipitate its equivalent of nickel on the cathode. But what did take place was this: If you take a solution of a single salt of nickel—chloride, sulfate, bromide or iodide—and electrolyze it you will first get exactly what Beckold did—a good deposit of metallic nickel. But after a while the deposit takes on a darker and darker color, until at last there is a little tint of green on the surface of the cathode; when that begins, more and more hydrogen is evolved at the cathode until finally the cathode is being covered slowly with a very green salt. But the addition of a little sulfuric acid to the solution causes it to begin depositing nickel again. Now, although all the single nickel salts give an acid reaction to litmus paper, if you electrolyze the solution until you get the green deposit on the cathode you will find that the solution is in a basic condition. To test the accuracy of the conclusion drawn from my experiments, that it was simply because of the basic condition of the solution and not because of any foreign substance, I electrolyzed a specially pure solution of nickel sulfate and before the deposit began to turn acid I added a little freshly precipitated hydroxide of nickel; instantly the deposit became green; I added a little acid and it became metallic nickel. Not satisfied with this I prepared extraordinarily pure nickel, taking great precautions to exclude every trace of potash, soda, alumina and lime, and I found that the solution acted exactly as did my first solution and the commercial sort. That led to the invention of a nickel anode and a new solution and gave me my really first great start.

The anode was made from grain nickel mixed with the minimum amount of carbon with a binder of tar or pitch, the whole thing being submitted to hydraulic pressure. After a long period of use if you broke the nickel-carbon electrode up you were rather astonished to find that although you had taken an enormous amount of nickel out of the electrode there was apparently no change in the size of the grains. The only difference observable was to be detected by the use of some sharp pointed instrument and then you could dig in and cut it out in a powdered condition. There is a colloid form of nickel and a crystalline one, and if you use a large cast anode for some time it will look just the same in size as it was originally even after you have used it for a year, but it will bend exactly like a piece of flexible sandstone. Examine it under a glass, and you will note that the colloidal portion has been dissolved out and only the crystals are left.

The solution used was sulfate of nickel, or chloride of nickel, to which boric acid had been added. I could have added any other acid and prevented the precipitation of the salt of nickel at the cathode and the change in the chemical condition of the solution, and, of course, got along fairly well, but there were certain pretty good sound reasons why I should not. If I added another acid which had a tendency to attack the positive metal to be coated I would have secondary reactions set up immediately upon my putting the electropositive metal into the bath, and it turned out that boric acid was the most suitable. The patent was unfortunately drawn so that afterwards others put in acetic acid. You can put in other acids—just keep the solution slightly acid and it will go.

Colloids in a nickel solution are often very dangerous, especially in the ordinary double sulfate solution or double chloride solution. I learned that in about 1870. Under the direction of a New York chemist, a firm in Newark had started a small nickel plating plant, but after it had been running a short time it began to give an extremely black, powdery deposit and large amounts of hydrogen. They could not get a regular metallic deposit. The chemist, who had furnished the solution, the anodes and I think also the batteries, was threatened with a suit and asked me if I could help him. I cross-examined the workmen at the plant but no one would admit doing anything to the solution; yet I could not correct it. Then I questioned them even more closely and finally they admitted that the tank had leaked and that they had saved the solution by transferring it to a barrel—a clean alcohol barrel. I could not imagine what there could be in an alcohol barrel except possibly some organic matter, probably glue. So I made a solution of permanganate of potash, stirred it into the plating solution until I got just the pinkish tinge, put an article in with an electrode, and the thing was all right. Several times thereafter I had similar experiences, and an investigation showed that as much as 0.1 per cent of foreign matter in the form of gelatin ruins a plating solution.

## DYNAMOS

You have, of course, seen in print a good deal about the dynamo and its inventors. The dynamo was originally invented by a man named Soren Hyjorth. I am not quite sure whether he was a Dane or a Swede. That was in 1855. He did not patent it in England in 1855, but showed a provisional specification in England in which he very fully described the machine and illustrated it. He allowed that to lapse, and in 1856 filed an application, which went through. However, Wilde, Siemens, Wheatstone and Varley all believed they had invented the dynamo, and it is generally so believed today. The invention is very extensively given to Siemens and Wilde in this country, and to Siemens in England. As a matter of fact neither of them invented it. Even Varley had it before Siemens, Wheatstone and Wilde. Varley came out with it in 1866, a year before anything was heard from Siemens or Wheatstone.

Originally, the platers had a very small equipment of batteries and these were very cheap. Fair-sized plating establishments could be run with about $15 or $20. The majority of the concerns did not pay much attention to the cost of upkeep. We did not then consider efficiency as we do now. Naturally, I became very well acquainted with the conditions of the plating business, and I could see that if I was going to build dynamos I had a very difficult problem as to the question of first cost. The first dynamo I built was used in my own place in Elm Street, New York. It had two armatures—one for exciting the field magnet, and the other for drawing the arm. That I adopted as a safeguard because I felt that I had to learn something about dynamos, and if I had control of the strength of the current flowing in the field magnet I could control the electromotive force of the other armature quite readily. The machine was built in Newark and it had a regulated rheostat consisting of the legs of the table on which it stood, that is the wires—German silver wires—were wound around the legs of the table, and we had a rheostat and regulator so we could regulate the current in the working armature. On the magnet-charging armature I had thin wire until I got the current down, and kept all the E. M. F. for running an arc light, so that I had a very powerful machine for my purposes. As soon as the success of that machine had been demonstrated the party who did the mechanical work, the same party I had helped out of solution difficulties, asked permission to make one, and I said, "You make it, and I will wind it at our place," so another one was started, and that dynamo ran continuously until a few years ago, when it burned in a fire. When I moved to Center Street, I built another type of single armature and that was

a better machine for efficiency, but still the efficiency from the power standpoint was rather poor. I thought, however, that that type machine might meet the requirements, and we built about twenty of them before I realized I never could make any success with such a type of machine. I made up my mind I had to get a cheaper machine than this if I was to reach the plating industries of the country with a dynamo. I started to design another machine. I had to reduce the amount of work to the minimum and also the amount of material. Hence, the machine was almost entirely made in a lathe—cylindrical work. There were only two parts in the machine which called for a milling machine or plane. After that machine was designed and built and tested we could see that we had something with which we had some possibility of success, but it would probably require a lot of hard work to introduce it and get people to buy it, so I designed two small machines: One was about 4 inches in diameter and about six inches long, to be sold for $65, to the little platers. The other size was about 8 inches in diameter and about 6 inches in length, the armature being somewhat larger, and that was to take care of a pretty good-sized plant, and to sell for $165. Later, of course, we built very much larger machines, up to 20 inches, the inside diameter of the cylinder carrying the radio magnets between the poles of which the armatures evolved. This machine had a tremendous output per pound of material and for unit cost, and so with it we stood a pretty good chance of getting the dynamo introduced.

Some of the difficulties we encountered were very amusing. But you must bear in mind, however, the point of view of the people at that time. First we encountered long time plating. The platers got ready during the day and ran the baths at night so there was on an average twelve to fourteen hours for plating. Of course, that could not be done with a machine because it would require the steam power all night. Necessarily, we had to change their solutions and methods in order to coat as thickly in about $2^1/_2$ to $3^1/_2$ hours as had been done in 12 to 14 hours. And solutions were a tender subject. Then the operators themselves did not like the machine for they regarded their skilful manipulation of their batteries as a part of their stock in trade. Again, the price was a very great difficulty. In one instance in Albany a Mr. Strickland, who had an unusually large business for tableware and fancy ware, would not even let me have anything to mount a machine on. However, I put it up and got it running, and started it. I stayed there two or three days so as to get the plater thoroughly posted on the operation, and told Mr. Strickland that if he did not like the machine in thirty days to send it back. In thirty days the check came. Mr. Strickland happened to be a relative of a gentleman in Newark with whom I was interested in the telegraph business. Mr. Strickland by chance asked him once whether he knew Weston. "Yes," was the answer. Mr. Strickland then said, "You tell that fellow that I did everything in the world to insult him when he was trying to do me a favor." When you get that kind of a customer you finally make headway, but it was dreadfully hard work.

Of course, in the efforts to separate gold from silver and refine copper that type of machine would not have been successful at all. There you have the question of efficiency. You do not have the battery to compete with.

### THE ARC LIGHT

In the arc light industry we were confronted with the opposition to the color of the light. I started with the long arc lamp, but it failed everywhere. I modified the light, as Dr. Backeland says, but that was for a double purpose. It was not for the color only, but to increase the power efficiency. The amount of light per horse power was very largely increased by the addition of the substances that caused the flaming arc, but there was also another very great advantage; they tended to hold the light steady. In the ordinary lamps with pure carbon—that is, nominally pure carbon—the arc traveled around all the time. The use of a cord carbon with something in the center to give a vapor of higher conductivity than pure carbon vapor locates the position of the arc definitely. Placing the substance on the outside as I did in that type of lamp, also keeps the arc in the shape of the carbon, and gives a flame very much like a gas flame in shape and of an enormously increased illuminating power for a given amount of energy.

Carbons were manufactured on a pretty large scale toward the end of my connection with the business, but when we started to work with the arc lamp here we paid $1.20 a dozen for carbons from France. Of course, that price was fatal to the introduction of the electric light. It was a chemical proposition throughout and it required a good deal of hard work. We sold them at from $12 to $14 per thousand when we sold the plant, and I think that they afterwards went down to from $6 to $8 per thousand. The whole affair was not the invention of a lamp—it was getting a lamp to compete with other things like gas.

The topic of carbons in incandescent lamps can be touched upon only in a general way. The incandescent lamp has been misunderstood from almost the start. It is misunderstood a good deal yet by the general public and frequently by a good many people in the business. There never was any difficulty in economically subdividing the electric light: that is nonsense. You have exactly the same proposition to contend with in the incandescent as you have in the arc light. People who wrote as Freece did and Fontaine did in the early eighties about the arc light and the incandescent light not being capable of being subdivided got entirely away from a simple proposition. You can all see this when you stop to consider that if you can produce one arc lamp with say half a horse power and are able to produce two arc lamps with one horse power, what in the world is there to interfere with your doing it? You could not expect to heat to a given temperature four materials with the same amount of heat required for two similar materials. That is obvious but it is where the early writers made their mistake.

What we were confronted with in the arc lamp was a really serious mechanical problem, that of getting the regulators to keep all the arcs always of the same length when they were in series, because there must be the same amount of energy on each lamp. Therefore, the resistances of the individual lamp must be almost exactly the same for equal lighting power. That difficulty was overcome in quite a variety of ways by both Brush and myself long before others were reading about the means of subdividing incandescent light. I discussed the whole subject in a paper before the National Electric Light Association a number of years ago.

### THE INCANDESCENT LAMP

With the incandescent lamp you have a different problem. The smaller the candle power the smaller the filaments must be. It does not make any difference whether they are in series or multiples. Here the chemical difficulties were vastly greater than the mechanical. You could never make a commercially successful incandescent lamp filament out of untreated paper or thread. For instance, with paper there is no uniform density. Moreover, tensile strengths and thicknesses of paper are variables and very thin strips give different amounts of electrical resistance per unit of length. The total resistance of the loop is one thing, but the total resistance of every loop of a given candle power should be exactly the same, and the total amount of matter in the separate lamps should be exactly the same. But there must not be slight resistance in some sections of a loop and large resistance somewhere else, *i. e.*, the loop must be entirely homogeneous. You will see at once that paper or wood fiber, in which the fibers differ, can not possibly furnish a material that will give an evenly distributed electrical resistance. Bamboo is better than any of the other fibers. If gelatine paper is used, you get a gelatinized fiber, as it binds the fibers of paper together and helps, but if you pass the current through such a loop in a vacuum the loop will become hot in some spots and will re-

main cool in others. But if you have a defective loop made from any of these substances, and put it into a hydrocarbon vapor and pass a current through it, the hydrocarbon vapor will be dissociated, and you will have a deposit of carbon forming on the hot spots, so that finally the loop will be repaired and will glow all over uniformly. The next step is to continue the deposition of carbon all over the loop so as to bring the resistance to exactly what you want it before it goes into the lamp. Thus you have chemical control of the resistance, not only of the bad spots, but of the loop as a whole.

The present metallic filament lamp has materially reduced the value of the carbon lamp and has almost driven it out.

Substantially, every incandescent lamp in the world is made by the above process of carbon treatments. There is a curious story in that connection. Who invented it? The courts ruled that I didn't. That is a strange fact. Hiram S. Maxim got the credit for it. Sawyer got the first patent on it. Sawyer and I had a terrible fight over this for a number of years. The courts decided that I had not made the invention. Such are the vicissitudes of an inventor's life. I had made it very early in the history of the work, long before Mr. Maxim or Mr. Sawyer had any knowledge of it whatever.

However, when filaments were treated by the hydrocarbon method they always failed at one spot—the initial weak spot that you first saw and tried to remove. We put a lamp between a powerful permanent magnet and passed an alternating current through it, and the loop vibrated at a rate corresponding with the rate of alternation of the dynamo. That was a severe test but it showed us whether we had completely eliminated the defective spots, because when the loop began to vibrate if there were any weak spots they would show. On obtaining the perfect lamp it became necessary to try to raise the efficiency of the lamp in order to increase possibility of the commercial competing with materials like gas.

I then took up the problem of producing the structureless carbon, a homogeneous thread, of uniform cross section, and of uniform electric resistance from end to end for any given section. That was a chemical problem, of course. At first I attempted to dissolve cellulose. After various expedients, finally including squirting through small openings, I finally came back to collodion film. If you pour a solution of pyroxylin in ether and alcohol on a glass plate it leaves behind a beautiful thin horny film. It has great strength if the cotton from which the collodion is made is good—about 16,000 to 20,000 pounds per square inch. Its tensile strength closely approaches that of some of the poorer metals and some of the rare, good metals. But if you attempt to use a filament of this material for an incandescent lamp the double solvent causes trouble. The alcohol-ether does not hold the pyroxylin in solution quite as well as it should, and shrinkage and pockmarking happen. We got over that by putting a frame of wood around the glass plate on which the liquid was poured and covering the top of the frame of wood with a very thin but very good filter paper. The vapor of the ether and alcohol traveled slowly through the filter paper and left a perfectly smooth film. Another way was to dissolve the pyroxylin in methyl alcohol and allow the solvent to evaporate. But this absorbed moisture from the atmosphere and caused a precipitate so that the film would turn milky—a result of cooling pyroxylin in a finely divided state in the film—called "chilling" in varnishes. A tray of anhydrous calcium chloride over the plate absorbed the vapor and allowed it to evaporate without the interference of moisture. We finally used ammonium sulfide hydrate to convert the material back again to cellulose.

After we got the film in that shape the next thing was to get the gases out of it without getting little explosions in the solid substance. That gave a lot of trouble. We placed the films in the usual apparatus for baking them and raised the temperature slowly and got films, but the bulk of them would be full of little volcanoes, caused by explosions of gas. We analyzed the gases and then we got along all right. That filament slowly displaced everything else. The process was later modified by squirting cellulose dissolved in chloride of zinc through a very fine tube into alcohol; the homogeneous carbon filaments were obtained and the method was within the limits of the invention as stated in the patent.

### ALLOYS

The alloys at our disposal for electrical measurement work were German silver and platinum silver, which was too expensive for use. German silver generally gave a resistance about thirteen times that of copper and a temperature coefficient of 0.004433. "German silver," of course, is only a common term for an alloy composed of a mixture of zinc, copper and nickel. German silver is used in the arts for all sorts of purposes, and is on the market with the nickel content varying from 4 per cent to 18 per cent. I found out quite early that it varied very much in resistance, and the temperature coefficient varied; so I took up the subject very carefully and found that if I increased the percentage of nickel in the German silver I increased the specific resistance in nearly the same proportion, and I reduced the temperature coefficient by nearly the same proportion. We went over the field carefully and made standard German silver, in which we used 30 per cent nickel; it had twenty-eight times the specific resistance of copper (about thirteen as given by Madison) and the temperature coefficient was almost half that of copper. These temperature coefficients were of course of very great importance to the electrical engineer and to other people in using electrical apparatus, because it was necessary where electrical instruments were used to give true results, whereas the results obtained from other alloys varied. The very best German silver that we could make was not good enough for instrument work, nor was it good enough for standard. It had to be used with very great care, and you had to be very careful about measurements. You can scarcely imagine what that means in a laboratory where thousands of electrical measurements are made in a day. Even the labor of calculating was frequently enormous and delayed the investigations, so that it became very urgent to try to find something that would give better results, so, as Dr. Baekeland has said, I took a large number of alloys, and out of all that I examined there was nothing which gave such a high specific resistance as manganilin, the resistance giving metal of all metals. Nickel stands next to it. Nickel gives very high specific resistance not only with copper but with other metals. On the other hand, the nickel alloys do not give as good a temperature coefficient as these manganilin alloys, and what is worse they have a relatively high thermoelectrical effect against copper and other metals.

### THE STANDARD CELL

My first efforts were devoted to the improvement of the Clark cell. I had imported the Clark cell from the other side of the Atlantic when I first started in the electrochemical field. Clark had done a great deal of work on this. According to Clark there was no difficulty in making or selling standard cells of this type. I found a great deal of difficulty when I got at it, and after quite a long investigation I abandoned the form of cell that Clark used. He recommended making the paste of zinc sulfate, mercurous sulfate and metallic mercury. I started my cadmium cell and after a long tedious job I finally succeeded But you had to wait hours before you could get rid of the lag. I reduced the temperature of that cell very much and got rid of the lag by using a known saturated solution of sulfate of zinc of known density and I had a very steady, absolutely reliable standard, but still it had a temperature coefficient. To avoid that I use a mercury cadmium amalgam on one side, and pure mercury with mercurous sulfate on the other. This cell, with a solution of sulfate of cadmium saturated at 4° C., shows practically no temperature coefficient.

## SOME OF DR. EDWARD WESTON'S ACHIEVEMENTS IN THE FIELD OF ELECTRICITY

By Carl Hering

The Perkin Medal is awarded principally for achievements in the field of chemistry. The contributions of Dr. Weston to the development of the practical application of electricity and in the science of electricity, have been of such importance that they should not pass unnoticed on the present occasion, especially as some of them have been of national importance and have brought him international fame.

It is not an exaggeration to say that the rapid development of the electrical industry is in no small part due to the direct-reading electrical measuring instruments which he contributed to the art, and which were of such a high order of accuracy, constancy, reliability, portability and simplicity of application, that it became not only possible but even quite easy to make really reliable measurements, whereby progress in the electrical industries was greatly facilitated. It may be said that the whole space of a laboratory room equipped with instruments, has now been reduced by him to a couple of coat pockets, in which the instruments for such measurements may now be carried.

Having myself been engaged in electrical work in that early and trying period when measuring instruments were so sorely needed, as so much of importance had to be discovered by measurements of currents and voltages, and when all but the crudest of these measurements were tedious, difficult, complicated and unreliable, and were generally limited to the use of the laboratory galvanometer, I can personally vouch for the statement that the advent of the Weston instruments marked a turning point in the development of the electrical industry.

More than that, it was a matter of even national interest, for prior to that time the "precision" instruments (in name though not in fact) were imported from abroad. Europe was ahead of America; but now Weston has turned the tables, and Europe imports large quantities of these instruments from us. Some years ago, in a visit to the German Reichsanstalt where some of the best research work in the world was being done with the best instruments the world could produce, I noticed, with no little national pride, that Weston instruments, made in America, were in universal use there, and this in that one of all the European countries which prided itself most on its development of the instrument art.

Weston early realized that in the successful manufacture of many of the articles used in the electric industry, especially when made on a large scale, such as incandescent lamps, it was essential that reliable and accurate electric measurements be made quickly and by inexperienced labor; he argued that such measurements should be as easy to make as those with the foot rule and the balance. Though considered Utopian in those early days, he persisted and finally succeeded in accomplishing it; the accurate measuring of amperes and volts became as simple as reading the dial of a spring balance, and the accuracy and reliability greatly exceeded it. Indeed it may be justly said that he created the art of practical electrical measurements in the industries, with direct reading, portable instruments requiring no trained experience, to a degree of accuracy equal to and often exceeding that formerly obtained with far more complicated apparatus in laboratories, by skilled and experienced men.

One of the essential factors in making such rapidly repeated measurements in the manufacturing industries, was the avoidance of having to make the troublesome correction calculations, such as those due to changes of temperature. As existing metals and alloys were very inadequate in this regard for resistance materials, on account of their temperature corrections, Dr. Weston, with the determination, persistence and indefatigability which are so characteristic of all his work, and with rare courage in attacking especially difficult problems, set himself the task of finding something better, and as usual he succeeded, giving to the world the alloy now known as manganine, a copper, manganese, nickel alloy, which combined the two very desirable features of a very small temperature coefficient and a high resistivity. The importance of this alloy is shown by the fact that it is now used and adopted internationally. Though the Germans for a time claimed priority in its discovery or invention, they seem now to give him the credit, even to the extent of suggesting calling it "westonine."

Having succeeded in what he was determined to find or produce, Dr. Weston does not rest, as most men do; on the contrary, he at once starts to get something still better; he is his own strongest and most determined competitor. The world was glad to get manganine, but he wanted something more; he wanted an alloy of practically no temperature coefficient, and having then gotten this, he wanted still more, a negative coefficient, something which there was no reason to think existed. As usual, he succeeded in producing it, but still was not satisfied until he had found several of them. The vastness of this metallurgical research will appeal to one when it is considered that there are quite a number of available metals, and that the various possible combinations of these in groups of two, three, four and more in different proportions, is practically infinite.

Nor did it satisfy him to find an alloy that had this desired quality, as it would be useless if it could not be drawn into a wire. Many of these alloys were stubborn and various thermal and mechanical operations had to be found before these otherwise desirable alloys could be made to yield to the wire-drawing process. The thermo-electric properties when in contact with other metals also were an important factor and added to the complications.

The best standard cell known in those early days, for serving as a concrete voltage standard, was not considered by him to be up to his standard of ideals, and indeed it was a troublesome apparatus to use; so he gave himself the task of producing a better one, one which was more easily reproducible and had a lower temperature coefficient; the fact that many others all over the world had tried it but were unsuccessful, rather encouraged than discouraged him. As in other problems which he undertook, he succeeded, and gave to the world something far better than the best it had had, and the world recognized it by making it the international standard; even the Germans now call it the Weston standard cell, though for years they contested the priority of invention. Its predecessor, the Clark cell, is now fast finding its way to the shelves of the museums.

Not satisfied with this standard of reference in which the solution was saturated at all temperatures, he also produced a working cell, the so-called unsaturated one, which saves the user some correction calculations, as it has a still better temperature coefficient.

That his instruments were ranked by electrical engineers as of the highest standard is best shown by the fact that the best claim that competitors could make was that their instruments were "as good as a Weston," whether true or not. It was the pride of laboratories to be equipped with Westons. Disputed measurements were settled by using Westons. When a particular measurement was difficult or troublesome to make, Weston was appealed to to make an instrument to do it easily. Even electrical capacities can now be measured with a portable, direct-reading Weston dial instrument, and perhaps a like simple method of measuring inductances will come next. So great was the demand that his list now includes about 4500 different types and ranges of instruments.

Though the credit for developing the fundamental, typical Weston instrument was disputed for years, the patent courts have given sweeping decisions in his favor.

Years prior to what might be termed the electrical age, which may be said to have started about 1880, Weston was making and selling dynamos. And as I understand that one or more of them are still in use, or were until recently, they must have been very serviceable. At first, about 1872, they were for electroplating; later, about 1874, for arc lamps, and from about 1880 on, for incandescent lights and power. Although in 1878 a noted and well-known Englishman, now deceased, who was later knighted for his achievements in the field of electricity, made a public statement that it was theoretically impossible to run arc lamps in series, Weston had been doing it on a commercial scale for about four years. Hundreds of arc lamps had by that time been made and installed by him, including the dynamos, as a regular commercial product, and in the earlier days as many as six arcs were run in series, though at the Centennial Exposition in 1876, the leading French company was still running a separate dynamo for each arc.

As early as 1878 he devised and patented what has recently been revived and called the flaming arc. He also described the cored carbon at about that time. He made arc-lamp carbons in large quantities in 1875. He was apparently the first to copper plate them, as was shown in a later litigation.

In the field of incandescent lighting he was also one of the earliest, beginning in 1875, and was the first to recognize the importance of, and produce commercially a successful homogeneous carbon filament, as distinguished from those of fibrous structure advocated by others, but which he claimed were wrong in principle. He abandoned the metal filament as early as 1877, recognizing that carbon was a far better material The great trouble with carbon filaments at that time was to get them uniform; this important problem was solved by him in 1875–6 by the hydrocarbon treatment process, which later came into almost universal use. In this ingenious process, defects cure themselves; carbon deposits itself just where it is needed, because the filament becomes hottest where it is weakest, and when heated by a current while surrounded by a hydrocarbon, carbon is deposited where it is hottest. This was also used to do what was otherwise practically impossible, namely, get all the filaments alike in resistance, hence in their candle power, the carbon-depositing process being continued until their resistance became what was wanted.

The production of a homogeneous filament was largely a chemical problem. Without permanently changing its chemical structure, though accomplished by a chemical process, he changed the physical structure of fibrous cotton to that of a horny, transparent sheet having neither cellular nor crystalline structure, and which could be rolled like a metal. It was a modified collodion and named tamadine. The large "mogul" lamps installed by him about 1884 were of this material.

In the development of the dynamo he also made early and very important contributions. He skilfully and intelligently analyzed the internal losses in dynamos, which in those early days were rather great, and showed how they could be reduced or avoided. He seems to have been the first to laminate the armature cores, which he did in 1879. When others devised the compound winding to correct for some internal losses, Weston adopted the much wiser principle of avoiding the losses themselves by low armature resistance and reaction. He patented one of the first drum windings which was symmetrical, hence electrically balanced.

Nothing was good enough for him if there was any possibility of improving it, and nothing seems to be too difficult for him to undertake. When the best manufacturers of this country or abroad, including the finest watchmakers, found it too difficult to meet his exacting requirements for some of the parts of his instruments, he undertook the task himself. To beat the best gave him pleasure. When he wanted a wire drawn to half a mil in diameter, he made it himself, as no manufacturer would undertake such a task. He wanted a screw thread of 500 to the inch, on a 10 mil rod; no one had come more than half way to this, but he accomplished it, originating the taps and dies himself. Not very long ago machine work to a thousandth of an inch was considered the highest class of work, but this was not good enough for Weston who now works to the millionth.

A characteristic of his work is that he insists upon completely finishing a piece of work in the privacy of his laboratory before it is brought before the public, which is in marked contrast with the more usual course of publicly proclaiming in the daily press the great things one intends to do, and which may never materialize. Instead of selling futures he sold finished products. His high ethical principles were shown when in the early days of incandescent lighting he insisted on the equity of rating the lamps by their mean spherical candle power, instead of deceiving the purchasers by measuring them in the direction of maximum light, as was not infrequently done by others.

Among his other early achievements may be mentioned the use of an arc furnace in 1875–6 for melting platinum and iridium, hence prior to Siemens whose arc furnace is usually cited as the first. Dr. James Douglas, who was the first in this country to refine copper electrolytically on a large scale, credited his success to the advice and assistance of Weston in 1878, when very erroneous ideas about its practical impossibility were prevalent among others.

His personality only those of his personal friends who have had the good fortune to have been guests at his home and have been intimately associated with him, can truly appreciate. The same laudable extremes to which he aspires in perfecting his products, he shows in his kindness and loyalty to his friends and associates, as also in defending himself against his enemies. His high ethical principles have made for him both staunch friends and bitter enemies. To profit from losses to those who have shown confidence in his work is repulsive to him; what gives him pleasure is to please them.

On whatever balances a man's life-work may be weighed, the scale of last resort for measuring it, and the one which even his enemies should use, is the question: "In what way has the world benefited by his having lived in it?" The summary of Dr. Weston's work, as given here tonight, answers this.

929 CHESTNUT STREET, PHILADELPHIA

# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

## SAFETY ENGINEERING

An address dealing with the growth and aims of safety engineering was delivered by O. P. Hood of the U. S. Bureau of Mines as vice-president and chairman of Section D of the A. A. A. S. [*Science*, 41 (1915), 154.]

In dealing with the history of this branch of engineering, the address pointed out that its recent rapid development was due not to any new fact or discovery but to the strong accent now placed on the feeling that every industry should receive its workers each day in fit condition and should return them to their homes whole and in like fit condition and to laws supporting this sentiment. While each mechanical, electrical, civil or mining engineer is now asked to look at his work from a new angle, and protective devices are added where it is perfectly evident they should have existed before, this is the merest superficial treatment of the problem, the attack of which de-

mands statistical information about all the circumstances of accidents and the success of safety devices. This solution has produced the safety engineer.

One great need now is for standardization of safety appliances, a standardization such as is demanded of fire prevention equipment and electrical installations. This can be brought about by the preparation of standard detailed specifications covering each case or by requiring the use of protective devices approved by some recognized investigative body. The latter is the simpler system and is similar to that applied in mining, under which the government approves certain types of materials and apparatus.

Safety engineering demands some means for general investigation, since the causes of some types of accidents are sufficiently hidden to require more research than individual industries can support. Several such agencies already exist, potentially or actually; among them are: coöperative agreements between industrial groups and existing federal, state and educational laboratories; university and professional school engineering laboratories, state engineering experiment stations; casualty insurance companies. To these must be added the Federal Bureau of Mines, in whose province is the investigation of safety conditions in mining, quarrying, metallurgical and other mineral industries.

## LIQUID AIR IN INDUSTRY

It will be surprising to many who have not followed the growth of the manufacture of liquid air to learn the extent to which it is used.

By far the greater part is utilized in the production of pure oxygen. But a rapidly increasing number of installations are being made for the manufacture of nitrogen, while the neon which is readily extracted as a by-product, is finding a useful application in industrial lighting. Experiments, giving good results, have also been made with liquid oxygen explosives; and a number of liquid-air plants have been installed for the production of hydrogen.

In the manufacture of oxygen, the liquid-air process has superseded almost all others, chiefly owing to the low cost of production which it permits.

The old barium oxide process may now be regarded as extinct; and the only rival to the liquid-air method is that depending on the electrolysis of water. For small plants the latter process is convenient, and where the hydrogen produced can be sold, it may be accounted a rival of liquid air.

According to *Engineering*, **99** (1915), 98, the cost of producing 1000 cu. ft. of oxygen by the electrolytic process is about $4 for power (on a basis of 0.7 cent, per brake horse power hour), and the total cost, including all other direct charges, except depreciation and interest on capital, and assuming no hydrogen to be sold, is about $4.58. With the liquid-air process on the same basis, the total cost is only $0.87; a plant to produce 40,000 cu. ft. of oxygen per twenty-four hours would require 100 brake horse power, and the initial cost of such a plant, including the motive power and gas holder, is about $37,500.

The increase in the consumption of oxygen is almost entirely due to the successful application of the oxy-acetylene blow-pipe for welding and cutting metals. In 1911 the consumption of oxygen in Germany was 150,000,000 cu. ft., in France 100,000,000 cu. ft., and in England about two-thirds of that amount, and it is estimated that at least 90 per cent of these totals was used for oxy-acetylene work, about one-half of this amount for welding and one-half for cutting. There are, it is stated, some fifty liquid-air oxygen plants at work on the Continent of Europe, and the British Oxygen Company in England has all of its eight factories equipped in this fashion. In the United States only five liquid-air oxygen plants had until recently been built, although there are in operation at least two electrolytic installations. The oxy-acetylene blow-pipe, it is interesting to note, is also used for melting silicon, and for exactly imitating rubies, sapphires, and topazes by fusing appropriate mixtures of alumina and metallic oxides.

Besides the blow-pipe, pure oxygen is required for a number of other purposes. One of the most interesting is the superoxygenizing of the air for blast furnaces. Experiments made on a 100-ton furnace at the Ougrée-Marihaye Works, in Belgium, show that by increasing the percentage of oxygen in the air only from 21 to 23 per cent, a saving of over 1 cwt. of coke is effected in smelting 1 ton of iron, and at the same time the output of the furnace is increased by from 10 to 15 per cent.

The market for nitrogen among makers of artificial manures is a large and growing one. At present the world's consumption of nitrogenous fertilizers is upwards of 4,000,000 tons annually, and liquid-air plants are in existence whose combined capacity will produce enough nitrogen to make 250,000 tons of calcium cyanamide yearly. The cyanamide is made on the Frank-Caro principle, by passing pure gaseous nitrogen through retorts containing calcium carbide, heated to about 800° C. For this purpose a purity of 0.997 is demanded, and a purity of 0.998 and over has, on the Claude and Linde processes, been obtained. On the Claude system nitrogen selling at $0.20 can be produced for $0.10 to $0.12 per kilogram.

Neon is produced as a residuum from the Claude apparatus in no inconsiderable quantities. In fact, from a plant with a capacity of 50 cu. m. of oxygen per hour, about 100 liters are produced per day, the proportion present in the atmosphere being 1 in 66,000. It is well known from the experiments of Ramsay and Collie that neon offers an exceptionally small resistance to the passage of the electric discharge. This property inspired M. Claude with the idea of using the gas obtained from his apparatus in lamps, similar to the Moore nitrogen tubes, and after some difficulties he has met with a fair measure of success. Neon lamps made by him were used to illuminate the colonnade of the Grand Palais des Champs Élysées on the occasion of the Automobile Exhibition in 1910, and fifty of his neon tubes, each 6 meters long, decorated the church of St. Ouen at Rouen during the fêtes of the Norman Millenary.

The use of liquid oxygen in explosives also promises to be considerably developed in the future.

## ALUMINUM IN THE GAS INDUSTRY

The growing use of aluminum for many widely different purposes as a substitute for brass, copper and other metals, is described in the *J. Gas Lighting*, **128** (1914), 732. Most of the experiments with the metal are conducted not so much for discovering its advantages, which are well known, as for finding out whether it has neutralizing disadvantages.

Aluminum is now used to some extent in the making of gas lamps. In some instances it is employed for the outside casings, in others for the tops, and in yet others for the inner portion of the lamps. An aluminum casing is handsome in appearance, and light; but, of course, care has to be taken that it does not get dented, an accident to which the softness of the metal renders it somewhat more liable than steel or copper. Aluminum chimneys do not chip or flake, and do not rust, neither do they induce condensation when cooling; and with these, and tops and reflectors, the consideration of lightness again comes in. The products of combustion do not affect the metal; and inquiry in several directions goes to show that experience generally is satisfactory as regards the effect of the atmosphere. There are many installations of outside lighting in which the lamps are provided with aluminum cases or parts; so they may be said to have been fairly tested.

In connection with a visit to a mantle works some time ago, reference was made in our pages to a new aluminum machine that was being used in the process of impregnating the stock-

ings, this particular metal having been chosen on account of its non-liability to corrode. Almost two years have elapsed since the visit alluded to; and the machine has been found to answer the expectations formed in respect to it.

Aluminum resists corrosion by sulfurous gases and fumes of ammonia—characteristics which, in their view, constitute its most important advantages for use with gas, though economy and lightness are also striking features in its favor. Aluminum conductors have been proved in every way suitable for use in gas works and over producer plants (where copper conductors in many cases on record have to a large extent been eaten into). An excellent example of their use in the latter connection is illustrated in the works of a large British engineering firm. The cables transmit several thousand horse power at low tension from a centrally situated gas-driven power house to the various shops containing electrically-driven machinery. Immediately outside the power house, the whole of the cables are carried across a large yard, in which are situated the producer-gas plant supplying gas to the engines in the power house. Originally, covered copper conductors were employed; but the fumes from the producers had such a powerful corrosive action on both the metal and its coverings, that copper had to be abandoned, and was replaced by bare aluminum. These aluminum cables have now been at work for four or five years, and they have so far proved entirely satisfactory, and show no signs of deterioration.

Aluminum has only one-third the weight of copper, and the same consideration applies when it is compared with brass or steel. In the case of electric conductors, a larger conductor is used, because the conductivity of aluminum is about 62 per cent that of copper, but even taking this into account, an aluminum conductor of equal resistance to one of copper has only one-half the weight of metal and works out in normal circumstances to anything in the neighborhood of 30 per cent of economy in price. Aluminum is more ductile than copper; and this means that bar and rod connections are more easily bent into position. As a matter of fact, when installing round aluminum rod, for instance, one can get most elaborate bends on the spot, by the aid of an ordinary benzoline blow-lamp.

Other uses of aluminum in relation to gas include the making of siphon pumps and of tubes, while the light weight of corrugated sheeting of this metal, with the other qualities already mentioned, makes it very useful. The replacement of brass parts of meters is thought to be another opening for aluminum, and its application even to taps and cocks is held to be only a question of determining the right alloy to use.

## LIFE OF TREATED RAILROAD TIES

Some data collected during the past year by J. H. Waterman, Superintendent of Timber Preservation, Chicago, Burlington and Quincy, on the service of treated ties were presented at the American Wood Preservers' Convention held recently at Chicago; they are quoted in the *New York Evening Post* for January 28, 1915. Out of 550 red oak ties treated with zinc chloride, which were placed in the Burlington experimental track near Mystic, S. D., in 1900, 50 were taken out at the last inspection on October 7, 1914, on account of decay. Previous to this time three had been taken out for the laboratory and eighteen on account of decay, making a total of seventy-one removed, or a little less than 13 per cent. These ties are laid on a 3 per cent grade and a 12 degree curve. All gave a life of 12 years, 87 per cent will certainly give fifteen years life, and there is reason to believe that 50 per cent will be in track at the end of eighteen to twenty years. In the two-mile section between Sidney, Neb., and Peetz, Col., 6,354 ties were laid in the fall of 1900 and the winter of 1900–1901. These ties were also treated with zinc chloride and are laid on a tangent in gravel ballast. Up to and including 1913, 285 of these ties had been removed on account of decay, and at the last inspection on October 6, 1914, 103 additional were removed, making a total of 388. This means that 94 per cent of these ties have already given fourteen years service in a dry western climate.

On the Chicago & Eastern Illinois, 24,271 red oak ties treated by the Wellhouse process, using zinc, glue, and tannin, were inserted in 1900 between Cypress, Ill., and Joppa. A count of these ties in June, 1914, showed 18,045, or practically 75 per cent., still in the track. Mr. Waterman also reported that he had observed that ties treated with creosote or with a mixture of creosote and zinc chloride show less mechanical wear under the rail than ties treated with zinc alone, on account of the action of the oil on the surface which lubricates the tie and the rail and results in less rail-cutting and surface wear.

## THEORY OF THE COKING PROCESS

Experiments by E. Donath, on the theory of coking, are described in a recent number of "*Stahl und Eisen*," **34**, 60. A sample of coal from Rossitz, near Brunn, containing ash 4.64, water 9.66, nitrogen 1.32, hydrogen 4.86, carbon 82.88, total sulfur 3.35, sulfur in ash 0.32, and combustible sulfur 3.03 per cent, when heated in an experimental coke oven gave a molten product sufficiently fluid to run from a small opening at the base of the oven. This product quickly solidified to a shining black mass, containing ash 10.47, water 0.50, nitrogen 0.14, hydrogen 2.99, carbon 76.86, total sulfur 3.63, sulfur in ash 2.18, combustible sulfur 1.45, oxygen 7.59 per cent. The whole of the organic constituents were volatilized when the product was heated in a covered crucible, leaving only the ash. This behavior resembles that of tallow, wax, and paraffin, and some resins; and the author concludes that during the coking of a coal of this type a mixture of compounds, consisting of the degradation products of the resinous and fatty constituents of the original coal-forming materials and also the pitch-like polymerized products of distillation under pressure, is completely melted, and decomposes on further heating without leaving any carbon residue. The decomposition products react chemically with the degradation products of the cellulose and protein constituents of the coal-forming material, cementing them into a carbon-like compound or mixture of compounds. At higher temperatures the protein degradation products in the coal soften; and during the complete gasification of the coal, stable compounds are formed containing sulfur and nitrogen, and these compounds are present in the coke.

## COAL, COKE, AND RESIDUALS MARKETS IN GERMANY

A recent market report, quoted from the *Journal für Gasbeleuchtung* in the *J. Gas Lighting*, **129** (1915), 131, states that there was a brisk demand for coal in Germany—especially the northern and eastern districts, which commonly receive large supplies from England. The gas works in these districts in particular were finding great difficulty in obtaining the necessary supplies. The Upper Silesian coal owners were unable to meet all demands; the Westphalian Coal Syndicate could barely supply its usual customers; and the output of the Staar coal fields had been reduced by nearly 50 per cent of its normal quantity. Gas works, moreover, were often unable to obtain coal of the grade to which they have become accustomed; and this put them at a further disadvantage in meeting the competition of the forced production of oven-coke. Coal prices for the first quarter of the present year are fixed at an advance of at least 24 cents per ton at the pit's mouth; whereas oven-coke is 36 cents per ton lower in price.

The embargo which the German Admiralty has laid on tar has resulted in the accumulation of immense stocks in tar-works, gas-works, etc., and there is an agitation, stimulated by the roofing-felt makers, for a big reduction in the selling price of tar.

Since the demands of the roofing-felt industry have fallen off by 50 per cent, and export of crude tar rom Germany has been prohibited, it will be impossible, the German Journal remarks, to prevent a considerable drop in the market value of tar; but the writer of the report considers that a reduction of more than 15 per cent should not be entertained by gas works.

High prices are ruling for sulfate of ammonia—*viz.*, in the vicinity of the Elbe and west of it, for lots of 5 tons and upwards, from about $67.50 per ton for ordinary grade (25 per cent ammonia) to $68.75 for the 25.5 per cent grade; east of the Elbe about $1.25 per ton above these prices.

## COKE-OVEN GAS FOR BALTIMORE

Some time ago *The Iron Age* contained particulars of two new batteries of by-product coke ovens which have been installed at the works of the Maryland Steel Company, and from which gas is piped to Baltimore for lighting purposes. The work was designed and installed by the Koppers Company.

About 5,800 cubic feet of rich gas per ton of coal carbonized, having an average heating value of about 620 B. t. u., are delivered to Baltimore, and about 4,450 cubic feet of lean gas, of about 490 B. t. u., are used for coking. So of the total quantity of 10,250 cubic feet of gas produced per ton of coal, only a little more than 43 per cent is used for carbonization, while nearly 57 per cent is surplus gas. Reduced to the B. t. u. basis, the requirements for coking are only 38 per cent, while 62 per cent of the total heat value of the gas is available for outside purposes.

At the present time, with only one battery in operation, the total surplus gas is furnished to Baltimore. Provision is made, however, for future use of a portion of the surplus gas in the steel plant. To this end a gas by-pass is installed between the mains for rich gas and lean gas after the final coolers. This by-pass is equipped with a gas seal to permit the gas to travel only in one direction, so that rich gas may flow into the lean-gas main while it is impossible for lean gas to find its way back into the rich-gas main. This feature serves to provide an automatic adjustment of the quantity of rich gas furnished to Baltimore according to the demand. Since the by-pass is located between the final coolers and the benzol washers, the benzol is extracted also from the portions of the rich gas which, owing to reduced demand on the part of the city, enters the lean-gas system through the gas seal.

## LABOR CONDITIONS IN ENGLAND

The effect of the war on the labor market in England—particularly that produced in some cases by the shortage of men due to enlistment—is of interest for comparison with the winter condition of the labor market in this country. *Engineering*, **99** (1915), 102, quotes details from the English *Board of Trade Labor Gazette* on "The State of the Labour Market in December."

Trades affected by war contracts, such as engineering, shipbuilding, cutlery, woolen, worsted, hosiery, boot, saddlery, and wholesale men's clothing, continued very busy, with much overtime. In several industries a shortage of male labor, especially of skilled labor, was reported.

The cotton trade showed a further improvement, and there was also an upward movement in the other textiles, and in the coal-mining and iron and steel industries. The building trades were, on the whole, well employed for the time of the year, especially carpenters, plumbers, and laborers. There was little change in the pig-iron, tin-plate, printing, furnishing, pottery, and glass trades. The tailoring, dressmaking, and hat trades continued to be adversely affected.

Compared with a year ago, when employment was good generally, there was an improvement in the building, engineering, shipbuilding, boot, woolen and worsted, hosiery, and wholesale men's clothing trades—all of which were more or less busy on Government orders. The cotton, lace, linen, tin-plate, pottery, brick, and slate trades showed a marked decline.

The changes in rates of wages reported as taking effect in December were all increases, and amounted to nearly $18,500 per week on the wages of 50,000 work-people. The most important changes affected 5500 coal miners in the Forest of Dean, 20,000 iron workers in the Midlands, 17,000 work-people in engineering works at Birmingham and Leicester, and 3800 laborers, etc., in ship-repairing establishments at Cardiff, Barry, and Penarth.

The number of disputes beginning in December was 17, and the total number of work-people involved in all disputes in progress during the month was 3065, compared with 8061 in November, 1914, and 59,026 in December, 1913. The estimated total aggregate duration of all disputes in progress during the month was 49,200 working days, compared with 84,500 in November, 1914, and 907,700 in December, 1913

Cases dealt with during the month included cotton operatives, Lancashire, boot and shoe operatives, Kettering; iron fitters, Falkirk; armature winders, London County Council Tramways; and tinsmiths, Edinburgh.

The average weekly number of vacancies notified to all Labour Exchanges for the four weeks ended December 11, 1914, was 32,088, as compared with 31,932 in the previous four weeks, and with 22,147 in the four weeks ended December 12, 1913. The average weekly numbers of vacancies filled for the same periods were 23,822, 24,220, and 17,168 respectively.

## GASOLINE SUBSTITUTES

Data on the calorific value of several liquid fuels gathered from various sources by the *Journal für Gasbeleuchtung* and specifications for substitute fuels printed in the same journal were published in the *J. Gas Lighting*, **128** (1914), 727.

The efficiency or consumption per horse power developed is approximately proportional to the calorific power of the fuels. The net calorific power (water as vapor) in B. t. u. per pound is given by Mohr for various fuels, as follows: Petroleum spirit (benzine), 18,000 to 18,900; pure benzene, 17,208; commercial 90 per cent benzol, 17,100 to 17,280; pure alcohol, 11,452; 95 per cent alcohol, 10,575; pure naphthalene, 16,722.

The following are the specifications for substitutes:

I—Benzol-Spirit. (*a*) 95 per cent methylated spirit, 70 parts; benzol, 30 parts. The benzol is poured slowly into the spirit with agitation—not the spirit into the benzol. (*b*) 90 per cent, or ordinary, methylated spirit, 50 parts; commercial acetone or acetic alcohol, 20 parts; benzol, 30 parts. The spirit and acetone are first mixed, and the benzol added gradually to them.

II—Benzoline-Spirit. (*a*) 95 per cent methylated spirit, 70 parts; Benzoline, 30 parts. The benzoline is poured slowly into the spirit with agitation—not the spirit into the benzoline. (*b*) 90 per cent, or ordinary, methylated spirit, 50 parts; commercial acetone or acetic alcohol, 20 parts; benzoline, 30 parts. The spirit and acetone are first mixed, and the benzoline added gradually to them.

III—Spirit-Ether. (*a*) 95 per cent methylated spirit, 90 parts; sulfuric ether, 10 parts. (*b*) 95 per cent. methylated spirit, 90 parts; sulfuric ether, 10 parts; naphthalene, 1 part.

IV—Acetone-Spirit. (*a*) 95 per cent methylated spirit, 70 parts; commercial acetone, 30 parts. (*b*) 90 per cent, or ordinary methylated spirit, 50 parts; commercial acetone, 50 parts.

V—Petroleum Mixtures. Petroleum and benzoline (petroleum spirit) mixed in the proportion of two to one; or petroleum 3 parts, acetone 1 part; or petroleum 90 parts, ether 10 parts, with 1 part of naphthalene dissolved in it.

# NOTES AND CORRESPONDENCE

## NOTE ON THE NEWBERRY RAPID LIME DETERMINATION

Although there has been a published statement[1] that a reflux condenser is unnecessary in the Newberry, or Acid and Alkali Volumetric Lime Determination, no data are given, and directions for the method still include its use. Repeating tests made some time ago by Mr. J. T. Abbott,[2] the writer became convinced that results are identical, with and without a condenser, and he therefore carried out the investigation described in this paper.

Considerations of Physical Chemistry indicate that a condenser should not be needed to prevent loss of the acid in boiling very dilute solutions of hydrochloric acid. The results obtained by Wanklyn, Regnault, Brown, Young,[3] and others, on the distillation of liquid mixtures may be cited. Sufficient for the purposes of this paper are the facts that in the system Hydrogen chloride–Water, the vapor phase, with concentrations approaching 100 per cent water, consists of nearly pure water vapor. On boiling, the loss of water increases the concentration of acid in both the liquid and vapor phases, until a concentration of 20.2 per cent acid in the liquid is reached, when a constant boiling mixture at 110° C. results.

For these experiments, a 4-ft. condenser tube was bent at the stopper to an angle of 45° below the horizontal and passed through a cold water jacket: 0.4 *N* solutions of hydrochloric acid and sodium hydroxide, exactly equivalent when drawn from standardized burettes, were prepared. To determine approximately the quantity of acid in the distillates, a simple optical

TABLE I—STANDARD TUBES

| No | Concentration 1 drop in | HCl content in grams | Equivalent to difference in lime value on av. "mix" | Per cent error of lime |
|---|---|---|---|---|
| 1 | 50 cc. | 0.00073 | 0.10 | 0.20 |
| 2 | 100 cc. | 0.00036 | 0.05 | 0.10 |
| 3 | 200 cc. | 0.00018 | 0.025 | 0.05 |
| 4 | 300 cc. | 0.00012 | 0.016 | 0.033 |
| 5 | 400 cc. | 0.000091 | 0.012 | 0.025 |
| 6 | 500 cc. | 0.000073 | 0.010 | 0.020 |
| 7 | 800 cc. | 0.000045 | 0.006 | 0.013 |
| 8 | Clear Water | None | None | None |

plan, based on the Nephelometric Method described by Richards and Wells[4] was employed: 8 × 1 inch test tubes marked to contain 50 cc. were used to collect the distillates, and 5 drops of a standard silver nitrate solution were added in each case.

From the calculation of lime by the Newberry formulae, it appears that a percentage error of 0.2 per cent (about 0.1 difference in the lime value of an average "Raw Mix") would be produced by the loss of the equivalent of from 0.5 to 0.2 cc. of 0.4 *N* acid, depending on the lime content of the material being analyzed. The magnesia value, as calculated, would be unaffected by loss of acid in the first boiling. Taking 0.5 cc. of 0.4 *N* acid as representing the minimum loss of acid to be reckoned with, and since the acid burette in use delivered a drop of exactly 0.5 cc., standard solutions were prepared by adding 1 drop of 0.4 *N* acid to 50, 100, 200, 300, etc., cc. of distilled water, and placing 50 cc. of each with 5 drops of the silver nitrate solution in the observation tubes. Comparison with these tubes would thus give concentrations of acid in terms of percentage error of the lime value. The standard tubes are given in Table I.

Obviously, the stronger the acid, the longer the period of boiling, or the lower the lime content of the material being analyzed, the greater the tendency of acid to pass over into the distillate. As a preliminary observation, 50 cc. of 0.4 *N* acid were boiled for 5 minutes in an open 500 cc. Erlenmeyer flask. The residue, cooled as for a determination, and titrated against the alkali with phenolphthalein as indicator, showed no loss of acid, except that on the addition of 50 cc. of alkali, the red color of the endpoint was a shade lighter than that obtained without boiling: 50 cc. of acid boiled for 5 minutes with the condenser attached gave a distillate of 9 cc. to which were added the usual condenser washings. This operation was repeated a number of times, and the opalescence observed in the distillates placed the acid content between Nos. 3 and 2 of the standard tubes. In one case only the opalescence was very slightly more than No. 2, but the average fell as stated, showing a loss of acid less than 0.00036 g., or about 0.5 drop of 0.4 *N* acid. A sample of rock low in lime gave about the same result, although on comparison it could be easily seen that the opalescence of the clear acid distillate was greater. In these experiments the period of boiling was counted from the time boiling actually commenced. Observations of opalescence by the method employed gave sharply defined results, those made by the writer being readily and accurately checked by others.

The practice in this laboratory has been to place the Erlenmeyer flasks on a hot plate till brisk boiling takes place, and then to allow to simmer or boil slowly at one side of the plate for 5 minutes. This plan, as tested in the above manner, gives excellent results, the distillates in all cases showing no loss detectable by phenolphthalein, and a maximum loss of 0.00012 g. by nephelometry. This method is recommended as giving the best solvent action with the least loss of acid. A great saving of time is effected, not only by doing away with the condenser, but also, as many analyses may be boiled at the same time as there is room for flasks on the hot plate, *i. e.*, 5, easily, on a 12 × 18 in. Hoskins electric plate.

For 0.2 *N* acid the loss due to boiling is so slight that it can scarcely be detected even by nephelometry. A boiling of 7 minutes was required to produce a visible opalescence with the clear acid. The practice of rinsing down the sides of the flask before boiling dilutes the acid and gives a smaller loss. The significant fact is that in nearly 100 determinations, covering all reasonable variations of conditions, not one gave a distillate containing as much acid as one drop of 0.4 *N* solution, and in all cases approaching actual practice, very much less.

A selection from the results obtained is given in Table II, one interesting feature being the test of condenser washings alone, showing that if a condenser is used, nothing is gained by washing it back into the flask after boiling.

TABLE II—EXPERIMENTAL RESULTS

| No | Samples and Treatment | Amount of acid boiled Cc. | Time of boiling Min | Comparison of Opalescence with standard tubes by number | Approximate acid content of distillates Gram | Equivalent to a max. % error in lime value | Fraction of 0.2% error allowed in commercial practice |
|---|---|---|---|---|---|---|---|
| (1) | 0.4 *N* HCl, vigorous boiling | 50 | 5 | > 3 < 2 | 0.000364 | 0.100 | 1/2 |
| (2) | 0.2 *N* HCl, vigorous boiling | 50 | 5 | > 8 < 7 | 0 | 0 | 0 |
| (3) | Condenser washings after (1) was boiled again | 41 | 1 | 8 | 0.000091 | 0.025 | 1/8 |
| (4) | 0.5 g. lime rock (32.10%), 0.4 *N* HCl, vigorous boiling | 25 | 5 | > 3 < 2 | 0.000364 | 0.100 | 1/2 |
| (5) | Same as No. 4, 0.4 *N* HCl, boiled, then digested | 25 | Digest 5 | > 7 < 6 | 0.000073 | 0.020 | 1/10 |
| (6) | 0.5 g. "raw mix" (41.68%), 0.2 *N* HCl, vigorous boiling | 50 | 5 | > 8 < 7 | 0 | 0 | 0 |
| (7) | Same as (6), 0.4 *N* HCl, vigorous boiling | 25 | 3 | 4 | 0.00012 | 0.033 | 1/6 |
| (8) | Same as (6), 0.4 *N* HCl, boiled, then digested | 25 | Digest 5 | > 7 < 6 [6] | 0.000073 | 0.020 | 1/10 |
| (9) | Condenser washings after (8) was boiled again | 20 | 1 | > 8 < 7 | 0 | 0 | 0 |
| 10) | 0.5 g. standard "mix", 0.4 *N* HCl, boiled, then digested | 25 | Digest 5 | 4 | 0.00012 | 0.033 | 1/6 |

[1] Meade, "Portland Cement," Last Edition.

[2] Chief Chemist, Union Portland Cement Co.

[3] Young's "Fractional Distillation."

[4] *Am. Chem. Journal*, **1904**, p. 235.

SUMMARY

From theoretical considerations as well as by actual tests, a condenser is unnecessary. The plan of slow boiling without a condenser for 5 minutes, or any shorter period, found to be sufficient for the materials analyzed with 0.4 *N* solutions is recommended. With 0.2 *N* solutions, there is absolutely no danger from loss of acid, unless boiling is continued longer than 10 minutes.

The error introduced by loss of acid due to boiling is less than other sources of error in the method.

Assistance rendered by Professor W. C. Ebaugh, of the University of Utah, and Dr. Joel H. Hildebrand, of the University of California, is gratefully acknowledged.

EDWIN G. PIERCE

UNION PORTLAND CEMENT COMPANY
DEVIL'S SLIDE, UTAH, December 10, 1914

## PRELIMINARY NOTE ON ARTIFICIAL ZEOLITE—PERMUTIT

As a result of a careful study of the artificial zeolite—permutit—I have developed a new method by which I can produce a very effective substitute at a much less cost than that now offered in the market. My product can be made by crushing previously set hydraulic cement to the proper size and extracting the granular material with dilute inorganic or organic acids. The efficiency of the product thus obtained is about three or four times that of the permutit products now on the market.

I am at present working towards the perfection of my method of manufacture and anticipate a more complete publication at a later date.

STEPHEN J. KOCSOR

36–38 WHITEHALL ST., NEW YORK
February 1, 1915

## PETROLEUM EXHIBIT—SAN FRANCISCO PANAMA-PACIFIC INTERNATIONAL EXPOSITION FEBRUARY 20 TO DECEMBER 4, 1915

The United States produced in 1913 crude petroleum and natural gases having a total value of approximately $324,847,000. This is 71 per cent of the value of the total world's production during this period.

The United States Bureau of Mines has been studying the chemistry of natural gases and petroleum in the laboratory for about seven years and methods for the conservation of natural gases and petroleum in the field for about three years.

Realizing the necessity of more practical field studies than had heretofore been possible not only in the chemistry of oils and gases but also in the drilling for oil and gas, their transportation and storage, their refining, testing and using, the Bureau wished to develop a petroleum exhibit at the Panama-Pacific International Exposition where all of these studies would be adequately demonstrated.

The moneys voted by Congress for the uses of the United States Bureau of Mines, however, did not contemplate any such exhibit nor did the fund voted by Congress for the uses of the Government Board at the Panama-Pacific International Exposition contemplate this exhibit. It was necessary therefore to turn to the petroleum industry for help and the Petroleum Exhibit has been made possible by direct contributions from the governing boards of the oil-producing counties of California, especially Fresno, Kern, Santa Barbara and Orange Counties, by the companies and individuals interested in the petroleum industry, by the Commissioner-General of California State Exhibits, by societies concerned with petroleum studies, and by the Departments of the Government studying petroleums for the United States Government, or using the products of petroleum. The organization of this exhibit is largely the work of the United States Bureau of Mines, through whom the aid of various companies and individuals has been enlisted.

The principal part of the Petroleum Exhibit will be located in the open, outdoor space belonging to the Department of Mines and Metallurgy situated east of the Palace of Machinery and will cover about 52,700 sq. ft. of ground. This space is well located, right in the center of the activities between the Main Exhibit Palaces and the Amusement Zone.

Two auxiliary exhibits, each occupying a space of approximately 600 square feet, will be installed in the Palace of Mines and Metallurgy and in the Palace of Machinery.

The Petroleum Exhibit will consist of nine principal divisions:

1. PICTORIAL—Photographs, transparencies, motion pictures and maps of the important oil fields of the world.

2. GEOLOGICAL—Relief models, models of the developed oil fields in the U. S., a collection of rocks and fossils typical of the oil-bearing formation of the important fields of the various states, fossils and oil-bearing formations and marine life, specimens, micro-photographs, large models of microscopic oil-producing organisms, and peg models showing the oil-well development of some of the more important fields of the industry.

3. STATISTICAL—Illustrations of the growth of the industry by graphic curves, mass models, comparative maps, charts, etc.

4. LIBRARY—A library and bibliography of petroleum literature.

5. TECHNICAL—A working oil camp with tool shop, drilling wells, equipment showing transportation facilities such as pipelines, tank cars and tank boats, storage facilities, protection against loss by fire, a refinery, a testing laboratory, appliances showing the uses of the products and an exhibit of the products.

A special exhibit will be made in coöperation with several of the Fire Underwriter Boards of the United States, when, from April 18th to 24th, an "Insurance Week" will be held. The International Fire Waste Congress will convene from October 7th to 9th and the World's Petroleum Congress from October 25th to 30th.

There will be a complete testing refinery with a capacity of about one carload per week, through which will be actually run typical crudes from the important oil fields of the country and from which will be obtained all the products possible to be made from the crude. It will be possible to make these products in such quantities that it will be practicable to use them as lubricants or fuels in the machines in the Palace of Machinery.

There will be model, fully equipped testing laboratories showing the latest and most approved methods of testing and the instruments and apparatus used. These will include laboratories for: checking and controlling the refinery runs; photometric study and development of lamps and lamp oils; critical study of methods and material; the examination of natural and artificial oil-gases both illuminating and producer; study of road oils and asphaltum paving materials. Actual testing will be carried on during the entire time of the Exposition. Some of the products produced in the refinery, such as the lubricants and fuels, will be supplied to the engineers in charge of the gas and oil engines running in the Palace of Machinery for use in their engines; critical data as to the quality and quantity of these oils will be kept in order that all runs may be considered test runs.

Careful and complete data will be kept of all information about the oil from the beginning of the drilling operations to the end of its uses in its transit through the plant. From the engineering data obtained by the engineers working on the machines in the Palace of Machinery, using the fuels and lubricants, together with the chemical and physical data obtained from the chemical and physical examination of the crudes and their products in the laboratory, combined with the knowledge as to how the products have been prepared or refined in the refinery and with the knowledge of the history and source of the crudes it will be practicable to obtain all the information possi-

ble in regard to the crude, together with full information regarding all the possible products to be made from it.

6. SAMPLES—There will be an exhibit of all types of the crude petroleum produced in the United States and some from abroad. There will be a display of samples of practically all refined products from the 250 odd refineries in the United States, and the crude oils from which these samples have been made will also be shown. The commercial composition, chemical composition and the physical characteristics of these products will be indicated. The companies are sending 5-gallon samples of each of their products. These will be shown in attractive glass bottles properly illuminated and labeled with data of interest. The excess of samples will be used for critical scientific examinations, which will develop valuable information as to the comparative quality of the oils produced from various districts and of various origins. This will be of great commercial, economic and scientific importance.

7. HOUSING AND SANITATION—Studies of the sanitation of isolated camps. Model cottages will be shown, built with practicable conveniences, with gardens, yards and all necessary outbuildings.

8. LECTURES—Illustrated by views and moving pictures by eminent men interested in the petroleum industry.

9. FIRE HAZARDS and methods of preventing and fighting fires; in coöperation with the Insurance and Petroleum Congresses mentioned below and with the Fire Departments of the Exposition and the City of San Francisco.

CONGRESSES

Three congresses of especial interest to the petroleum men will be held during the Exposition:

INSURANCE WEEK, APRIL 18TH TO 24TH—April 24th will be "Fire Prevention Day."

INTERNATIONAL FIRE WASTE CONGRESS, OCT. 7TH TO 9TH—Special studies and displays for preventing fire wastes will be made.

During these Congresses special displays of equipment for fighting oil fires will be demonstrated. This will show the best practice in using high pressure and low pressure water and steam sand and chemical extinguishers, together with the special equipment used. The precautions to be taken will be demonstrated, using burning tanks of oil on North Beach.

THE WORLD'S PETROLEUM CONGRESS, OCT. 25TH TO 30TH—This week has been reserved by the officials of the Panama-Pacific Exposition as a period for discussions and conferences on matters of interest to the men of the petroleum industry.

The program has been divided as follows:

Literature, Exploration, Development and Production, Transportation, Storage and Distribution, Properties and Characteristics, Refining, Utilization, Legal Rules and Regulations, Statistics.

SPECIAL EXCURSIONS to the great petroleum fields of California and Oklahoma are being arranged.

A DEMONSTRATION MINE has been installed in Block No. 6 of the Palace of Mines and Metallurgy by the United States Bureau of Mines, in coöperation with various mining companies and manufacturers of machinery, powder and mine safety appliances. This, under the floor of the building, is to illustrate various methods of mining practiced by the principal metal and coal mines of the country; it gives an excellent idea of the conditions to be found in the mines of the United States. First aid and rescue work will be a prominent feature of this exhibit.

## FIFTIETH MEETING OF AMERICAN CHEMICAL SOCIETY, NEW ORLEANS, MARCH 31 TO APRIL 3, 1915

The Fiftieth meeting of the American Chemical Society will be held in New Orleans from Wednesday, March 31, to Saturday, April 3, inclusive. The Grunewald Hotel, one-half block from Canal Street, with entrances on University Place and on Baronne Street, has been chosen as headquarters. The opening meeting and the Symposium of the Industrial Division will be held at the Tulane University of Louisiana, located on St. Charles Avenue, and reached by the St. Charles Belt cars from Canal or Baronne Streets. The meetings of Divisions will be held in the Grunewald Hotel.

The chairmen of the committees appointed by the local section to make arrangements for the meeting are as follows:

W. L. Howell, *Executive Committee.*
C. S. Williamson, Jr., *Finance Committee.*
B. P. Caldwell, *Program and Entertainment.*
J. L. Porter, *Transportation and Excursions.*
P. Asher, *Press and Publicity.*
G. B. Taylor, *Reception and Registration.*
L. A. Beenel, *Banquet.*
S. J. Tremoulet, *Smoker.*
Mrs. E. J. Northrup, *Entertainment of Visiting Ladies.*

The following provisional program has been issued:

WEDNESDAY, Mar. 31, *Morning and Afternoon,* Excursions about the city.

*Afternoon,* Excursion on Mississippi River; Smoker on the Steamer. Ladies especially invited.

THURSDAY, April 1, *Morning and Afternoon,* Industrial Symposium. Luncheon at the Tulane refectory, tendered by the University. Inspection of the University.

*Afternoon,* Personally conducted walk through the Vieux Carre for visiting ladies.

*Evening,* Public address by Bernhard C. Hesse on the "Chemists' Contribution to the Industrial Development of the United States—A Record of Achievement." Reception at the Round Table Club, tendered by the Club.

FRIDAY, April 2, *Morning and Afternoon,* Meetings of Divisions.

*Afternoon,* Motor ride for visiting ladies. Visit to the New Orleans Water Purification plant by the Water, Sewage and Sanitation Section.

*Evening,* Subscription dinner, Grunewald Hotel.

SATURDAY, April 3, Excursion to the Salt Mines at Avery's Island. (Minimum number, seventy-five persons.)

A feature of the meeting will be a symposium by the Industrial Division, which was originally planned for the Montreal meeting. A large number of papers have been promised, giving a resumé of the progress of American chemistry during the history of the American Chemical Society. The symposium is to be opened by an address by A. D. Little, presenting broadly and adequately some of the vast opportunities open to the South in the Chemical Industry. It is to be closed by a public address to the people of New Orleans by Dr. Bernhard C. Hesse on Thursday evening. Papers by such prominent men as J. B. F. Herreshoff, James Lewis Rice, E. T. Bedford, W. P. Mason, R. C. Schuepphaus, H. Walker Wallace, Franklin W. Hobbs, R. L. Bentley, F. R. Hazard, David Wesson, G. S. Brown, W. D. Horne, G. D. Thevenot, W. H. Teas, are assured.

Special attention should be directed to the proposed excursion to the Salt Mines at Avery's Island, scheduled for Saturday, April 3. This excursion can be given only if seventy-five people signify their intention to be present and procure tickets during the early part of the meeting. The excursion will take a full day, but members will return to New Orleans in time to catch the evening trains for the north.

The mines themselves are well worthy of a visit, being of peculiar geological formation and interesting historically. The immense chambers hollowed out in the salt some 500 feet under ground and the unusually pure quality of the salt itself have rendered these mines famous. The trip to Avery's Island, which is approximately 130 miles from New Orleans, carries one into the Teche country, made famous in the story of Evangeline, and through now fertile lands only recently reclaimed from the marsh by means of scientific irrigation. The mines are being worked 500 feet below the surface and the supply of salt is practically inexhaustible.

All titles for papers should be in the Secretary's hands on or before March 16th, or in the hands of the secretaries of divisions by March 14th, in order to be placed on the final program. By vote of the Council, no papers can be presented at the meeting, the titles of which are not printed on the final program.

ADDRESSES OF DIVISIONAL AND SECTIONAL SECRETARIES

*Agricultural and Food Chemistry*, G. F. Mason, H. J. Heinz Company, Pittsburgh, Pa.

*Biological Chemistry*, I. K. Phelps, Bureau of Chemistry, Washington, D. C.

*Fertilizer Chemistry*, F. B. Carpenter, Virginia-Carolina Chemical Company, Richmond, Va.

*Industrial Chemists and Chemical Engineers*, S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa.

*Organic Chemistry*, C. G. Derick, 619 Indiana Ave., Urbana, Ill.

*Pharmaceutical Chemistry*, A. P. Sy, University of Buffalo, 24 High Street, Buffalo, N. Y.

*Physical and Inorganic Chemistry*, R. C. Wells, U. S. Geological Survey, Washington, D. C.

*Water, Sewage and Sanitation*, Harry P. Corson, State Water Survey, Urbana, Ill.

The Water, Sewage and Sanitation Section will be organized as a division at this meeting if the Council permits. Facilities have been offered by the Sewage and Water Board of New Orleans for inspecting its works. The system treats effectually 20,000,000 gallons of Mississippi River water per day by the lime and iron process of mechanical filtration to effect both purification and partial softening. The main drainage system has an eventual capacity of 7,000,000,000 gallons per day, all of which is pumped. A matter of importance will be the report of the Committee on Standard Methods of Water Analysis.

No special rates have been granted to the meeting. South of Washington interchangeable mileage books can be purchased to advantage. Winter excursion rates approximately the same as mileage rates can be obtained from the north.

Special cars will be provided from any points where a sufficient number of members can warrant same. A special car from Washington accommodating members in the Atlantic States has already been arranged for. Write the Secretary early for space, taking regular trains to Washington. Car will leave Washington 10.45 P.M., March 29th. Special car from Cincinnati will probably be available for members from Ohio, West Virginia, Western Pennsylvania, and Western New York. A special car from Chicago or St. Louis is also under consideration.

The final program will be sent to all members of the Louisiana Section, to members of the Council, and to all members who make special request therefor by postal card to this office. Other members will find it printed in the Society's journals.

Box 505, Washington, D. C.
February 19, 1915

CHARLES L. PARSONS,
*Secretary*

## THE USE OF HYDROMETALLURGICAL APPARATUS IN CHEMICAL ENGINEERING—A CORRECTION

In my article under the above title, THIS JOURNAL, 7 (1915), 119, the following corrections should be made:

In Table II, page 122, and on page 125, all dimensions marked "inches" should read "feet."

On page 127 the "$0.76 per ton of ore" near top of Column 2 should read "$0.076 per ton of ore."

In the table at the top of page 129, in the last per cent column, "0.94" should read "0.90."

30 Church St., New York

JOHN V. N. DORR

# PERSONAL NOTES

The new building which will form the permanent home of the Mellon Institute of Industrial Research and School of Specific Industries of the University of Pittsburg, was formally dedicated on February 26th. This building, which was erected at a cost of $350,000, is the gift of Messrs. A. W. and R. B. Mellon, of Pittsburg. A full account of the dedicatory exercises and a detailed description of the building will appear in the April number of THIS JOURNAL.

Dr. William D. Crumbie died at his home in East Orange, N. J., on January 16th, aged 60 years. He was born at Milburn, N. J., and was a graduate of the Columbia School of Mines. He devoted himself to metallurgical chemistry and had been for thirty-two years in the New York Custom House, where his services as metallurgist and expert examiner were highly valued.

Mr. F. Lee Mickle presented a paper on "Modern Purification of Swimming Pools," before the Connecticut Valley Section of the A. C. S., on February 13th.

The suit of the Chadeloid Chemical Company against the Wilson Remover Company and John MacNaull Wilson for alleged infringement of the Ellis paint remover patent of December, 1902, was determined in January in favor of the complainant by Judge Hand in the United States District Court at New York. The claims for royalties are placed by the complainant's counsel at about $120,000.

The Third Midwinter Convention of the American Institute of Electrical Engineers was held in New York City on February 17th, 18th and 19th. The program was as follows: "The Characteristics of Electric Motors Involved in their Operation," by R. B. Rushmore. "Effect of Moisture in the Earth on Temperature of Underground Cables," by L. E. Imlay; "Oil Circuit Breakers," by K. C. Randall. "Comparison of Calculated and Measured Corona Loss Curves," by F. W. Peek, Jr. "A 100,000-volt Portable Substation," by Charles I. Burkholder and Nicholas Stahl. The subject of "The Status of the Engineer" was considered, the opening address being presented by Mr. Lewis B. Stillwell. "Distortion of Alternating-Current Wave Form Caused by Cyclic Variation in Resistance," by Frederick Bedell and E. C. Mayer; "Dimmers for Tungsten Lamps," by Alfred E. Waller; "Searchlights," by C. S. McDowell. One session was devoted to the subject of "Electrical Precipitation," the opening address being given by Dr. F. C. Cottrell. E. E. F. Creighton presented a paper on "Electrical Porcelain." The afternoon of the 18th was devoted to a trip to the new power station of the United Electric Light and Power Co., 201st Street and Harlem River.

Prof. Robert Hallowell Richards, of the Massachusetts Institute of Technology, will be presented, on March 18th, with the annual gold medal of the Mining and Metallurgical Society of America, in recognition of his services in the advancement of the art of ore-dressing.

The sum of $40,000 has been given by Mr. Andrew Carnegie to Allegheny College for a chemical laboratory to replace the one recently destroyed by fire.

Mr. George Skelton Yuill, of London and Australia, has given a sum of $20,000 to the University of Aberdeen to found a scholarship in chemistry in the memory of the arts class of 1864–68, of which he was a member. The scholarship will be held by a student of the university for the purpose of research within it, or for the study of the practical applications of chemistry elsewhere.

On April 3, 1915, an examination will be held in the State of Illinois at Anna, Carbondale, Chicago, Dunning, East St. Louis, Elgin, Jacksonville, Kankakee, Lincoln, Macomb, Mt. Vernon, Peoria, Pontiac, Springfield, Urbana and Watertown to provide an eligible list for the position of Food Bacteriologist in the

Chicago office of the State Food Commission. Circular and application blanks may be secured by addressing the State Civil Service Commission, Springfield, Illinois.

Dr. A. A. Noyes, of Boston, has been elected recipient of the Fifth Willard Gibbs Medal, and will address the Chicago Section of the A. C. S. at the regular April meeting. Previous recipients of the Medal are: Svante Arrheniu , T. W. Richards, L. H. Baekeland and Ira Remsen.

The speaker for the May meeting of the Chicago Section of the A. C. S. will be Dr. R. F. Bacon, director of the Mellon Institute of Industrial Research, Pittsburg, Pa.

Prof. Andrew C. Lawson has been appointed dean of the School of Mining of the University of California to succeed Professor Samuel B. Christy, recently deceased.

Stephen T. Mather, the Chicago manufacturer of chemicals, has been appointed by Secretary of the Interior Lane to take administrative charge of all of the National Parks. Mr. Mather was chairman of the Chicago Section of the A. C. S. in 1911.

Dr. Harry M. Ullmann has been made professor of chemistry at Lehigh University, in charge of the department.

The New York Sections of the American Electrochemical Society, the American Chemical Society and the Society of Chemical Industry held a joint meeting at the Chemists' Club on February 5th. The subject of the evening was, "The Electrochemical Production of Organic Compounds;" the speakers were: F. A. Lidbury, Manager, Oldbury Electrochemical Co.; Harold Hibbert, of the Mellon Institute of Industrial Research; Geo. Shannon Forbes, Professor of Electrochemistry, Harvard University.

The February meeting of the Philadelphia Section of the A. C. S. was held at the Engineers' Club on the 18th. The program was: "A Study of the Reproducibility of the Cadmium Electrode," by Frederick H. Getman and V. L. Gibbons, and a Symposium on Enzymes by the following speakers: Donald D. Van Slyke, Rockefeller Institute for Medical Research, New York City; Alonzo E. Taylor, Department of Physiological Chemistry, University of Pennsylvania; Joseph S. Hepburn, formerly of the Department of Biological Chemistry, Columbia University; John A. Kolmer, Laboratory of Experimental Pathology, University of Pennsylvania.

The new radium laboratories, Manchester Infirmary, Eng., which contain radium of the value of £20,000 raised by public subscription a few months ago, have been formally opened by the mayor of the city. A staff of experts will specialize on efforts to apply the radium for the arrest and elimination of cancer.

Charles Waldo Wright died in January, aged 31 years at his home in Rock Island, Illinois, after a lingering illness said to have been due to poisoning contracted in his work as chemist at the Rock Island Arsenal. During the two years of his employment at the arsenal he was able to substitute for the $5 per pound German flux used in welding the aluminum canteens for the U. S. army a composition of his own devising that can be produced at 46 cents per pound. Mr. Wright graduated from Indiana University in 1908.

Announcement was made on February 18th that the McKeesport Tin Plate Company will break ground for the erection of twenty additional modern tin plate mills which are expected to cost about $1,800,000. The new mills will constitute an extension of the present plant at Port Vue near McKeesport, Pa., where the company owns 16$^2/_3$ acres of land. It is planned to have the mills completed and ready for operation by March 1, 1916. When completed, they will make a 42 mill plant, the largest in the world, the company having 22 mills in operation at the present time. The production of the company will be virtually doubled by this addition, making it about 3,500,000 boxes of tin plate per year. The whole plant, with the new addition, will represent an expenditure of $4,000,000.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### BUREAU OF STANDARDS

**Specific Heat of Copper in the Interval 0° to 50° C. with a Note on Vacuum-Jacketed Calorimeters.** D. R. Harper, 3rd. Scientific Paper 231. 71 pp. A review of the previous determinations of specific heat of copper is given in extended form and the author's method for the measurement and operating results are described in detail. The method used is essentially the heating of the specimen with a measured quantity of electrical energy and determining the rise of temperature by the change in resistance of the specimen itself. The use of a vacuum-jacketed calorimeter is not strongly recommended by the experiments reported in the appendix.

**Insulating Properties of Solid Dielectrics.** Harvey L. Curtis. Scientific Paper 234. 62 pp. Methods of measuring very high resistances are discussed, and diagrams given showing how they may be applied to the measurement of volume resistivity and surface resistivity. The volume resistivities of more than 60 materials are tabulated. The effect of the humidity of the surrounding air, of the temperature of the specimen, and of the magnitude and length of application of the impressed voltage is discussed. The surface resistivity is shown to be due to a surface film, usually of water or oil, on the insulator. About 75 curves are given showing the change of surface resistivity with humidity for various materials. The effect of temperature and of exposure to light are also treated.

**Studies on the Silver Voltameter.** G. A. Hulett and G. W. Vinal. Scientific Paper 240. 18 pp. The work reported was done in the laboratories of Princeton University with the idea of comparing the methods of this institution with the methods previously used by the Bureau of Standards. The work includes a study of methods of preparing the electrolyte, the preparation and preservation of the porous cup, and the methods of washing and weighing the deposits. Original differences were reconciled after completion of the preliminary investigation.

**A Vibration Electrometer.** Harvey L. Curtis. 18 pp "An electrostatic instrument, called a vibration electrometer, is described. It is capable of detecting alternating currents of low frequency having a value as small as $10^{-11}$ ampere. The theory of this instrument is developed mathematically and the conclusions verified by experiment."

**The Emissivity of Metals and Oxides. II. Measurements with the Micropyrometer.** G. K. Burgess and R. G. Walten-

BERG. Scientific Paper 242. 15 pp. "The micropyrometer has been shown to be an instrument comparable in accuracy and range with much more elaborate experimental installations for the determinations of monochromatic emissivity. Starting with the cold substance, measurements of emissivity and of its temperature coefficient, accurate to about 1 per cent, may be taken at high temperatures (900 to 3000° C.) within a few minutes with a mass of less than 0.01 mg. presenting a surface of 0.25 mm$^2$."

"Measurements of emissivity with red and green lights have been made of 23 metals in hydrogen and 12 oxides in air."

**The Emissivity of Metals and Oxides. III. The Total Emissivity of Platinum and the Relation between Total Emissivity and Resistivity.** PAUL D. FOOTE. Scientific Paper 243. 6 pp. "A definite relation has been found to exist between the total emissivity and the volume resistivity of a metal. This relation follows directly from the Maxwell theory of reflection and absorption. Experimental determinations of the total emissivity of platinum have verified the derived relation."

**Hydration of Portland Cement.** A. A. KLEIN AND A. J. PHILLIPS. Technologic Paper 43. 71 pp. "This investigation included the preparation of cement minerals in conditions as nearly pure and homogeneous as possible. They consisted of the following compounds: Free lime, tricalcium aluminate, 5 : 3 calcium aluminate, monocalcium aluminate, beta-calcium orthosilicate, gamma-calcium orthosilicate, and tricalcium silicate. The hydrations took place on microscopic slides with an excess of water, in a cylinder with steam at atmospheric pressure, and in the autoclave with steam at various temperatures and pressures. The compounds were also molded with quantities of water, approximately those used in normal-consistency mixtures. Lime water and calcium sulfate solutions were also used as hydration media."

### BUREAU OF THE CENSUS

**Census of Manufactures, 1914. Classifications by Industries.** This tabulation indicates the 350 classes into which industries will be divided for proposed or census reports. The report is of chemical interest only as showing industries which are independently considered in the census work.

### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Wholesale Prices of Leading Articles in United States Markets, January 1913 to October 1914.** Miscellaneous Series No. 19. Paper, 5 cents. This publication gives weekly prices for, the period indicated for the following substances: Silver, coffee, leather, rubber, manila, sisal hemp, jute, jute butts, cotton middling, cottonseed oil, wool, mohair, iron, steel, petroleum, auto naphtha in wood, gasoline, breadstuffs, oleostearin, tallow, sugar, raw silk, lake copper, Straits tin, lead, speltzer (zinc), and tin plates.

### COMMERCE REPORTS—JANUARY, 1915
### Superseding "Consular Reports"

**Note**—Annual Reports from consular officers including import and export statistics are now published as supplements to Commerce Reports. Those issued in January are numbered: Philippines, 80*a*; British South Africa, 66*a*; Malaysia, 56*a*; Australia, 60*a*, French Indo-China, 54*a*.

The status of the German trade in **dyestuffs** is briefly as follows: Exceptions to the embargo on dyestuffs are made for American vessels, in amount not to exceed the average former exports to the United States (about 2300 tons per month). The increased demand in Germany for nitric acid for explosives tends to limit the manufacture of dyestuffs. (P. 5.)

During the first 10 months of 1914, 385 cases of **lead poisoning** (including 24 deaths) were reported in England, under the factory and workshop act, in addition to 210 cases of lead poisoning and 32 deaths in the painting and plumbing trades. Both show a decrease over 1913. (P. 25.)

The exportation of **rubber** from any British territory or possessions is strictly prohibited. (P. 36.)

A new modern **sugar** mill is about to be erected in Venezuela. (P. 51.)

Efforts are being made to develop or expand the following industries in India, *viz.*: **dyes, perfumes, cement, iron, glass, matches, sulfuric acid, alcohol, paper, and starch.** (P. 74.)

The British government has offered to assist in the formation of a stock company to manufacture **dyestuffs.** (P. 83.)

The use of American machinery in Chinese **cottonseed** mills is increasing. (P. 89.)

To assist the **Kauri-gum** industry of New Zealand the government is advancing cash on gum held for later sales. (P. 101.)

The war has caused an increased demand for **natural indigo** from India. (P. 104 and 340.)

The terms **"nickel silver"** and **"nickel steel"** are now used in England instead of "German silver" and "German steel." (P. 106.)

The use of red **beet pulp** for **paper** has been suggested in Spain, on account of the scarcity of wood pulp. (P. 109.)

The present status of the **iron and steel industry** in Germany is discussed. (P. 114.)

A new **carbide** factory is to be erected in Norway. (P. 119.)

Attempts are being made to renew shipment of Florida **phosphate** to Germany. (P. 113.)

Much of the **pongee silk** recently exported from China has been adulterated by loading with rice paste or coloring with sulfur fumes. (P. 151.)

**Radium ore** has been discovered in British Columbia. (P. 153.)

Efforts are being made to promote the **beet sugar** industry in England. (P. 162.)

The estimated world's production of **sugar** for 1914–15, and the actual figures for the last two years, are given. (P. 164.)

Experimental boring for **petroleum** by the Standard Oil Company in the province of Shensi, China, has resulted in a flow of 2000 barrels per day at a depth of 400 feet. (P. 194.)

Arrangements have been made for sale of **rubber** from the British Empire to American dealers, who must sign a guaranty not to export it to Europe except through the United Kingdom. (P. 195.)

The Chilean **nitrate industry** shows a marked falling off. (P. 196.)

The **menthol** and **peppermint** industry of Japan are discussed. (P. 220.)

The German government has established maximum prices for **copper, brass, bronze, aluminum, nickel, antimony,** and **tin.** (P. 230.)

The market for **sulfur** and for **iron** in Japan shows a marked falling off. (P. 244.)

The **importation of drugs and chemicals,** which fell off markedly at the beginning of the war, is now equal to or in excess of the normal, especially in the case of dyes, creosote oil, quebracho extract, camphor, chicle, gambier, sodium cyanide, sumac, vanilla, vegetable and mineral wax, quinine, and cinchona bark. Those which are still below normal include carbolic acid, fusel oil, magnesite, and potassium carbonate. (P. 250.)

The **olive oil** industry of Tripoli is described. (P. 259.)

Inspectors have been sent through the Philippines to enforce the recent law regarding the grading of **manila hemp.** (P. 286.)

American imports of **potash salts** in December, 1914, were considerably less than in December, 1913, except for the hydrate, which showed a slight increase. (P. 293.)

Efforts are being made to develop the **soap industry** in India. (P. 298.)

STATISTICS OF EXPORTS TO THE U. S. (AND IN SOME CASES TO EUROPE). (PP.)

LATIN AMERICA—10
Rubber
Hides
Copper
Sugar
Nitrate
Tin
Bolata gum
Rum
Phosphate rock
Whale oil

COLUMBIA—128
Platinum
Hides
Rubber
Gold
Ivory nuts
Tannin extract
Ipecac
Sugar
Balsam Jolu

CANADA—213
Feldspar
Graphite

PHILIPPINES—(Supplement 80a)
Manila hemp
Copra
Cocoanut oil
Sugar

MALAYSIA—(Supplement 56a)
Mangrove bark
Benzine
Cubebs
Cutch
Gambier
Gum copal
Gum damar
Gutta-percha
Hides
Cocoanut oil
Rubber
Tin

ARGENTINE—305
Hides

UNITED KINGDOM—376–382
Iron and steel
Glass
Chemicals
Hides
Ammonium chloride
Bleaching powder
Earthenware
China
Liquors
Linoleum
Ammonia
Creosote
Dyes
Fertilizer
Castor oil
Linseed oil
Rape oil
Brass
Copper
Rags
Palm oil
Tin
Rubber
Ferromanganese
Glycerine
Antimony
China clay
Platinum

DEMANDS FOR AMERICAN GOODS BECAUSE OF THE WAR. (PP.)

CHILE—3
Agateware

PHILIPPINES—102
Potassium cyanide

IRELAND—112
Leather belting

COSTA RICA—426
Cast iron pipe
Paints
Drugs

LIBERIA—118
Salt
Kerosene
Condensed milk
Benzine
Beer
Methyl alcohol
Vinegar
Soap
Whiskey
Matches
Motor oil
Quinine

JAPAN—120
Phosphorus

COLUMBIA—128
Drugs
Glassware
Beer
Paints
Varnishes
Rubber tires

BRAZIL—322
Caustic soda

A plant is to be erected in Argentine to extract the **oil from grape seeds,** with a capacity of 600,000 pounds of oil per year. The oil may be used both for edible purposes and for soap. (P. 317.)

A market is desired by India for **vegetable tallow,** formerly shipped to Antwerp for making candles and soap and as an edible fat. (P. 335.)

Efforts are being made to develop the **gypsum** deposits of British Columbia. (P. 339.)

The process of manufacturing **alcohol** from the "nipa" palm in the Philippines is described, and the possibilities of making **sugar** instead, are discussed. (Pp. 362–4.)

The **beet-sugar** factory at Raymond, Alberta, has not been successful, owing to the failure to furnish sufficient beets. (P. 371.)

Mexican **petroleum** is principally of an asphalt base, and is more difficult to refine than the paraffin oils. It contains more sulfur than the Eastern United States oils, and yields much less gasoline. It is not suitable for making high grade lubricants, and is chiefly used for fuel. (P. 383.)

**"Firth's stainless steel,"** claimed to be non-rusting and non-tarnishing, is being manufactured into cutlery in Sheffield, England. (P. 405.)

### BUREAU OF THE MINT

**Report on the Production and Consumption of Gold and Silver in the United States during the Calendar Year 1913.** Part II of the Report of the Director of the Mint for the Fiscal Year Ending June 30, 1914. Cloth, 35 cents. "The official estimate upon the production of gold and silver in the United States is made by the Bureau of the Mint and the Geological Survey working in conjunction, the latter making a mine canvas in each State and the former working backward from mint deposits through refineries, smelters, and other reduction works to the figures of the mine production made by the survey. The two systems thus verify and support each other.

"The gold production of the United States, including its insular dependencies, for the calendar year 1913 is estimated to have been $88,884,400, and the production of silver is estimated at 66,801,500 fine ounces.

"The output of gold in the United States, including its outlying territories, in 1913 fell $4,567,100 below the output of 1912 and $8,005,600 below that of 1911. Of this decline over $6,000,000 was in the State of Nevada and about $1,000,000 in Colorado. The other gains and losses were unimportant.

"The construction of a Government railway into Alaska is looked forward to as a step likely to have great influence upon future developments in that Territory. Otherwise there is nothing in sight upon which to base a prediction as to an expansion or falling off of mining operations except that the effect of the European war in controlling copper and lead production will have the incidental effect of reducing the yield of gold and silver from copper and lead ores."

There are given full data for the production by states, the exports, imports, the foreign production by countries, and the mint consumption for foreign countries, for the period in question.

### GEOLOGICAL SURVEY

**Mineral Resources of the United States, Calendar Year 1913. Part I. Metals.** 1074 pp. Cloth, 70 cents. This bound volume, which includes the numerous short articles which have previously been reviewed, has just been issued.

**Geology of the Hanagita-Bremner Region, Alaska.** F. H. MOFFIT. 56 pp. "Although the author's survey was of a reconnaissance character, it was sufficiently detailed to outline the geography, general geology, and geologic history of the region and to obtain information about the occurrence and distribution of the gold and copper deposits. The Hanagita-Bremner region includes some mineral deposits which, though almost undeveloped, give promise of becoming commercially valuable, now that they have been made comparatively accessible by the railroad recently completed up the Copper River Valley."

**Contribution to Economic Geology, 1913. Part I.** The following four additional separates from Bulletin 580 have been issued:

1. **The Rochester Mining District, Nevada.** F. C. SCHRADER. *Bull.* 580-M, 325–72.

2. **The Elliston Phosphate Field, Montana.** R. W. STONE AND C. A. BONINE. *Bull.* 580-N, 373–83.

3. **The Rutile Deposits of the Eastern United States.** T. L. WATSON. *Bull.* 580-O, 385–412.

4. **Publications by Survey Authors on Metals and Nonmetals except Fuels.** Compiled by I. P. EVANS. *Bull.* 580-P, 413–455

**Reconnaissance of the Geology and Oil Prospects of Northwestern Oregon.** C. W. WASHBURNE. 111 pp. The author concludes that there is no good reason for believing that oil will be found in the northern part of the Coast Range of Oregon. A map of northwestern Oregon showing gas and oil prospects accompanies the report.

**Geology and Underground Waters of the Southeastern Part of the Texas Coastal Plain.** ALEXANDER DEUSSEN. 365 pp. In addition to the geological information, there is included a discussion of the quality of the water and the artesian conditions in this district.

**Gems and Precious Stones in 1913.** DOUGLAS B. STERRETT. Mineral Resources of the U. S., 1913. Part II, pp. 649–708. This separate is principally of interest in consideration of gem stones, but certain data regarding these stones is of some chemical interest. The 1913 production of precious stones in the United States was valued at $319,000. There were imported during the same period precious stones amounting to over $45,000,000.

**Statistics of the Clay-Working Industries in the United States in 1913.** JEFFERSON MIDDLETON. Mineral Resources of the U. S., 1913. Part II, pp. 545–637. This article shows the extent of the production of manufactured clay products. The total value of these productions in 1913 was over $180,000,000, an increase of approximately 5 per cent. The brick and tile industries show a more marked increase than the pottery in-

dustry; the production of common brick decreased materially. For each branch of the industry full statistics are given as to production, imports, and exports. These are arranged both by character of the material and by states in which the material is produced.

**Notes on the Occurrence and Use of Flint Clay.** J. H. HANCE. Mineral Resources of the U. S., 1913. Part II, pp. 639–48. This separate indicates typical analyses of flint clay, describes the uses, geologic occurrence, methods of sampling and testing, and methods of commercial development of deposits. There is included a bibliography of the occurrences of flint clay.

**The Production of Borax in 1913.** CHARLES G. YALE AND HOYT S. GALE. Mineral Resources of the U. S., 1913. Part II, pp. 521–36. The 1913 production of crude borate materials was valued at $1,500,000, a material increase over the previous year. Practically all of this material consisted of the mineral colemanite in various degrees of purity, and all of the material came from Southern and Southeastern California. The imports for 1913 were valued as follows: Borax $500, calcium and sodium borates $1,025, and boric acid $17,000. A full bibliography of publications relating to borax and borates is given.

**The Production of Lime in 1913.** RALPH W. STONE. Mineral Resources of the U. S., 1913. Part II, pp. 309–24. "The lime manufactured in the United States in 1913 amounted to 3,595,390 short tons, valued at $14,648,362. This was an increase of 65,928 tons, or 1.87 per cent, in quantity and of $678,248, or 4.85 per cent, in value, when compared with the output for 1912. The average price per ton in 1913 was $4.07, as compared with $3.96 in 1912, and with $4.03 in 1911. The increase in average price was general for the entire country, increased cost of labor and supplies and scarcity of labor being given as the reason by the majority of producers. The value given represents the value of bulk lime f. o. b. at point of shipment and does not include any weight or cost of barrel or package."

There are included in this separate, tables which show the number of kilns and the kind of fuel used in lime manufacture, and proposed standard specifications (not published here for the first time) are given.

**The Source, Manufacture, and Use of Lime.** ERNEST F. BURCHARD AND WARREN E. EMLEY. Mineral Resources of the U. S., 1913. Part II, pp. 1509–93. An extended discussion of the varieties and sources of commercial limestone and a description of the commercial methods of manufacture, the properties of commercial interest, and suggestions regarding the proper use of lime in various classes of work.

**The Production of Natural Gas in 1913.** B. HILL. Mineral Resources of the U. S., 1913. Part II, pp. 1411–1507. "The total gas production in the United States in 1913 is estimated at 581,898,239,000 cubic feet, valued at $87,846,677, an average price of 15.10 cents per thousand cubic feet, as compared with a production of 562,203,452,000 cubic feet, valued at $84,563,957, an average price of 15.04 cents in 1912, this being an increase of 19,794,787,000 cubic feet in quantity and of $3,282,720, in value. Of this total product, about 32 per cent was utilized for domestic purposes, or 184,885,662,000 cubic feet, valued at $50,522,415, an average price of 27.33 cents per thousand cubic feet, and 68 per cent was utilized for industrial purposes, or 397,012,577,000 cubic feet, valued at $37,324,262, an average price of 9.4 cents per thousand cubic feet."

There is given a tabulation of 1500 analyses and properties of samples of natural gas combined from a large number of sources.

The quantity of gasoline produced by extraction from natural gas amounted to more than 24,000,000 gallons, valued at $2,500,000, a marked increase over the previous years.

The use of natural gas for manufacture of carbon black is discussed and this practice is defended on the ground that in the regions where carbon black is now manufactured from natural gas it can be done with comparative efficiency; and it is generally made from gas for which there is no other convenient market available. There is given here a very complete description of the method of manufacture of lamp and carbon black.

**The Production of Petroleum in 1913.** DAVID T. DAY. Mineral Resources of the U. S., 1913. Part II, pp. 921–1284. The 1913 production of petroleum was the largest ever known, amounting to 248,000,000 barrels, more than the entire world production seven years earlier. The sources of the oil are indicated in considerable detail and full discussion of production in this country and abroad is given. There is also included a tabulation of analyses and tests of 750 samples of oil data are given for gravity, color, odor, distillation, and analysis, including sulfur, paraffin, asphalt, water, and unsaturated hydrocarbon.

**The Stone Industry in the United States in 1913.** ERNEST F. BURCHARD. Mineral Resources of the U. S., 1913. Part II, pp. 1285–1410. Principally a description of interest in the building trades and to the economic geologist.

### SMITHSONIAN INSTITUTION

**Annual Report.** This report includes a number of brief articles, most of which have been previously printed; but some of those of chemical interest are not generally accessible elsewhere. Those of most direct chemical interest are the following:

(1) **Recent Developments in Electromagnetism.** EUGENE BLOCH. Pp. 223–41. The discussion is confined to the following topics: 1—The dynamics of the electron and electromagnetic mass. 2—The principle of relativity. 3—Electromagnetism and radiation. 4—The magneton. 5—The production and nature of gaseous ions. 6—Photoelectric effect (Hertz and Lenard effects).

(2) **Oil Films on Water and on Mercury.** HENRI DEVAUX. Pp. 261–73. A summary of the author's researches during the last 10 years.

(3) **Flameless Combustion.** CARLETON ELLIS. Pp. 639–52. No original experiments reported.

(4) **The Work of J. H. van't Hoff.** G. BRUNI. Pp. 767–89. A full biographical sketch.

(5) **The Manufacture of Nitrates from the Atmosphere.** ERNEST K. SCOTT. Pp. 359–84. A well illustrated article describing the commercial processes now in use, particularly the apparatus used in the Schonherr and the Birkeland-Eyde processes. The production of calcium cyanamid is also described.

(6) **Problems in Smoke, Fume, and Dust Abatement.** F. G. COTTRELL. Pp. 653–85. This article, published here for the first time, reviews the author's experiments and describes the commercial application of his process in a large variety of plants; numerous illustrations both of the laboratory equipment and commercial applications are included.

### DEPARTMENT OF AGRICULTURE

**The Use of Radioactive Substances as Fertilizers.** WILLIAM H. ROSS. Department Bulletin 149, from the Bureau of Soils. 14 pp. The amount of radioactive material present in the residues proposed for fertilizer use is so small as to probably have no fertilizing value of itself. It is believed that the advantageous use of this material, when such is noted, is due either to the action of uranium on the plants through its chemical properties or to the fertilizing action of non-radioactive constituents such as soluble salts and free acids.

**The Manufacture of Acid Phosphate.** WILLIAM H. WAGGAMAN. Department Bulletin 144, from the Bureau of Soils. 28 pp. This article describes the character of the raw materials available, the reactions involved in the preparation of the acid phosphate, machinery and methods of handling used in the works, and discusses the cost of production and value of the product.

**The Clyde Series of Soils.** J. A. BONSTEEL. Department

Bulletin 141, from the Bureau of Soils. 60 pp. A discussion principally of geological and agricultural interest.

The *Journal of Agricultural Research*, 3 (1915), contains the following articles of interest: **Changes in Composition of Peel and Pulp of Ripening Bananas,** H. C. Gore, 187–203. **Assimilation of Colloidal Iron by Rice,** P. L. Gile and J. O. Carrero, 205–10. **Coloring Matter of Raw and Cooked Salted Meats,** R. Hoagland, 211–26. **Oil Content of Seeds as Affected by the Nutrition of the Plant,** W. W. Garner, H. A. Allard and C. L. Foubert, 227–49. **Studies in the Expansion of Milk and Cream,** H. W. Bearce, 251–68. **Moldiness in Butter** (with analyses) C. Thom and R. H. Shaw, 301–10. **Changes in Sweet Potatoes during Storage** (with analyses), H. Hasselbring and L. A. Hawkins, 331–42.

# BOOK REVIEWS

**Liquid Fuels: Die Flüssigen Brennstoffe (Ihre Bedeutung und Beschaffung).** By Ed. Donath und A. Gröger, an der Deutschen Technischen Hochschule in Brunn. Published by Friedr. Vieweg & Son, Braunschweig, 1914. 86 pp. Price, 2 Marks.

The four fields of liquid fuels are discussed as follows: 1—The generation of steam on ships and locomotives, and as a fuel in the chemical and metallurgical industries. 2—The Internal Combustion Engine, of the Diesel type, as a source of power to compete with the reciprocating or turbine engine. 3—The automobile type of engine. 4—The aeroplane type of engine, whose available fuel is practically limited to low boiling point gasolines.

Particular emphasis is placed on the high compression engine of the Diesel type. Unlike the aeroplane engine, it can use a variety of liquid fuels. One recognizes the German point of view in that tar oils are given equal, if not greater, attention than petroleum products. On pages 70–71 a table is given indicating the oils which are fit and those unfit for the Diesel engine. Stress is also placed on alcohol as a substitute for gasoline, with references (pp. 79–80) to tests made on various mixtures of alcohol and aromatic hydrocarbons, such as benzol, as a substitute for gasoline. Liquid fuels are divided into four classes, with the indicated number of pages devoted to each: Petroleum, 12–45. Tars resulting from efficient carbonization of peat and coal, 45–77. Alcohol, 77–82. Oils, 82–84.

The book contains no pictures and but a single sketch. The so-called practical man who is not a chemist would miss the customary tables indicating the weights of various gases, amount of air required for combustion, etc. No particular reference is made to the various mechanical appurtenances, such as burners, compressors, blowers, carburetors, pumps, and piping, required in the use of liquid fuels.

On the other hand, the book is a distinct relief from most fuel books in that it deals intelligently and clearly with the chemical and physical fundamentals so important in fuel consumption. The book is obviously academic. Nevertheless, it is a valuable contribution to our understanding of fuels.

W. F Rittman

**Water Supplies, Their Purification, Filtration and Sterilization. A Handbook for the Use of Local and Municipal Authorities.** Samuel Rideal, D.Sc., and Eric K. Rideal, Ph.D., New York. D. Appleton & Co., 1915. ix + 274 pp., 24 photographic plates. Price, $2.50.

"It is hoped that without too many technical details, the following pages summarize the science and practise of modern water supply and water purification in a way which may be of use to many readers." Undoubtedly this hope, expressed in the preface, will be realized, as the book as a whole is clearly written, and all the various methods of obtaining water and of purifying it are touched upon.

In some instances the discussions are not well balanced, too little emphasis being laid on the presence of harmful bacteria in water in comparison with the statements concerning inorganic impurities, and 60 pages devoted to water sterilization against 40 to filtration. The chapter on interpretation of analytical results could be greatly improved by the discussion of some concrete examples, as it is often necessary for "local and municipal authorities," for whom the book is mainly intended, to be able to interpret chemical and bacteriological data.

The subjects discussed cover sources of supply, distribution, storage, slow sand and mechanical filtration, softening—including the Permutit Process—and sterilization—including ozone and ultra-violet light as well as chlorine compounds and other chemicals. The appendix contains a large number of water analyses, a table giving the composition of numerous boiler scales and a comprehensive table showing the order of rocks and the characteristics of waters from them.

Although an English book, much of the material will apply to American practise, even if few municipalities would be able to consider the use of ozone for sterilization, which is described in considerable detail.

The preface gives credit to American engineers for the rapid development of the whole science of obtaining clean and wholesome water supplies. The volume is a welcome and valuable addition to the subject.

John F. Norton

**Clean Water and How To Get It.** By Allen Hazen. Second edition, revised and enlarged. John Wiley & Sons. Large 12mo. xii + 196 pp., 18 half-tones. Cloth, $1.50.

The scope and object of this publication are well set forth in the following extract from its preface: "This little volume deals with the means now used by Amercan cities to secure clean water.

"Some closely allied subjects are also touched upon, including some matters of general policy, pressure, fire service, the sale of water, and the financial management of water works..... Its object is to help beginners to understand some of the first principles. In the present edition chapters have been added on the red-water trouble and the disinfection of water supplies."

The author has succeeded admirably in accomplishing his object. The book is full of technical information presented in a non-technical and readable manner. The illustrations give much information concerning lay-out and construction which could not otherwise be given in a book of this size.

A. M. Buswell

**Assaying in Theory and Practice.** By E. A. Wright. pp. xi, 323. Longmans, Green & Co., New York. Price, $3.00 net.

About sixty per cent of the book is devoted to useful tables, laboratory plans, apparatus, minerals, sampling, fire assay, bullion, fuels, refractories, etc. The remainder takes up wet methods for iron, copper, zinc, aluminum, lead, bismuth, tin, tungsten, arsenic, antimony, manganese, chromium, sulfur, vanadium, uranium, molybdenum, cobalt, nickel and ore tests by cyanidation and amalgamation. The book contains nothing new, except the errors, and treats many subjects in a cursory manner, amounting to little more than suggestions. References are conspicuous by their absence and under the above mentioned condition their omission is unfortunate.

The methods probably represent certain English practices and the author is either ignorant of or does not accept work done in this country. It is certain, however, that many of his schemes

would not be accepted in the United States. Considering the author's position, it is surprising to note the character of inaccuracies too numerous to mention. An abstract of a few will illustrate the type: "$NaHCO_3$ has one-half the fluxing power of $Na_2CO_3$." It is not stated in molecular proportions. "Copper ores and products should be assayed by the wet and dry method." This is frequently spoken of as the combination method. And it has been known for a score of years that gold results so obtained are unreliable and generally worthless. "Arsenic and antimony sulfides dissolved with HCl and $KClO_3$ diluted to 120 cc. and evaporated with the addition of a little more HCl till all chlorine is expelled will completely remove the arsenic."

The description of the very creditable work done by Messrs. Wright and Teed on wet tin unquestionably forms the best chapter in the book. The fire assay for silver bullion is also treated much better than is usual. On the whole, however, it is difficult to designate the proper field for this work and also be complimentary.

E. J. HALL

# NEW PUBLICATIONS

By JOHN F. NORTON, Massachusetts Institute of Technology, Boston

**Agriculture: A Handbook for Farmers and Dairymen.** By FRITZ WILHELM WOLL and others. 6th Ed., revised. 16mo 490 pp. Price, $1.50. John Wiley & Sons, New York.

**Analysis: Nachweis, Bestimmung und Trennung der chemischen Elemente. 3 Bd. Kupfer, Cadmium, Wismut, Blei.** By A. RÜDISÜLE. 8vo. 762 pp. Price, $8.00. Drechsel, Bern.

**Analysis: Technical Methods of Chemical Analysis. Vol. 3.** English Translation edited by C. A. Keane. By GEORG LUNGE. 8vo. 1166 pp. Price, $18.00. D. Van Nostrand Co., New York.

**Analysis: Ubungsbeispiele zur quantitativen Analyse.** By W. MEIGEN. 2nd Ed. 8vo. 103 pp. Price, $0.75. Speyer and Kaerner, Freiburg

**Boilers: Boilers, Economisers and Superheaters: their Heating Power and Efficiency.** By R. H. SMITH. 8vo. 136 pp. Price, $2.00. C. Lockwood, London.

**Electricity: Alternating Current Electricity and Its Application to Industry.** By W. H. TIMBIE AND H. H. HIGBIE. 8vo. 534 pp. Price, $2.00. John Wiley & Sons, New York.

**Food: Principles of Food Preparation: a Manual for Students of Home Economics.** By MARY D. M. CHAMBERS. 12mo. 251 pp. Price, $1.00. Boston Cooking School Magazine, Boston.

**Gas: Gas Supply in Principle and Practice.** By W. HOSGOOD YOUNG WEBBER. 12mo. 199 pp. Price, $1.25. The Macmillan Co., New York.

**Gas: Technical Gas Analysis.** By GEORG LUNGE. 8vo. 407 pp. Price, $4.00. D. Van Nostrand Co., New York.

**General Chemistry: Einführung in die Elemente der allgemeinen Chemie.** By MAX ROSENFELD. 8vo. 153 pp. Price, $0.75. Veit & Co., Leipzig.

**Hygiene: Public Hygiene.** By THOMAS S. BLAIR. Vol 2. 8vo. Price, $10.00. Richard G. Badger, Boston.

**Iron: The Cementation of Iron and Steel.** Translated by J. W. Richards and C A. Rouiller. By FEDERICO GIOLETTI. 8vo. 407 pp. Price, $4.00. McGraw Hill Book Co., New York.

**Metallurgy: An Introduction to the Study of Physical Metallurgy.** By W. ROSENHAIN. 8vo. 368 pp. Price, $3.50. D. Van Nostrand Co., New York.

**Metallurgy: The Metallurgy of Non-Ferrous Metals.** By W. GOWLAND. 8vo. 296 pp. Price, $5.00. J. B. Lippincott Co., Philadelphia.

**Microbiology: Handbuch der technischen Mykologie für technische Chemiker, etc. Bd. 5, Brauerei, Brennerei, etc.** By FR. LAFAR. 2nd Ed. 8vo. 689 pp. Price, $5.00. Fischer, Jena.

**Milk: Text-book of Milk Hygiene.** By DE W. ERNST. 8vo. Price, $5.00. Baillière, London.

**Oils: Examination of Lubricating Oils.** By T. BLISS STILLMAN. 8vo. 125 pp. Price, $1.25. Chemical Publishing Co., Easton, Pa.

**Radio-activity: The Chemistry of the Radio-elements. Pt. 1. 2nd Ed., revised. Pt. 1, The Radio-Elements and the Periodic Law.** By F. SODDY. 8vo. 151 pp. Price, $1.75. Longmans, Green & Co., New York.

**Rare Earths: The Rare Earths, their Occurrence, Chemistry and Technology.** By S. I. LEVY. 8vo. 345 pp. Price, $3.00. Longmans, Green & Co., New York.

**Sewerage: American Sewerage Practice. Vol. 1. Design of Sewers.** By LEONARD METCALF AND HARRISON P. EDDY. 8vo. 747 pp. Price, $5.00. McGraw-Hill Book Co., New York.

**Technology: Industrial Chemistry.** Edited by ALLEN ROGERS. 2nd Ed. 8vo. 1025 pp. Price, $5.00. D. Van Nostrand Co., New York.

**Water: Untersuchung und Begutachtung von Wasser und Abwasser.** By L. GRÜNHUT. 8vo. 473 pp. Price, $1.25. Akadem. Verlagsgesellschaft, Leipzig

## RECENT JOURNAL ARTICLES

**Adsorption: The Adsorptionsfähigkeit der Talke und Kaoline.** By RAUL ROHLAND. *Kolloid-Zeitschrift*, Vol. 15, 1914, No. 5, pp. 180–2.

**Asphalt: Beiträge zur Kolloidchemie des Asphalts.** By A. ROSINGER. *Kolloid-Zeitschrift*, Vol. 15, 1914, No. 5, pp. 177–9.

**Concrete: Microscope Opens New Field in Study of Concrete.** By NATHAN C. JOHNSON. *Engineering Record*, Vol. 71, 1915, No. 4, pp. 98–102.

**Concrete: Standard Practice Instructions for Concrete Testing Laboratory.** By RALPH E. GOODWIN. *Engineering News*, Vol. 73, 1915, No. 5, 202–8.

**Concrete: The Action of Boiling Water on Concrete.** By E. R. MATTHEWS. *Concrete and Constructional Engineering*, Vol. 10, 1915, No. 1, pp. 29–31.

**Copper: Ueber die Hartlotnähte für Kupferblech verbindungen und ihre Unzulässigkeit für Kupferne Dampfässer.** By ERNST GALZ. *Chemische Apparatur*, Vol. 1, 1914, No. 23, pp. 305–6.

**Cyanidation: The Development of Continuous Counter-Current Decantation in Cyanidation of Slime.** By H. G. PENTLAND. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 2, pp. 105–7.

**Evaporators: An Experimental Study in Multiple Effect Evaporation.** By NOEL DEERR. *The International Sugar Journal*, Vol. 17, 1915, No. 193, pp. 31–6.

**Fat: Proposed Uniformity in Methods of Fat Analysis.** By W. FAHRION. *The Journal of the American Leather Chemists' Association*. Vol. 10, 1915, No. 1, pp. 7–18.

**Fats: Some Oleaginous Seeds and Fruits.** By E. RICHARDS BOLTON AND ENID M. JESSON. *The Analyst*. Vol. 40, 1915, No. 466, pp. 3–9.

**Filter: A New Continuous Filter.** ANONYMOUS. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 2, pp. 125–7.

**Filtration: Bemerkungen über Filtration und Auslangung.** By OSKAR NAGEL. *Chemische Apparatur*, Vol. 1, 1914, No. 22, pp. 293–4.

**Food: Ueber die Volksernährung im Kriege.** By EDMUND PAROW. *Zeitschrift für angewandte Chemie*, Vol. 28, 1915, No. 1, pp. 1–2.

**Gas: The Removal of Carbon Bisulfide from Coal Gas.** By E. Y. EVANS. *Journal of the Society of Chemical Industry*, Vol. 34, 1915, No. 1, pp. 9–14

**Gypsum: Die Entwässerungs-produkte des Gipses.** By R. GRENGG *Zeitschrift für anorganische Chemie*, Vol. 90, 1914, No. 2 u. 3, pp. 327–60.

**Hides: The Bating of Hides and Skins.** By ALLEN ROGERS. *The Journal of the American Leather Chemists' Association*, Vol. 10, 1915, No. 1, pp. 52–7.

**Iron: Recent Developments in Cast-iron Manufacture.** By J. E. JOHNSON, JR. *Journal of the Franklin Institute*, Vol. 179, 1915, No. 2, pp. 171–213.

**Markasite: Einfluss von Temperatur und Säuregrad auf die Bildung von Markasit und Wurtzit.** By E. T. ALLEN AND I. L. CRENSHAW. *Zeitschrift für anorganische Chemie*, Vol. 90, 1914, No. 1, pp. 107–49.

**Nitric Acid: On the Boiling Point of Aqueous Solutions of Nitric Acid at Different Pressures. Part I.** By H. J. M. CREIGHTON AND J. H. GITHENS. *Journal of the Franklin Institute*, Vol. 179, 1915, No. 2, pp. 161–70.

**Photography: The Physics of the Photographic Process.** By C. E. KENNETH MEES. *Journal of the Franklin Institute*, Vol. 179, 1915, No. 2, pp. 141–60.

**Pyrite: Stokes Methode zur Bestimmung von Pyrit und Markasit.** By E. T ALLEN AND I. L. CRENSHAW *Zeitschrift für anorganische Chemie*, Vol. 90, 1914, No. 1, pp. 81–106.

**Rectifiers: Die periodisch arbeitenden Rektifizierapparate in Theorie und Praxis.** By HUGO SCHRODER *Chemische Apparatur*, Vol. 1, 1914, Nos. 22, 23, and 24, pp. 294–7, 307–11, and 321–4.

**Refrigeration: Brewery Refrigeration and Ventilation.** By PETER NEFF. *Refrigerating World*, Vol. 49, 1915, No. 1, pp. 37–8.

**Rubber: Estimation of Sulfur in Rubber.** By R. GAUNT. *The Analyst*, Vol. 40, 1915, No. 466. pp. 9–11.

**Sanitation: Sewage-Treatment and Garbage Reduction Works for Akron, Ohio.** ANONYMOUS. *Engineering News*, Vol. 73, 1915, No. 4, pp. 147.

**Sanitation: The Sanitation of Iquitos, Peru.** By C. M. CONVERSE. *Engineering News*, Vol. 73, 1915, No. 5, p. 201.

**Sewage: Buffalo Sewage Disposal and Water Supply in Relation to the Pollution of the Great Lakes.** By G. H. NORTON. *Engineering News*, Vol. 73, 1915, No. 1, pp. 8–9.

**Silver: Die Herstellung der Silberspiegel nach Liebig.** By EMIL LENK. *Zeitschrift für angewandte Chemie*, Vol. 28, 1915, No. 1, pp. 2–7.

**Steel: Limitations of the Electric Furnace in the Manufacture of Steel Castings.** By G. MUNTZ. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 2, pp. 108–10.

**Steel: Micrographic Inspection of Steel.** ANONYMOUS. *Iron Age*, Vol. 95, 1915, No. 5, pp. 292–3.

**Steel: Segregation in Steel Rails.** ANONYMOUS. *Iron Age*, Vol. 95, 1915, No. 5, pp. 309–10.

**Steel: Sound Steel for Rails and Structural Purposes.** By ROBERT A. HADFIELD. *Journal of the Franklin Institute*, Vol. 179, 1915, No. 2, pp. 119–40.

**Sugar: Chemical Control in the Cane Sugar Factory, using Boiling-House Balances of Both Sucrose and Total Solids.** By HORACE JOHNSON. *The International Sugar Journal*, Vol. 17, 1915, No. 193, pp. 27–31.

**Sugar: The Rational Imbibition (Maceration) of Bagasse in the Cane Sugar Factory.** By LÉON PELLET. *The International Sugar Journal*, Vol. 17, 1915, No. 193, pp. 20–6.

**Sugar: Using Cane Tops for Planting.** By ARTHUR H. ROSENFIELD. *The International Sugar Journal*, Vol. 17, 1915, No. 193, pp. 16–8.

**Tannin: Available Tannin in Various Tanning Materials.** By JOHN H. YOCUM AND THOS. A. FAUST. *The Journal of the American Leather Chemists' Association*, Vol. 10, 1915, No. 1, pp. 26–41.

**Tanning: Determination and Estimation of Tanning Materials in Admixture.** By F. H. SMALL. *The Journal of the American Leather Chemists' Association*, Vol. 10, 1915, No. 1, pp. 41–5.

**Tellurium: Ueber das Atomgewicht des Tellurs und seine Beziehungen zu den Gruppen-homologen.** By G. PELLINI. *Sammlung Chemischer und Chemisch-technischer Vorträge*, Vol. 21, 1914, No. 8–11, pp. 291–442.

**Ventilators: Eine neue Montierung für Ventilatoren aus säurefesten Steinzeng.** By ED FRITZWEILER. *Chemische Apparatur*, Vol. 1, 1914, No. 24, pp. 325–6.

**Wood: The Battle against Rot.** ANONYMOUS. *The Canadian Engineer*, Vol. 27, 1914, No. 21, pp. 664–8.

**Zirconia: A New Refractory.** By H. CONRAD MEYER. *Metallurgical and Chemical Engineering*, Vol. 12, 1914, No. 12, pp. 791–3.

## BIBLIOGRAPHY ON THE TRAINING AND EDUCATION OF THE CHEMIST AND CHEMICAL ENGINEER

FROM THE INFORMATION DEPARTMENT OF ARTHUR D. LITTLE, INC.
By Guy E. Marion

**American Institute of Chemical Engineers. Report of Committee on Chemical Engineering Education.** THIS JOURNAL, **3** (1911) 863. **Synopsis of the Course in Chemical Engineering.** *Ibid.*, **2** (1910). 430.

**Atkinson, F. W. The Development of the Chemist as an Engineer.** *Chem. Eng.*, **13**, 8.

**Benner, R. C. Technical Training.** *Met. and Chem. Eng.*, **9** (1911), 68.

**Booth, W. M. The Chemical Engineer and Industrial Efficiency.** *Sci. Am. Suppl.*, April 5 (1913), 210.

**Borrowman, George. Chemistry and the Engineer.** THIS JOURNAL, **3** (1911), 186.

**Briggs, T. Lynton. Education of the Professional Chemist.** *Science*, **25**, 681–93; *C. A.*, **1** (1907),1760.

**Brown, J. C. University Training of Technical Chemists.** *J. Soc. Chem. Ind.*, **28** (1909), 329.

**Burgess, Charles F. The Efficiency of College Training of Men for the Chemical Industries.** *J. Am. Chem. Soc.*, **33** (1911), 611.

**Cazeneuve. The Technical Preparation of Expert Chemists.** *Ann. fals.*, **3**, 1–8; *C. A.*, **4** (1910), 1063.

**Coethen. The Training of Engineers for Enamel Works at Friedrichs-Polytechnikum.** *Glashütte*, **41**, 309–10; *C. A.*, **5** (1911), 2711.

**Dennis, Louis M. To What Extent Should College Training Confer Practical Efficiency along Technical Lines?** THIS JOURNAL, **1** (1909), 194.

**Donnan, F. G. The University Training of Technical Chemists.** *J. Soc. Chem. Ind.*, **28** (1909), 275.

**Duncan, Robert Kennedy. Industrial Fellowships.** THIS JOURNAL, **1** (1909), 600–3; discussion in *J. Soc. Chem. Ind.*, **28** (1909), 684–90. **On Certain Problems Connected with the Present-Day Relation between Chemistry and Manufacture in America.** *Ibid.*, **3** (1911), 177. **(The) Industrial Chemist. What Opportunities for Achievement Are Offered Him?** *Sci. Am.*, Sept. 16 (1913), p. 249.

**Dunlap, Oscar. Training Technical Graduates.** *The Dodge Idea* Oct. (1912), p. 933.

**Eames, C. H. Technical Education—Its Function in Training for the Textile Industry.** *Chem. Eng.*, **14**, 363–5; *C. A.*, **5** (1911), 3623.

**Ellis, Wm. M. The Chemical Education of the Engineer.** *Science*, **27**, 882–5; *C. A.*, **2** (1908), 2287.

**Fabre, L. Instruction in Chemistry and Electrochemistry at the Technische Hochschule, Dresden.** *Rev. gén. chim.*, **13**, 65; *C. A.*, **4** (1910), 2894.

**Frankforter, George B. Teaching of Chemistry in the State Universities.** *Science*, **26**, 303.

**Frary, Francis C. The Use of the Blue Print in the Teaching of Industrial Chemistry.** *J. Am. Chem. Soc.*, **33** (1911), 628.

**Guttmann, Oscar. The Works Chemist as Engineer.** *J. Soc. Chem. Ind.*, **26** (1907), 864.

**Herreshoff, J. B. F. Training of Technical Chemists.** *Science*, **19**, 561.

**Hunicke, H. August. The Chemical Engineer.** Presidential Address delivered before the St. Louis Chemical Society, Jan. 14, 1907.

**James, J. H. Chemical Education for the Industries.** *Proc. of Soc. for the Promotion of Engineering Education*, **19** (1912). **(The) Four-Year Course in Chemical Engineering.** *Trans. of the Am. Inst. of Chemical Engrs.*, **4** (1911).

**Kaempffert, Waldemar. The Business Side of German Science, VIII. Making Money with the Aid of Technically Trained Men.** *Sci. Am.*, July 20 (1912), p. 54. **The Industrial Need of Technically Trained Men, I. Scientific Manufacturing and the Opportunities it Offers.** *Sci. Am.*, Mar. 15 (1913), p. 252.

**Kallir, J. The Course of Instruction for Food Chemists.** *Z. öffentl. Chem.*, **16**, 396; *C. A.*, **5** (1911), 721.

**Kaselitz, O. The Preparatory Education of Chemists.** *Z. angew. Chem.*, **21**, 5–7; *C. A.*, **2** (1908), 1031.

**Kerr, J. G. Technical Education in Scotland at the Franco-British Exhibition.** *Eng.*, **86**, 198; *C. A.*, **3** (1909), 103.

**Kippenberger, C. The Question of the Proper Training of a German Food Chemist.** *Chem. Ztg.*, **34**, 745–6; *C. A.*, **4** (1910), 2850.

**Kreutz, A. Should the Requirements of a Practical Training for Food Chemists Be Changed?** *Chem. Ztg.*, **34**, 493; *C. A.*, **4** (1910), 2041. **The Regulations of February 22, 1894, Concerning the Examination of Food Chemists.** *Chem. Ztg.*, **34**, 821; *C. A.*, **5** (1911), 531.

**Lachman, A. Some Suggestions for the Improvement of Instruction in Technical Chemistry.** *Science*, **15**, 775.

**Le Chatelier, Henry. Higher Technical Instruction: Its Purpose and its Methods.** *Rev. métal.*, **8**, 397; *C. A.*, **5** (1911), 2705.

**Louis, H. Relations between Practical Training and College Education for Engineers.** *Electrician*, **67**, 622; *C. A.*, **5** (1911), 3326.

**Lunge, Georg. Education of Industrial Chemists.** *J. Am. Chem. Soc.*, **15** 1893), 481

**Mabery, Charles F. Education of the Professional Chemist.** *Proc. Am. Assn. for the Advancement of Science*, 56th and 57th Meetings, held at Ithaca, N. Y., June 28 to July 3, 1906, and New York City, Dec. 27, 1906 to Jan. 2, 1907.

**Magruder, Wm. T. The Good Engineering Teacher, His Personality and Training.** *Science*, Aug. 1 (1913), p. 137.

**Marre, F. The Practical Character of Chemical Instruction in the United States.** *Rev. chim. ind.*, **20**, 103–5; *C. A.*, **3** (1909), 1954.

**McMurtrie, Wm. The Attitude of Technical Institutions to Post-Graduate Study.** THIS JOURNAL, **1** (1909), 196. **(The) Condition, Prospects, and Future of the Educational Demands of the Chemical Industries.** *J. Am. Chem. Soc.*, **23**, 71.

**Nichols, Wm. H. The Efficiency and Deficiencies of the College-Trained Chemist, when Tested in the Technical Field.** THIS JOURNAL, **1** (1909), 102.

**Nowak, Carl A. The Training of the Fermentologist.** *Ibid.*, **5** (1913), 502.

**Noyes, A. A. A Talk on Teaching.** *Science*, **8**, 657–65.; *C. A.*, **3** (1909) 388.

**Palmer, Charles S. Chemical Engineering.** THIS JOURNAL, **6** (1914), 768.

**Pemberton, Jr., Henry. The Education of Industrial Chemists.** *J. Am. Chem. Soc.*, **15** (1893), 627.

**Richardson, Clifford. A Plea for the Broader Education of the Chemical Engineer.** *Science*, **27**, 81–9; *C. A.*, **2** (1908), 1031.

**Richardson, W. D. The Analyst, the Chemist and the Chemical Engineer.** *Science*, **28**, 396–402; *C. A.*, **2** (1908), 3265.

**Rogers, Allen. A New Step in Industrial Education.** THIS JOURNAL, **2** (1910), 25. **Educating Foremen to Coöperate with Chemists.** *The Dodge Idea*, Oct. (1912), p. 927.

**Snyder, H. The Training of the Agricultural Chemist.** U. S. Bureau of Chem., *Bull.* **122**, 110.

**Stewart, John. A Plan for the Support of Chemical Research and for the Better Teaching of Industrial Chemistry.** THIS JOURNAL, **4** (1912), 616.

**Talbot, H. P. The Outlook for a Better Correlation of Secondary School and College Instruction in Chemistry.** *Science*, **31**, 561–74; *C. A.*, **4** (1910), 3028.

**Taylor, F. W. May Boys in Industries Appreciate the Diplomas of Universities and Technical Schools?** *Rev. métal.*, **7**, 648–54; *C. A.*, **5** (1911), 771.

**Volhard, J. Liebig's Methods of Instruction.** *Z. angew. Chem.*, **21**, 2449–54; *C. A.*, **3** (1909), 734.

**Von Meyer, Ernst. The Growth of Chemical Instruction in the Nineteenth Century, More Especially in Germany.** ("In His History of Chemistry." London, **1906**, p. 332.

**Walker, Wm. H. and Lewis, W. K. A Laboratory Course of Chemical Engineering.** *J. Am. Chem. Soc.*, **33** (1911), 618.

**Weber. Do the Prescriptions as to the Practical Training of Food Chemists Require Change?** *Chem. Ztg.*, **34**, 577; *C. A.*, **4** (1910), 2333.

**Whitaker, M. C. The Training of Chemical Engineers.** THIS JOURNAL, **3** (1911), 36; *Met. and Chem. Eng.*, **9** (1911), 9.

**Wichelhaus, H. Technology for Chemists and Jurists in German Universities.** *Z. angew. Chem.*, **21**, 7–10; *C. A.*, **2** (1908), 1031.

**Wilson, Thomas. Training Engineers at Yale.** *Power*, **37** (1913), 772.

**Withrow, James B. Points of View in the Teaching of Industrial Chemistry.** *J. Am. Chem. Soc.* **33** (1911), 624.

**Woy, Rudolph. Industrial Chemists and the Agricultural Experiment Stations.** *Z. öffentl. Chem.*, **17**, 22; *C. A.*, **5** (1911), 1481.

**Chemical Engineering.** Editorial in *Chem. Trade J.*, **43**, 393–4; *C. A.*, **3** (1909), 389.

**Chemical Engineering at the University of Wisconsin.** *Electrochem. and Met. Eng.*, **7** (1909), 209.

**Chemical Engineering Education.** Editorial in THIS JOURNAL, **2** (1910), 397.

**College Training and the Works.** *Chem. World*, **3** (1914), 33.

**Conference on the Education and Training of Engineers, 1911.** *Electrician*, **67**, 543, 583; *C. A.*, **5** (1911), 3326.

**Education.** Editorial in THIS JOURNAL, **1** (1909), 147–8

**Education of the Chemist.** *Z. angew. Chem.* **22**, 1845–6; *C. A.*, **3** (1909), 2099.

**Educational and Economic Importance of Chemistry and the Social Status of Chemists.** *Z. Nahr.-Genussm.* **18**, 1–88; *C. A.*, **3** (1909), 2869.

**Society for Promotion of Engineering Education.** (Report of 21st Annual Meeting, giving digest of various papers.) *Electrical World*, July 5 (1913), p. 12.

**Symposium on the Education of the Technical Chemist.** *Chem. Eng.*, **1904–5**, pp. 71, 131, 210, 305, 357.

**Training of Industrial Engineers.** *J. of Political Economy*, June (1913), p. 494.

# RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Aluminum Glazed Black Powder. F. Sparre, Nov. 10, 1914. U. S. Pat. 1,116,944.** A coating of aluminum is applied to granulated uncoated black powder.

**Treating Rosin. F. E. Mariner, Nov. 17, 1914. U. S. Pat. 1,117,584.** Rosin from which the turpentine has previously been separated is distilled over in a vacuum of approximately 22 in. and at a temperature between 290° C. and 310° C. The distillation is continued until substantially all the rosin has been distilled over, whereby a grease-set high in abietic acid is produced.

**Removing Oxygen from Water. R. Gans, Nov. 17, 1914. U. S. Pat. 1,117,831.** A reducing sulfur compound and a salt of copper is added to the water to be freed from oxygen.

**Leather. O. Roehm, Nov. 17, 1914. U. S. Pat. 1,117,912.** Glacé leather is produced by treating depilated skins with a tanning liquid and then with a sulfonated oil free from soap and containing a volatile substance soluble in oil.

**Smelting Zinc Ores. J. M. Hyde, Nov. 24, 1914. U. S. Pat. 1,118,012.** Zinciferous ores mixed with a flux and a reducing agent are heated in an externally heated retort to a temperature sufficient to reduce the metallic constituents of the ores. The molten materials are collected in a bath beneath the charge and the zinc vapors are removed from the retort above the molten bath, kept molten by being applied directly to its surface.

**Recovering Molybdenum. F. D. S. Robertson, Nov. 17, 1914. U. S. Pat. 1,118,150.** Molybdenum is produced in the form of pure molybdenum trioxid by subjecting ores containing molybdenum to a volatilizing temperature in an atmosphere having an excess of oxygen.

**Manufacturing Fusel-Oil. J. Scheckenbach, Nov. 24, 1914. U. S. Pat. 1,118,238.** Fusel oil is produced by means of bacteria by subjecting a solution of a carbohydrate to the exclusive action of such bacteria as are capable of standing the heat of saturated steam at 100° C. for about half an hour.

**Pyroxylin Solvent. F. Kniffen, Nov. 24, 1914. U. S. Pat. 1,118, 498.** The solvent comprises equal parts of ethyl acetate and benzol.

**Hydrogen. B. Spitzer, Nov. 24, 1914. U. S Pat. 1,118,595.** A mass of iron ore is heated by means of producer gas and air and reduced by means of water gas. Steam to be decomposed is then passed through the reduced mass.

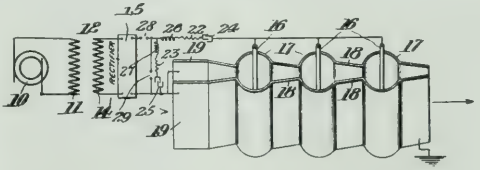
**Ammonia. C. Bosch and A. Mittasch, Nov. 24, 1914. U. S. Pat. 1,118,628.** A mixture of hydrogen and nitrogen is passed over a catalytic mixture containing tungsten and nickel

**Pure Zinc Oxid. H. W. de Stucklé, Nov. 24, 1914. U. S. Patent 1,118, 894.** A dissolved zinc salt is reacted upon with ammonium sulfite in the presence of caustic ammonia or ammonium carbonate. The precipitated zinc sulfite is calcined and the evolved sulfur dioxid utilized for regenerating the ammonium sulfite.

**Method of Distilling Hydrocarbons. R. E. Humphreys, Dec. 1, 1914. U. S. Pat. 1,119,700.** The liquid residue of the paraffin series of petroleum distillation having a boiling point of upward of 500° F. is distilled under a pressure of over four atmospheres. All the vapors passing from the still are cooled while passing through an inclined conduit or run-back, and which is kept under a pressure of over four atmospheres, which automatically returns the condensed heavier fractions to the still, where they undergo further treatment. The light vapors, which are of the same series as the original material but of lower boiling points, are led off and condensed.

**Removing Particles of Suspended Matter from Bodies of Gas or Fluid. W. W. Strong and A. F. Nesbit, Dec. 1, 1914. U. S. Pat. 1,119, 469.** Suspended matter is removed from bodies of gases or fluids by means of an apparatus, as illustrated, which consists of grounded electrodes formed by oppositely disposed

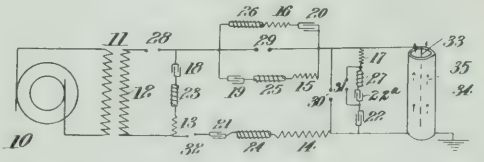
Fig. 1.



members having bulging sides that form cells connected by constricted passages. The electrodes are maintained at a high difference of potential and means are provided for the proper disposal of the material collected and for keeping the cells clean.

**Separating Finely-Divided Particles of Solids or Liquids from a Gas. W. W. Strong and A. F. Nesbit, Dec. 8, 1914. U. S. Pat. 1,120,561.** This improvement in the separation of solids or liquids from a gas depends upon the fact that the precipitation produced by an ordinary high tension alternating corona discharge may be greatly increased by the introduction of a spark gap in series with the active or grounded electrode; this spark gap greatly extends the luminous region about the elec-

Fig. 1.



trode. Fig. 1 shows the relative positions of the spark gaps in one arrangement of apparatus. It was also found that, contrary to the usual view, iron cored inductances may be used to exert a noticeable adjustment of the circuits. In practice an alternating current of high frequency is used; the amplitude and damping of the oscillations are controlled by predetermined and adjustable values of resistance, self-inductance and capacity. One or more spark gaps are used and flame discharges in the spark gaps are prevented by suitable means.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF FEBRUARY, 1915

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid | Lb. | 50 | @ | 52 |
| Acetic Acid (28 per cent) | C. | 1.75 | @ | 2.00 |
| Acetone (drums) | Lb. | 18 | @ | 20 |
| Alcohol, denatured (180 proof) | Gal. | 33 | @ | 35 |
| Alcohol, grain (188 proof) | Gal. | 2.52 | @ | 2.56 |
| Alcohol, wood (95 per cent) | Gal. | 45 | @ | 47 |
| Amyl Acetate | Gal. | 2.50 | @ | 2.60 |
| Aniline Oil | Lb | 63 | @ | 67 |
| Benzoic Acid | Lb. | 1.10 | @ | — |
| Benzol (90 per cent) | Gal. | 40 | @ | 50 |
| Camphor (refined in bulk) | Lb. | 41 | @ | — |
| Carbolic Acid (drums) | Lb. | 1.00 | @ | 1.25 |
| Carbon Bisulfide | Lb. | 7 | @ | 8 |
| Carbon Tetrachloride (drums) | Lb. | 12 | @ | 13 |
| Chloroform | Lb. | 30 | @ | 35 |
| Citric Acid (domestic), crystals | Lb. | 55 | @ | 57 |
| Dextrine (corn) (carloads, bags) | C. | 3.18 | @ | — |
| Dextrine (imported potato) | Lb. | — | @ | |
| Ether (U. S. P., 1900) | Lb. | 15 | @ | 20 |
| Formaldehyde | Lb. | 8 1/2 | @ | 9 1/2 |
| Glycerine (dynamite) | Lb. | 21 3/4 | @ | 22 |
| Oxalic Acid | Lb. | 12 1/2 | @ | 14 |
| Pyrogallic Acid (bulk) | Lb. | 1.90 | @ | 2.10 |
| Salicylic Acid | Lb. | 1.10 | @ | 1.35 |
| Starch (cassava) | Lb. | 3 1/4 | @ | 4 |
| Starch (corn) (carloads, bags) | C. | 2.40 | @ | - |
| Starch (potato) | Lb. | - | @ | — |
| Starch (rice) | Lb. | — | @ | — |
| Starch (sago) | Lb. | 2 7/8 | @ | 3 |
| Starch (wheat) | Lb. | 5 | @ | 10 |
| Tannic Acid (commercial) | Lb. | 60 | @ | 66 |
| Tartaric Acid, crystals | Lb. | 37 | @ | 38 |

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lead (brown, broken) | Lb. | 7 1/4 | @ | 7 1/2 |
| Acetate of Lime (gray) | C. | 2.00 | @ | 2.05 |
| Alum (lump) | C. | 2.50 | @ | 3.00 |
| Aluminum Sulfate (high-grade) | C. | 1.75 | @ | 2.00 |
| Ammonium Carbonate, (domestic) | Lb. | 8 1/4 | @ | 9 |
| Ammonium Chloride, (gray) | Lb. | 5 1/2 | @ | 6 1/2 |
| Aqua Ammonia (drums) 16° | Lb. | 2 1/4 | @ | 2 1/2 |
| Arsenic (white) | Lb. | 4 | @ | 5 |
| Barium Chloride | Ton | 45.00 | @ | 50.00 |
| Barium Nitrate | Lb. | 15 | @ | 16 |
| Barytes (prime white, foreign) | Ton | 19.00 | @ | 25.00 |
| Bleaching Powder (35 per cent) | C. | 1.30 | @ | 1.50 |
| Blue Vitriol | Lb | 5 1/8 | @ | — |
| Borax, crystals (bags) | Lb. | 4 3/4 | @ | 5 |
| Boric Acid, crystals (powd.) | Lb. | 8 3/4 | @ | 9 |
| Brimstone (crude, domestic) | Long Ton | 22.00 | @ | 22.50 |
| Bromine (bulk) | Lb. | 40 | @ | 50 |
| Calcium Chloride (lump) | Ton | 11.70 | @ | 12.00 |
| Chalk (light precipitated) | Lb. | 4 1/2 | @ | 5 1/2 |
| China Clay (imported) | Ton | 14.00 | @ | 16.00 |
| Feldspar | Ton | 8.00 | @ | 14.00 |
| Fuller's Earth (powdered, foreign) | C. | 80 | @ | 90 |
| Green Vitriol (bulk) | C. | 30 | @ | 32 |
| Hydrochloric Acid (18°) | C. | 1.15 | @ | 1.65 |
| Iodine (resublimed) | Lb. | 3.75 | @ | 4.00 |
| Lead Nitrate | Lb. | 8 | @ | — |
| Litharge (American) | Lb. | 5 | @ | 5 1/4 |
| Lithium Carbonate | Lb. | 1.00 | @ | 1.10 |
| Magnesium Carbonate | Lb. | 4 1/2 | @ | 4 3/4 |
| Magnesite "Calcined" | Ton | 40.00 | @ | 50.00 |
| Nitric Acid (36°) | Lb. | 3 7/8 | @ | 4 1/4 |
| Phosphoric Acid (sp. gr. 1.75) | Lb. | 28 | @ | 28 1/2 |
| Phosphorus | Lb. | 35 | @ | 95 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate | Lb. | 13 | @ | 15 |
| Potassium Bromide | Lb | 70 | @ | 80 |
| Potassium Carbonate (calcined), 80 @ 85% | C. | 8 1/4 | @ | 9 |
| Potassium Chlorate, crystals | Lb | 25 | @ | 30 |
| Potassium Cyanide (bulk), 98–99% | Lb | 19 | @ | 21 |
| Potassium Hydroxide | Lb | 9 1/2 | @ | 10 |
| Potassium Iodide (bulk) | Lb | 3.15 | @ | 3.25 |
| Potassium Nitrate (crude) | Lb. | | @ | — |
| Potassium Permanganate (bulk) | Lb | 18 1/2 | @ | 21 |
| Quicksilver, Flask (75 lbs.) | | 60.00 | @ | |
| Red Lead (American) | Lb | 5 1/2 | @ | 6 |
| Salt Cake (glass makers') | C. | 55 | @ | 65 |
| Silver Nitrate | Oz | 31 | @ | 33 |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash (48 per cent) | C. | 67 1/2 | @ | 72 1/2 |
| Sodium Acetate | Lb. | 4 | @ | 4 1/2 |
| Sodium Bicarbonate (domestic) | C. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate (English) | Lb. | 3 1/2 | @ | 4 |
| Sodium Bichromate | Lb. | 4 3/4 | @ | 5 |
| Sodium Carbonate (dry) | C. | 60 | @ | 80 |
| Sodium Chlorate | Lb. | - | @ | — |
| Sodium Hydroxide (60 per cent) | C. | 1.55 | @ | 1.57 1/2 |
| Sodium Hyposulfite | C. | 1.60 | @ | 1.90 |
| Sodium Nitrate (95 per cent, spot) | C. | 2.10 | @ | - |
| Sodium Silicate (liquid) | C. | 85 | @ | 1.15 |
| Strontium Nitrate | Lb. | 15 | @ | 17 |
| Sulfur, Flowers (sublimed) | C. | 2.20 | @ | 2.60 |
| Sulfur, Roll | C. | 1.85 | @ | 2.15 |
| Sulfuric Acid (60° B) | C. | 85 | @ | 1.00 |
| Talc (American) | Ton | 15.00 | @ | 20.00 |
| Terra Alba (American), No. 1 | C. | 75 | @ | 80 |
| Tin Bichloride (50°) | Lb. | 11 | @ | 12 |
| Tin Oxide | Lb. | 42 | @ | 44 |
| White Lead (American, dry) | Lb. | 5 | @ | 5 1/4 |
| Zinc Carbonate | Lb. | 8 1/2 | @ | 9 |
| Zinc Chloride (granulated) | Lb. | 5 | @ | 5 1/2 |
| Zinc Oxide (American process) | Lb. | 5 3/8 | @ | 6 3/8 |
| Zinc Sulfate | C. | 2.35 | @ | 2.50 |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax (pure white) | Lb. | 45 | @ | 57 |
| Black Mineral Oil, 29 gravity | Gal. | 12 1/2 | @ | 13 |
| Castor Oil (No. 3) | Lb. | 8 1/4 | @ | 9 |
| Ceresin (yellow) | Lb. | 10 | @ | 25 |
| Corn Oil | C. | 6.15 | @ | 6.25 |
| Cottonseed Oil (crude), f. o. b. mill | Lb. | 6.07 | @ | 6.13 |
| Cottonseed Oil (p. s. y.) | Lb. | 7 1/8 | @ | 7 1/2 |
| Cylinder Oil (light, filtered) | Gal. | 20 | @ | 25 |
| Japan Wax | Lb. | 10 3/4 | @ | 12 |
| Lard Oil (prime winter) | Gal. | 92 | @ | 94 |
| Linseed Oil (raw) | Gal. | 56 | @ | 58 |
| Menhaden Oil (crude) | Gal. | 35 | @ | — |
| Naphtha, 68 @ 72° | drums | — | @ | 16 |
| Neatsfoot Oil (20°) | Gal. | 96 | @ | 98 |
| Paraffine (crude, 120 & 122 m. p.) | Lb. | 3 1/8 | @ | 3 1/4 |
| Paraffine Oil (high viscosity) | Gal. | 22 | @ | 23 |
| Rosin ("F" grade) (280 lbs.) | Bbl. | 3.52 | @ | 3.55 |
| Rosin Oil (first run) | Gal. | 25 | @ | — |
| Shellac, T. N. | Lb. | 14 | @ | 14 1/2 |
| Spermaceti (cake) | Lb. | 26 | to | 27 |
| Sperm Oil (bleached winter), 38° | Gal | 70 | @ | 71 |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid (double-pressed) | Lb. | 9 1/2 | @ | 10 1/2 |
| Tallow (acidless) | Gal. | 62 | @ | 63 |
| Tar Oil (distilled) | Gal. | 30 | @ | 31 |
| Turpentine (spirits of) | Gal. | 45 | @ | 46 |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum (No. 1 ingots) | Lb. | 19 | @ | 19 1/2 |
| Antimony (Hallet's) | Lb. | 19 | @ | 20 |
| Bismuth (New York) | Lb. | 2.80 | @ | 2.90 |
| Bronze powder | Lb. | — | @ | — |
| Copper (electrolytic) | C. | 14 1/2 | @ | 14 5/8 |
| Copper (lake) | C | 14 5/8 | @ | 14 7/8 |
| Lead, N. Y. | C. | 3.85 | @ | — |
| Nickel | Lb. | — | @ | — |
| Platinum (refined) | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | 48 7/8 | @ | — |
| Tin | C. | 37.00 | @ | — |
| Zinc | C. | 9.00 | @ | — |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | C. | 3.10 | @ | — |
| Blood (dried) | Unit | 2.65 | @ | — |
| Bone, 4 1/2 and 50 (ground, raw) | Ton | 30.00 | @ | — |
| Calcium Cyanamid | Unit of Ammonia | 1.90 | @ | — |
| Calcium Nitrate (Norwegian) | C. | — | @ | — |
| Castor meal | Unit | — | @ | — |
| Fish Scrap (domestic, dried) | Unit | — | & | — |
| Phosphate, acid (16 per cent bulk) | Ton | 7.00 | @ | — |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble (68 per cent) | Ton | 2.25 | @ | 2.50 |
| Tennessee (70–80 per cent) | Ton | 5.00 | @ | 5.50 |
| Potassium, "muriate," basis 80 per cent | Ton | | nominal | |
| Pyrites (furnace size, imported) | Unit | 12 1/2 | @ | — |
| Tankage (high-grade) | Unit | 2.65 | & | 10 |

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# EDITORIALS

## ANOTHER GREAT DISCOVERY

A discovery of enormous potential importance to the chemical profession has been made within the last few months by the general public. Hundreds of newspapers and periodicals are devoting editorial space to the discussion of the chemists and chemical engineers and their relations, and especially their obligations, to the coal-tar dye industries. The public acknowledgment of our responsible connection with this important industry is a great accomplishment for our profession when we recall that only six months ago the chemist was known chiefly by the drug store he kept. Every worker thrives upon public recognition of his achievements. The chemist is no exception to this rule, yet from the obscure and involved nature of his work and his natural secretive instincts he has received less public acknowledgment than the workers of any other profession. It matters little whether the chemical profession comes into view riding the spectacular coal-tar dye hobby, whether it is "trimmed" by the public press for its lack of initiative in seizing opportunities, or whether it is charged with an utter absence of business acumen, so long as it comes to be publicly recognized as an important and an essential factor in the industrial development and councils of this country.

If the newspapers make mistakes in discussing our intricate scientific and industrial problems, we should not be content to blink and chuckle in our superior wisdom, but should come out in the open and set them right. If legislative styles point unmistakably to pension log-rolling, bureaucratic log-rolling, tariff log-rolling, it is our duty to teach legislators the value of rolling the logs that will develop the industries which support our profession.

The public have been left to their own resources to figure out the function of the chemical profession. We publish one thousand copies of our Journals each day in the year, but they are for the chemists, and are free from matters of public interest. The directory of our Society—the largest technical society in the world—gives no hint of the vast and varied field of professional activity of the chemist. Our public work is obscured by impenetrable technical detail and our industrial achievements are cut off from public view by high factory walls. Public sources of information as to the field of activity of the chemist are thus limited to the signs displayed on the corner drug stores. We have labored for years under cover. Is it any wonder, then, that we were still undiscovered when the foreign crisis disclosed to the public the fact that some of our great industries depended for their development and continuance upon the work of the chemist? Nevertheless, there are many other fields of activity besides those which have recently become of interest to the public, in which the chemist and the chemical engineer have contributed much to industrial wealth.

The time seems ripe for coming out in the open and showing the public in clear and authoritative form the place of the chemist in industry. We publish in THIS ISSUE a series of papers written by eminent specialists—chemists, chemical engineers, administrative officials and industrial managers—who see and present from various angles the contributions of the chemical profession to our industrial development. These papers cover but a few of the industries benefited by the science of chemistry. We hope to publish many others of the same kind and thus bring to light a better understanding of the world's work of the industrial chemist and the chemical engineer.

## ON SYNTHETIC DYESTUFFS AND OUR EXPLOSIVES

Under the title of "The Dyestuff Situation and Its Lesson," we printed in the March number of THIS JOURNAL an address by our ex-president, Arthur D. Little. Were it not for the prominent position occupied by him, in view of the many reports and papers written, we would make no comment, as the subject has become threadbare. From a standpoint of patriotism, however, if for no other reason, we challenge his conclusions. While he is stopping the "wasting precious ammonia" the no less precious benzol, toluol, carbolic acid, etc., are to go to waste, or be exported to be returned to us as finished products.

It is admitted that we can have a dyestuff industry in this country if it is protected with an *ad valorem* duty of 30 per cent, plus a specific duty of $7\frac{1}{2}$ cents per pound. Let us see what this means to the mind of the man or woman who is called upon to pay the tax. Dr. Hesse tells us: that the cost of the dyestuff, including this duty, would not be over 15 cents per annum per capita of our population; that the dyestuff entering into a suit of clothes costing $25.00 would not buy a good cigar, and, including the proposed duty, would be less than 5 cents per suit.

He asks why then "should we duplicate them (*i. e.*, German Color Works) only to plunge into an industrial warfare against the most strongly fortified industrial position in the world." In answer, let us quote from what Dr. Schweitzer says in an article on German militarism.

"The industry for the recovery of the by-products from the coking process, which we already mentioned as a source for sulfate of ammonium, has also been highly developed because German militarism needed some of the resulting coal-tar products for the manufacture of explosives. Benzol, toluol, carbolic acid, metacresol and diphenylamine are starting materials used in the manufacture of ammunition."

Bearing this in mind let us see what Dr. Hesse says on the subject in a report which was read into the records of the House of Representatives, dated December 10, 1914, by Hon. Samuel Wallin:

"The best information your committee has so far been able to gather is that this country can produce so-called coal-tar raw material in amounts sufficient for the needs of a complete domestic coal-tar chemical industry, inclusive of explosives

and dyes, provided there is a certainty of outlet as to volume and continuity.

"There is no inherent defect in our coke industry with regard to the actual making of these things; the only question involved is whether it be more profitable to burn the benzol, toluol, and the like, contained in the gas, as a fuel, than to separate them from each other for purposes of sale.

"The materials of the preceding paragraph are the ones used in the coal-tar explosive industry, as well as in the coal-tar medicinals and dyestuffs industries. Each of these three industries coöperates with the others to make full use of those materials; alone none can fully make use thereof nor succeed; the correct and proper utilization of these materials require successful coexistence of all three industries in one and the same country."

In a statement made by H. A. Metz, before the Committee of Finance of the U. S. Senate, 62nd Congress, on the matter of duty on Aniline Oil and Salts, he said: "or if the foreigners did not drop their prices the articles would probably be made here, and provide the basis for a real coal-tar (chemical) industry, etc."

Here we find the motive for the opposition by the foreign manufacturer and their agents, because if the dyestuffs industry was assisted by proper protection in this country they know that in ten years we would compete with them in the markets of the world.

T. B. Wagner has given us a text on the subject when he stated in his address before the American Institute of Chemical Engineers that:

"Strange as it may seem, the starting of industrial enterprises is not always due to the chase of the almighty dollar, as is generally and perhaps pardonably assumed, but in many instances it is directly caused by the enactment of laws with more or less restrictive tendencies."

Switzerland produces neither coal, coke nor coal tar, and yet of the 16.6 per cent of dyestuffs not obtained from Germany in the year 1913 by this country the major part was obtained from Switzerland. Switzerland then could hold us at her mercy because of her ability to supply herself, or other nations who might be at war with us, with explosives. We can read between the lines.

There is no secret whence the success of the foreign coal-tar chemical industry. It is fully set forth in the report of the U. S. Tariff Board dated February 7, 1912, pages 225 and 226:

"The German chemical industry knows practically no competition between individual establishments engaged in the manufacture of the same products; and the elimination of competition and general tendency toward combination observable in all industrial countries, but especially pronounced in Germany, has in that country gone further in the chemical and allied industries than in any other manufacture. This has been accomplished by the formation of 'syndicates,' 'cartels,' 'selling associations,' and to a lesser degree by the absorption of, or amalgamation with, rival concerns, formed secretly or openly for the purpose of controlling output and prices. The law puts no obstacle in the way of such consolidation, and in several instances governmental agencies operating large chemical establishments form a party to the agreements. * * * * Practically all the important manufactures of the chemical industries and many products of lesser importance are under some form of syndicate control, more or less strict, and more or less extensive as to production, prices, supply of raw materials or division of territory. Chemical manufactures lend themselves more readily to consolidation than any other, because within a given line the products from one source are not visibly different from those of other sources, and, on the same basis of purity, do not differ at all. The products, therefore, carry little if any individuality, which is the principal basis of competition. Quite a number of these organizations are bound by agreements of some kind to international 'cartels,' the object of which is to control the international markets."

Should the American manufacturers use similar methods, indictments would promptly follow. Were they permitted to use them, however, the foreigner would unquestionably be beaten at his own game. If then it is not the desire of the people of this country to foster its aniline industry, let us, at least, as a matter of patriotism, demand that our Government enter into the manufacture of the necessary explosives derived from the coal-tar chemical compounds, although in so doing our ammunition of the character described by Dr. Schweitzer and quoted above will cost the country many, many times what it could be supplied for by an established and protected aniline industry in the United States.

T. J. PARKER

# SYMPOSIUM ON THE CONTRIBUTIONS OF THE CHEMIST TO AMERICAN INDUSTRIES

Papers presented at the 50th Meeting of the AMERICAN CHEMICAL SOCIETY, New Orleans, March 31 to April 3, 1915

## CONTRIBUTIONS OF THE CHEMIST TO THE WINE INDUSTRY

By CHARLES S. ASH

Demonstrating the value of chemistry and chemists to an old established industry, which has been commercially successful without either, is never an easy matter. To attempt such a demonstration to the wine industry of California fifteen years ago seemed like an almost hopeless as well as an entirely thankless task.

The California wine industry had been established by European wine makers some thirty years before and for that length of time had been conducted by "thumb and screw" rules. While wines of good quality were not turned out each year, the results obtained by the wine maker were entirely satisfactory to the dealer. Spoilt and poor wine was attributed to a "poor vintage."

The arguments which could be advanced at that time showing the value of the chemist to other industries had little effect. When the chemist looked for employment in the wine industry he was naturally asked what he could do for the benefit of the industry. On replying that he could make an analysis of the wine, he was met with this answer—"Well, after I know the composition of the wine what good does it do me? Can you tell me whether the wine is good, bad or indifferent? An expert taster can tell all these things." Of course, a chemist knowing nothing about wine could not interpret the analysis he had made, and an analysis without an interpretation is useless, while an incorrect interpretation is fatal. So the stand taken by the wine merchant was absolutely correct, as far as his knowledge went. The fallacy of his position at that time (15 to 20 years ago) was that he unknowingly did depend upon the chemist. Chemical preservatives were in common use all over the world, their preservative value having been discovered by chemists. All wine having a sufficient quantity of preservative was sterile and, therefore, gave no trouble after shipment.

The chemist begins to be of value to the wine industry only when he becomes familiar with the wine business and becomes a wine man. When that happens he will know that as wine is a natural and not a synthetic product, he must adjust his scientific knowledge to the nature of the product and not try to change the character of wine to meet his scientific views. As the chemist becomes familiar with the wine he will be able to interpret his analyses correctly, to segregate the sound from the unsound wines and to anticipate their stability. This was most desirable and useful to the wine merchant. Pure food laws were coming into effect in European countries. Salicylic acid (the preservative commonly used) had to be abandoned and the chemist was instructed to look for a preservative that could not be detected. At that time benzoates were very difficult of detection and benzoic acid was adopted as a preservative. But analytical science soon caught up, and benzoates also were of no value. The chemist is still looking vainly for a preservative that cannot be detected.

As wine makes itself spontaneously when the grapes are crushed, it was considered a purely natural product and its goodness or badness the result of chance. So we have to this day the much-abused phrase, "the fine vintage of 188–." The reasons for good and bad vintages were unknown. To be sure, Pasteur had made his classic researches and his views had slowly made themselves felt throughout the world. Where pure yeast was planted in sterile media, as in beer, the quality of the resulting product was largely dependent upon the quality of the yeast. In the manufacture of wine, it is obvious that the must cannot be sterilized in the same way that beer can be. The chemist at this time, being able to anticipate the stability of a natural wine, concentrated his effort upon the production of wines of sufficient stability to keep in a warm climate rather than the finding of a preservative that could not be detected. The use of a preservative in such a wine would only add to the cost and do little, if any, benefit. It holds good in all food industries, I think, that the need for preservatives decreases as knowledge of the product increases. Through the efforts of the writer, wine was shipped without preservatives as an experiment: the first car was shipped with many misgivings. It was expected that every barrel would blow up, and the entire carload be lost. This was a very trying time for the chemist, as his theories were on trial and a failure meant a return to the old régime. The car, however, gave perfect satisfaction and nothing was heard afterwards. From that time on, the use of preservatives decreased and methods for improving the vintage increased; in fact, a chemist's knowledge took the place of preservatives in the business.

The production of stable wine—that is, a wine that does not deteriorate on shipment—is a most complex problem. To go into the problem is outside the province of this short paper. It can be said, however, that if the chemist has been of any benefit to the wine industry he has been of benefit here. To the direct question—"What has the chemist done for the wine industry?"—one can with justice reply:

1—By proper methods of handling he has made the use of preservatives unnecessary.

2—He has insured the uniformity of the product as completely as seasonal differences will allow.

3—He has reduced the quantity of spoilt wine from 25 per cent to less than 1 per cent (about 0.46 per cent average).

4—He has reduced the quantity of inferior wine from 25 per cent to 5 per cent. (Some grapes always give inferior wine no matter what care is given to the products. Usually these grapes are those grown on over-irrigated ground and over produce.)

One of the most important duties of the chemist is, as we have said, the production of a uniform product, without which uniformity no business can be successful. Some details may not be out of place. There is no difficulty in turning out, for example, a uniform sugar, but a uniform wine is less easy. Every vintage is slightly different, yet if a brand of wine be established it is necessary to supply your customer always with wine of exactly the same type. Otherwise, the consumer, being used to the one wine, objects to the other. The wine chemist has to help in the attaining of uniformity. As the blending of wines is the final operation, and as these blends compose at times 100 different wines, this is perhaps one of the most important duties of the wine chemist. Blends are usually made up first in sample, analyzed, blended as nearly as possible to the composition of the previous blend of this type, and the directions for the blends then distributed to the winery which is to make them up. After blending, samples are again sent to the laboratory where the chemist again analyzes them to see whether the blends have been properly and uniformly made.

The following samples show the method of checking the blending. The analyses of the sample blend made in the laboratory, and the actual blend made in the cellar must agree; otherwise, the blend is not uniform and must be reblended.

| | Per cent alcohol by volume | Grams per 100 cubic centimeters Total acidity | Volatile acidity | Reducing sugar | Tannin |
|---|---|---|---|---|---|
| Winehaven Claret—Blend No. 485 (265,000 gallons) | | | | | |
| Sample blend | 12.29 | 0.500 | 0.060 | 0.145 | 0.135 |
| Finished blend | 12.37 | 0.510 | 0.060 | 0.150 | 0.140 |
| Wahtoke Port—Blend No. 482 (144,500 gallons) | | | | | |
| Sample blend | 20.78 | 0.390 | 0.043 | 6.60 | 0.070 |
| Finished blend | 20.78 | 0.390 | 0.046 | 6.63 | 0.079 |

Besides this, the wine chemist has duties in common with all chemists. He must analyze the water and soils of the vineyards owned by his company, analyze the supplies used in the wineries or in the vineyards, advise as to fertilizers to be used and devise means to gather as many by-products as possible.

I must say, in conclusion, that the wine chemist, in spite of temporary discouragements, is having more intimate relations with the Wine Industry. He is, in fact, becoming quite friendly, and he has hopes of being on the same good terms as his brothers in the sugar, dyeing, oil, petroleum, gas, soap and other industries, which the chemist has made famous.

MONADNOCK BUILDING, SAN FRANCISCO

## CONTRIBUTIONS OF THE CHEMIST TO THE COPPER INDUSTRY

By J. B. F. HERRESHOFF

Vice-President Nichols Copper Company and Consulting Engineer General Chemical Company

During the last forty years there has been an enormous increase in the copper mined, smelted and refined in the United States. The following figures clearly show this increase:

| | |
|---|---|
| In 1874 the United States produced | 17,500 long tons |
| 1884 | 64,708 long tons |
| 1894 | 158,120 long tons |
| 1904 | 362,739 long tons |
| 1912 | 563,700 long tons |

Of the 17,500 tons produced in 1874, Calumet & Hecla produced 87 per cent. This was before the producing days of Montana and Arizona copper, which began in about 1883.

It is fair to assume that there were very few, if any, chemists employed in the copper industry in the United States in 1874. At that time, among the few laboratories in New York City, the largest one made only one or two copper analyses per year, and it was known then that Calumet & Hecla had employed one of the very few expert chemists in the country to help them, if possible, out of some chemical difficulty.

About 1884 a few chemists were employed in the earlier work of developing going on in Montana and Arizona. You will notice the marked increase in the output of copper from the years 1884 to 1894. It was not until after 1890 that the real value of chemists in improving operations in mining, as well as in concentrating, roasting, smelting and refining copper was fully appreci-

ated. From that time to the present the value of chemists in the mining and metallurgical work in the production of copper has very greatly increased, and the number of chemists employed is greater in proportion than the enormous increase in copper produced.

In the large copper mines of this country chemical analyses are made and used to very great advantage in the control of mining operations and also in connection with sorting the ore before crushing. Ores from different parts of a mine have varying percentages of copper and differ often to a great extent in their fluxing properties, so that a bedding system is sometimes employed, placing the various grades of ore in different beds of bins. All of this ore has to be analyzed and then careful chemical calculations are made by the metallurgists, so that the proper proportion from each bin is mixed when delivered in the smelter.

In the concentration of ores the process is, to a considerable extent, a mechanical one, although of late electricity for separation and concentration is employed, and also a process that uses a moderate amount of oil which facilitates a more perfect separation of the mineral from the gangue. Whichever method is employed, a control by chemical analysis is necessary to show the gains or losses in copper.

In the successful smelting operations at many of our large mines the metallurgist who calculates the best smelting mixture of ores and fluxes to be introduced into the smelter, has to be not only an able chemist, but should be a physicist and engineer as well, in order to obtain the most economical results. To carry out this important work a great many chemical analyses are necessary, for the best results in roasting ores in the modern roasters can be produced only by the full employment of chemical analyses and physical tests.

The United States mines more than 50 per cent of the copper of the world; 75 per cent of the copper of the world is refined in this country and the larger proportion of this refining is done by electrolysis. In carrying on this electrolytic work the chemist has been responsible for a very large proportion of the improvements that have been made in the last twenty years, so that chemistry has shown itself to great advantage not only in improving the electrolytic methods of refining, but also in the preceding methods of mining and smelting.

In the electrolytic refining of copper, samples representing 80 to 100 tons of blister copper are analyzed for copper, gold and silver in order to arrive at the value of the lot. Formerly the analyses of copper were not exact enough to satisfy the buyers and sellers. The chemists then came together and improved the methods so much that perfect satisfaction now exists. It is not unusual in a copper works laboratory to have two chemists make independent analyses of the same sample and turn in results, which agree to within 0.01 per cent on blister copper and 0.002 per cent on refined copper.

More than one-half of the copper refined is cast into wire bars and then rolled and drawn into wire, the bulk of which is used for electric conduction. A very small quantity of arsenic in copper greatly lowers its conductivity; a quarter of one per cent cuts down its electric conductivity from 101 to 45. Refined copper for this purpose should contain less than one-thousandth of one per cent arsenic in order to satisfy the consumer. The chemists have made such results possible by their able research work and also by their remarkable improvements in analytical methods for copper and arsenic and their wonderfully exact methods for determining quantitatively minute quantities of bismuth, antimony, tellurium and selenium in copper.

These results could not have been obtained twenty years ago, and forty years ago even the best chemist in the country could not have dreamed of doing such work. In the great improvements in the copper industry our chemists have performed a very important part in a very able manner. The great consumers of copper in large manufacturing industries of this and other countries, and the whole world, owe to the chemists connected with our copper industries a debt of thanks for their masterly work.

25 Broad Street, New York

## CONTRIBUTIONS OF THE CHEMIST TO THE CORN PRODUCTS INDUSTRY

By E. T. Bedford
President Corn Products Refining Company

The industry of glucose and grape sugar, or, as it is known in this country, the industry of corn products, is based upon an epoch-making discovery of a chemist—the conversion by chemical means of starch into reducing sugars. The chemist has been inseparably connected with this industry from its beginning. It was started in Germany a little over one hundred years ago, and due to the limitation of the products—there being only two, glucose and grape sugar—the field and the activities of the chemist were limited correspondingly, but conditions in this country afforded him much larger opportunities, and I am glad to be able to say that the American chemist did not overlook his opportunity, but was quick to make the most of it. Owing to the character of the raw material employed in this country—corn—our products are no longer limited to two; the chemist has added to them until their number now exceeds one hundred. We produce a large number of different grades of glucose, or corn syrup, suitable for every conceivable purpose, either as food or in the arts. Manifold as the technical uses are, they are overshadowed by the great value of glucose as a food. This fact is emphasized in these days of high-priced food. Its importance and significance as an ideal food for the masses was pointed out very forcibly by Prof. Graham Lusk, who showed conclusively that glucose is the cheapest food-fuel known. Grape sugar, or corn sugar, also is an important product, and is manufactured in a variety of grades. Due to the great care which the chemist exercises in devising ways and means of controlling the process of manufacture in all of its details, the quality of the articles produced is of such excellence as to have secured for this country by far the largest portion of the world's trade in these commodities.

While the chemist was most active from the very beginning in developing the process for making glucose and grape sugar and in steadily improving their quality, he also demonstrated his value to the industry by developing new staple products such as starches for culinary and technical purposes, of dextrins and gums and various sugars, which in point of purity rival cane and beet sugar. These products are now manufactured in this country in very large quantities and are being shipped to all parts of the world. A brief reference to statistics will illustrate the effect of such work. The corn manufactured into corn products in this country amounts to 50,000,000 bushels per year. It is converted into 800,000,000 pounds of corn syrup, 600,000,000 pounds of starch, 230,000,000 pounds of corn sugar, 625,000,000 pounds of gluten feed, 75,000,000 pounds of oil and 90,000,000 pounds of oil cake.

The chemist soon recognized the large possibilities which lay in the utilization of certain constituents of the raw material which were allowed to run to waste. First among these were the nitrogenous substances, commonly classified under the name of "gluten." Their running to waste was stopped; the product was collected, washed and dried, and put upon the market as a cattle feed of great nutritive value; it has materially increased the revenue obtainable from corn. I should like to say in this connection that I hope the chemist will again concentrate his attention upon this product and within a reasonable time convert it into an article of food to be used by man rather than by animals.

The recovery of the outer hull of the corn, the bran, followed next, and by applying practically the same methods it was ob-

tained in a dry state and soon became an article of commercial importance.

With the recovery of these products, the impetus was given to a further exploitation of the other ingredients of the corn, particularly its germ, which contains a large amount of the article, commercially so important, and known as "corn oil." The chemist observed that, due to its lighter specific gravity, the germ could be separated from the body of the crushed corn by a very simple method, and so sound was the reasoning of the chemist leading to an almost mathematical separation of the germ, that the same principle is today still employed, although the invention itself was made over 30 years ago.

The chemist next turned his attention to the soluble solids lost in the water which is used in the softening or steeping of the corn, which water formed an ordinary trade waste. These solids consist of nitrogenous matter, sugars and other carbohydrates, the valuable organic phosphorus compounds and the salts of magnesia and potash.

There are numerous other products which the chemist evolved; among them glycerine and fatty acids from the oil, soap stock from other oil-containing by-products, innumerable special starches for specific purposes, and dextrins and gums of great variety.

These developments have made the products of corn the equals of competing products obtained from wheat, potatoes, sago, rice and other amylaceous sources; and where the products from corn were looked upon at one time as substitutes for the more expensive starch products obtained from other sources, they are sold today upon their own merits, which are recognized and appreciated very keenly by the trade. It goes without saying that the development of our industry would not have made such rapid strides if it had not been for the excellent work of a highly efficient sales organization and for the coöperation of the engineering forces; nevertheless, the effects of the activity of the chemist are noticeable in every direction, and it is not an exaggeration to say that the great American industry of corn products owes its existence primarily to the chemist; while it may be admitted that further expansion of the business will be largely in the direction of commercial development, I am firm in my conviction that the chemist will continue making his influence felt in our industry, that the future holds in store a great evolution of the industry and that to this evolution the chemist will contribute, as in the past, a substantial share.

17 Battery Place, New York

## CONTRIBUTIONS OF THE CHEMIST TO THE ASPHALT INDUSTRY

By James Lewis Rake

Secretary The Barber Asphalt Paving Company

Chemistry, in the service of the asphalt industry, has converted it from one which originated on purely empirical lines into one which is now founded on a rational and highly scientific basis. The development and perfection of the industry from a technical point of view has been made possible only with the aid of chemistry, intelligently associated with practical experience and service tests. During the first two decades of its existence it was conducted on no fixed principle. The hard, refined Trinidad Lake asphalt was fluxed with a heavy petroleum oil, not manufactured especially for the purpose, to form an asphalt cement of a consistency determined solely by personal judgment. This was mixed with hot sand of varying degrees of fineness and with a certain amount of powdered limestone in purely haphazard proportions which were not rationally determined. These mixtures were laid and compressed in the street with most uncertain results, sometimes excellent and sometimes very bad. When the irregularity of such work was recognized, an appeal was made to the chemist, who selected typical samples of these old pavements and resolved them into their constituents by analytical methods. It was found that surfaces which gave good and those that gave poor service were of very different and distinctive characters and that the manner in which they behaved depended upon the original properties of the mineral matter, sand, and powdered stone, as well as the consistency of the asphalt cement used. The chemist devised means of controlling the consistency and regulating the size of the sand by means of sieves, evolving a rational method of construction, which has been followed for twenty years, making the industry, when carried out on such lines, an extremely reliable one, and all work, if controlled by definite tests and analyses, of highly satisfactory character.

The chemist has also given his assistance in the preparation of fluxes or heavy oils of suitable character, and in the fixing of a standard for the grading of the sand and the nature and amount of filler or powdered stone, which enter into an asphalt pavement.

Aside from this, he has studied the nature of the native bitumens which are the components of asphalt and has differentiated the various types which are found in nature. In fixing the characteristics of the asphalts and the various petroleums from which fluxes and residual pitches are obtained, he has made it possible to describe these materials with such accuracy in specifications that they are readily differentiated.

He has made a study of the behavior of asphalt surfaces under service tests, and has been enabled to draw valuable conclusions therefrom which are applicable to the improvement and development of the industry. He has studied the physical characteristics of the sand used and of the phenomena connected with its behavior in combination with fine powders. He has demonstrated the fact that the presence of large amounts of this fine powder and filler through the presentation of a very large surface for the adhesion of the bitumen, adds in an enormous degree to the success of an asphalt surface under heavy traffic, in which study the principles of physical chemistry are closely involved. Work along these lines is still being undertaken in the laboratory, and it would seem that equally interesting points are to be developed in the future as in the past, along the lines of chemistry and physics.

Results obtained in these directions have been on such a large scale that the data accumulated have been assembled in a book of more than 600 pages by an expert of the company with which the writer is connected.

Land Title Building, Philadelphia

## CONTRIBUTIONS OF THE CHEMIST TO THE COTTONSEED OIL INDUSTRY

By David Wesson

Manager of the Technical Department, Southern Cotton Oil Company

In 1834, an English traveler in this country, writing about cotton culture, said: "In many places it is usual to manure the fields with the seed not used for sowing; but of late years experience has taught the planters to set a higher value on it as it contains a considerable quantity of oil which is extracted by pressure and is suitable both for burning and painting. This oil may, in the course of years, become an additional source of wealth to the planters."

About twenty years afterwards—shortly prior to our Civil War—one or two mills were started in New Orleans. The industry, interrupted by the war, acquired a start shortly afterward, and in 1872 as much as 52,705 tons of seed were crushed. This amounted to 4 per cent of the entire crop of 1,317,637 tons. In 1913, with a production of 6,305,000 tons, 4,767,800 tons were crushed, or 75.6 per cent of the entire crop. The estimated average cost per ton was $25.35, and the total value of the seed alone was $120,840,000, while the value of the products was $156,600,000. Needless to say that the oil was used for something besides burning and paint.

The first refineries in this country were the Aldige, Union and

Maginnis in New Orleans, Union in Providence, and J. V. Lewis in Cincinnati. Most of the early product was used for adulterating olive oil, except when it was labeled and sold as that material.

In 1887, the writer had the privilege of visiting these refineries, which were probably operating then very much as they had been doing for years. The crude oil was refined with caustic soda, and the strength of lye was largely a matter of taste on the part of the refiner. The quantity used was left entirely to his discretion. The crude oil was judged by taste, color and smell, and caustic added till the required color was obtained on a filtered sample. There were as many styles of kettles and agitators as there were refineries. Most of the refiners were practical men, and they were chock-full of theories. One of these practical refiners mixed his lye in round-bottomed sugar cauldrons, and another judged the strength by rubbing a few drops between his thumb and fingers.

The crude oil mills were run very much like the refineries. The export trade liked soft, yellow cake, so some of the mills, trying to make what was wanted, would leave from 12 to 16 per cent of oil in the cake and meal. They also allowed large quantities of meats to go into the hulls, and annually sacrificed large amounts of perfectly good meal and oil in the form of settlings, which were allowed to ferment and were originally put in the soap kettles.

It was about this time that chemistry began to take the industry in hand. Crude oil, up to now, had been bought and sold as prime, or prime for the season, or off, and was passed upon by manufacturers and brokers, who looked at it, tasted it, then looked wise and gave their verdict. Then the chemist stepped in and found that the quality of the oil closely followed the free acid present, and started grading accordingly. This made a big stir. Some of the mill owners denied the possibility of free fatty acid being present in any of their oil, as they never had any fatty acids on their premises. The chemists then showed these same mill men how much oil they were losing in their cake and throwing away in their hulls, with the result that more oil was made per ton of seed.

The hulls were burned under the boilers and furnished the power for the mills. Every ton of seed furnished about 700 lbs. of hulls. The ashes, averaging about 10 lbs. per ton of seed were a valuable by-product, being rich in potash and phosphoric acid. The writer is in doubt whether it was a chemist or a cow that discovered that hulls were good for cattle food. At any rate, cows ate them with avidity, and analyses proved that they had the feeding value of low-grade hay. So the mills now get from $4 to $10 a ton for hulls which are worth about $1 to $2 per ton as fuel.

The cotton-seed soap stock in the early days was almost thrown away. Much was made into woolen and scouring soaps. About 1877, a bright near-chemist mixed some of this soap with soda ash, and made it into washing powder. The advertising man made a virtue of its yellow color, and the "twins did the work." Now, the soap stock is used largely as a source for white distilled fatty acids and glycerine, while the residual tar from the stills forms a base for paint and roofing materials.

The chemist's greatest service to the industry has been in the refining of the oil. Beginning with tests for acidity, followed up by laboratory refining tests to determine loss and color, and finally bringing into use the tintometer for measuring the color against standard glasses, the commercial practice has been put on a higher and more substantial basis.

The careful and scientific application of bleaching materials and selection of the oil has done much towards the development of the lard compound industry. The greatest factor in the advance of the industry as a whole has been the development of methods for deodorization and improvement of the flavor of the oil. The flavor of an alkali refined oil is largely dependent on the seed from which it is made. For this reason it was practically impossible to obtain a uniform oil. Bleaching with fullers' earth helped but little. Even the best oils made from selected crude and careful handling were open to objection. Certain volatile principles made a disagreeable odor when the oil was used for cooking, and created natural prejudices. Now all flavors are absolutely removed, and the resultant product is as pure as granulated sugar, regardless of the kind of crude oil from which it has been made.

The latest contribution has been the hydrogenization of the oil which converts it into a solid fat by the introduction of hydrogen into the molecules of the unsaturated acids. This enables the manufacturer of cooking fats to turn out compounds consisting entirely of vegetable fat, which are fast displacing the mixtures of oil with animal fats formerly employed.

The improvements given by the chemist to the cotton-seed industry may be summarized as follows:

I—Putting the refining of crude oil on a more rational basis.

II—Preventing loss in manufacture by making a physical audit by analytical methods of the work of mills and refineries.

III—By analyses of products their values have been shown, and the commercial practice has been placed on an accurate foundation.

IV—By improving refining methods, practically all cotton-seed oil, regardless of section, or season, has been converted into one of our most valuable food products, and the residue worked into valuable by-products.

V—By the new process of hydrogenation wholesome edible fats of the consistency of butter and lard are now produced entirely from what will probably continue to be our cheapest vegetable oil.

VI—While the chemist has worked to improve the manufacturing side of the industry, he has been the means of putting something like $125,000,000 every year in the hands of the farmers; or, in other words, he has added ten to twelve dollars to the value of the crop for every bale of cotton grown and has made possible an industry which provides means of livelihood for the thousands of people in hundreds of factories and on the road making and selling the products.

24 Broad Street, New York

## CONTRIBUTIONS OF THE CHEMIST TO THE CEMENT INDUSTRY

By G. S. Brown
President Alpha Portland Cement Company

Portland cement was manufactured in the United States in a small way 40 years ago. It occupied, however, a very minor position among the industries of this nation until the beginning of the present century. At this time the production of Portland cement is not far from 125,000,000 barrels, or 20,000,000 tons, per annum, and is, perhaps, next to the manufacture of iron and steel, the manufacturing industry which gives to the railroads their largest tonnage.

It is safe to say that the tremendous advance made in this industry has been, for the most part, due to the zeal and knowledge of the chemist.

Portland cement has been manufactured in Europe for very many years and in the latter part of the 19th century was imported into the United States in large quantities. The small amount of Portland cement manufactured in the United States at that time was of irregular composition and of, perhaps, doubtful quality; on this account there was instilled into the minds of the users of cement a strong prejudice against Portland cement of American manufacture.

Prior to 1890, investigations made by some of those interested in the manufacture of cement in the United States, convinced them that with proper care it would be possible to make from the materials available in the United States just as sound

a Portland cement as was made in Europe. These men turned the matter over to chemists, who were given entire charge of the manufacturing process. It was very soon demonstrated that American Portland cement manufactured in this manner was absolutely as good as the foreign cements which hitherto had enjoyed a much better reputation. There was still considerable prejudice in the minds of the users of the cement and in the minds of engineers and architects; they argued that, while the short-time tests were satisfactory, there was nothing to indicate that the cement would give normal tests for longer periods of time. Further work by chemists proved, to the satisfaction of all reasonable men, that the constituents of American Portland cement and Imported Portland cement were not very different and that there was every reason to believe that the long-time tests would be just as satisfactory as the short-time tests were. This conclusion was amply demonstrated.

Having proven that it was possible to manufacture cement really of a better quality than that hitherto imported, the next step before the manufacturers was to reduce the cost, so that Portland cement could be sold to consumers at a price which would warrant them in extending its use and substituting it for other forms of construction. In the original factories the clinker was burned with oil. The kilns were short and the process was very wasteful of fuel. Along towards the end of the 19th century the price of fuel oil began to go up and reached such a point that the life of the cement industry in the United States was seriously threatened. Again recourse was had to the chemist, and after many experiments the system of powdering coal and burning it in kilns was perfected. This powdered coal took the place of fuel oil and resulted in a very marked reduction in the cost of manufacturing cement. Further than this, experiments were also conducted along lines indicated by theory and longer kilns were built, this again effecting a reduction in the cost of cement.

Many other reductions in the cost of the manufacture of cement were made by reason of the investigations of the chemist, probably the most important being that of handling the raw material in large quantities direct from the quarry. This method took the place of the old scheme, whereby the stone of different compositions was gathered in separate bins and then distributed in proper quantities throughout the mill. The present practice is to mix the raw stone in the quarry, thus greatly reducing the cost of handling. So much for the manufacturing itself.

In the realm of the use of Portland cement the chemist has also done much. He has been particularly active in educating those who use cement to the necessity of seeing that the aggregates used with the cement are of proper quality. He has also given a great deal of time to the development of specifications which will protect the user of cement. Originally, each engineer had his own specifications and many of them were most peculiarly and wonderfully drawn. The energetic efforts of the chemist practically eliminated all of these freaks and we have today, through his efforts, standard specifications which insure to any user of cement an absolutely sound article.

Time would fail me to go into the detail of all the problems which have come up in our business and which have been successfully solved through the efforts of the chemist. Careless manipulation in mixing concrete often resulted in walls that were not water-proof. While it is easily possible, with careful attention to the aggregates and mixing, to get an absolutely water-proof concrete wall without the use of any so-called water-proofing, the fact remains that in the hands of the ordinary user of cement proper care may not be taken. The chemist, therefore, developed a water-proofing material which, when added to the concrete, prevents water from seeping through.

Problems in connection with the storing of clinker, sorting of cement, the operation of our power plants, quarry conditions, etc., all have been referred to the chemist and by him put in process of solution.

The fact that the chemist is responsible for the quality of the cement to such an extent that he controls the operation of the mill, is largely advertised by at least one of the larger cement manufacturing companies in the United States.

EASTON, PA.

## CONTRIBUTIONS OF THE CHEMIST TO THE SUGAR INDUSTRY

By W. D. HORNE
Consulting Chemist

Chemistry as a science has contributed so much toward the development of the sugar industry from the beginning that the association has been a continuous one and cannot be looked upon as having been abruptly formed at any particular time, but rather as having been the principal factor in the development of sugar manufacture.

Thus the influence this science has exerted upon the industry during the past quarter century should be viewed in relation to what has preceded and what will follow. Much of what chemistry is doing now is the development of earlier work and will continue to exert its influence upon the future. Every department of the industry has long been under searching chemical investigation in almost every detail. Agriculture, manufacture, refining and utilization in the arts have called for chemical assistance and have received noteworthy aid. Very many new processes have been developed, better methods of analysis have been devised and theoretical knowledge of the constitution of the sugars has been substantially advanced. A vast literature is maintained on the subject of sugar, the main division of which is chemical. The International Commission for Uniform Methods of Sugar Analysis, composed of leading sugar chemists from the principal sugar-producing countries of the world, has done a great deal of good work in revising analytical methods, prescribing standards for apparatus, calculating working tables and generally supervising the field of sugar analysis.

Emil Fischer introduced the use of phenylhydrazine as a reagent in studying the theoretical molecular constitution of the sugars. This reagent's property of reacting with the aldehyde or ketone group of a sugar molecule and the adjacent alcohol group has rendered the highest service in studying the constitution of the sugars, as pursued for many years by Fischer, Herzfeld, Mulliken, and many others.

The development of sugar in the cane has been carefully studied by Prinsen Geerligs in Java and the occurrence of the nitrogenous constituents in the beet by Saillard in France, not to mention an almost endless series of similar investigations by other chemists in every branch of plant physiology and development. The influence of soil composition and the effect of fertilizer ingredients has also received detailed study, including the remarkable effect on plant development caused by the action of minute quantities of manganese in the soil upon the enzymes in the growing plants. A great deal of work has been done on the development of new varieties of cane through raising seedling plants and selecting, largely through chemical analysis, the best individuals for further propagation. Thus the famous D 74 has been developed in Demerara and equally good varieties in Java and other countries. In Java, a few years ago, the sugar industry was threatened with destruction through the prevalence of insect pests and other troubles which beset the cane with accumulating force. The development of new varieties through chemical and biological work alone reclaimed the industry and placed it upon a very profitable basis.

In the manufacture of raw sugar, the past quarter century has seen great advance through bringing factories under chemical control, and the cane industry has caught up with and surpassed the beet industry through its scientific development on these lines. The consumption of sugar in the United States

has risen from 1,500,000 tons in 1890 to 3,750,000 tons in 1914 and the per capita consumption from 54 pounds to 84 pounds per annum. This has been partly due to the cheapening of sugar through scientific management in its production, raw sugar having fallen from 2.88 cents per pound (without duty) in 1890 to 2.03 per pound in 1914, and this, too, in spite of a rise in price of all other food staples, averaging considerably over 15 per cent.

In making raw sugar the proper defecation and clarification of the juice are chemical matters of first importance and during twenty-five years great improvements have been made in the double carbonation process both for beet and cane, the use of sulfitation of the thin carbonated juice, and the use of phosphoric acid and its salts as additional defecating materials. Kieselguhr has been introduced by Wiechmann as a clarifying agent and is now being used more and more extensively, especially since the development of the great Lompok deposit in California. Raw sugar factories are now producing white sugar directly from cane as well as from beet, due to chemical investigations of the matter and chemical control.

Raw sugar factories are now generally able to sell their molasses instead of throwing it away, because of chemically developed methods of converting it economically into alcohol, cattle foods when mixed properly with bagasse, peat moss, etc., and into other useful products. The sugar is all recovered from beet molasses by the Steffens process of conversion into tricalcium saccharate, and the by-products from this are going into fertilizers, cyanides, etc. Wax is recovered from scums and the residues utilized as fertilizers in the cane fields. Paper is made from the unused fiber of the cane and another by-product has been improved by the chemical investigations of the manufacture of rum.

In sugar refining, due to chemical research, invention and control, progress has been made all along the line. Better methods of enclosing samples of raw sugar have led to better agreement in tests through preventing changes in moisture. The establishment of the Sugar Trade Laboratory in New York, under Dr. C. A. Browne, has placed the polarization of sugar samples for seller and buyer upon a satisfactory scientific basis, free from bias.

Well-equipped laboratories are maintained by all factories and refineries where routine testing and analytical work are carried on constantly and where investigations are made. The Bates polariscope with adjustable sensitiveness is a recently developed aid of great value to all this work. Anhydrous subacetate of lead, introduced by Horne, has simplified the polarization of impure solutions and greatly reduced the time and labor of making tests. New analytical methods are constantly being developed along with more convenient apparatus. The refineries have given up the use of blood as a defecating agent in favor of acid phosphates, and the tendency is towards the use of flocculating agents which will produce no objectionable side products. Certain solutions containing invert sugar are cleared of this constituent in the Batelle process of heating with sufficient lime to destroy the invert sugar without harming sucrose. The Weinrich dry-lime process undertakes, by treating concentrated impure sugar solutions with pulverized lime at low temperatures, to effect a nice differentiation between organic non-sugars and invert sugar, whereby the former are largely removed along with some salts and most of the color, without affecting the valuable invert sugar. Progress has been made in electric defecation, but objectionable features of expense still await surmounting. Liquid sulfurous acid has to some extent beneficially replaced the gas, while the hydrosulfites of soda and of lime are used by many in massecuites and in syrups for improving color and yield. The practice of boiling back the syrups from previous massecuites has greatly developed, due to the increasing facility in testing all products in the laboratory and the increased precision of work possible because of this more intimate knowledge of the purity of every part of material in operation. Crystallization in motion has been developed to a fine point with great increase in yields. A more thorough exhaustion of the sugar from molasses has been arrived at, partly through the light thrown on this subject by chemical investigations such as that made by Prinsen Geerligs on the subject. Potash salts are more thoroughly removable through the permutit process which employs alkaline silicates similar to the natural zeolites for the purpose. Water supplies can be purified by the same process. New dyes have been developed to take the place of ultramarine, sometimes used to give a certain tone of white to some refined products.

The treatment of bone-black has been improved by the gentle oxidation obtained in the Weinrich decarbonizer. The increasing price of bone-black has led to the invention of various carbonaceous substitutes, among which can be mentioned Norit or Eponite favorably reported upon by the late Dr. Strohmer, and which its manufacturers claim to be capable of yielding white sugar direct from cane juices. Patterson has contributed materially to our knowledge of the composition of bone-black, but much remains to be learned concerning this material.

The last 25 years have witnessed the giving up of the attempt to commercialize sorghum sugar and the enormous development of the beet sugar industry within the United States, in both of which credit falls to Dr. Wiley, aided by many other well-known chemists.

What chemistry will do for the sugar industry in the future is a question of deep interest, and the answer will probably be found in simplified processes of defecation, cheapened materials for color removal, etc., more energetic chemical treatment of low-grade intermediate products and a better utilization of such by-products as are inevitable. The service of chemistry in the past leaves no misgivings for the years that are to come.

175 Park Avenue, Yonkers, N. Y.

## CONTRIBUTIONS OF THE CHEMIST TO THE INCANDESCENT GAS MANTLE INDUSTRY

By Sidney Mason
President of the Welsbach Company

No article more strikingly emphasizes the importance of the science of chemistry than does the incandescent gas mantle, which owes both its inception and development, up to the towering output in the United States alone of upwards of 80,000,000 mantles annually, to the untiring effort of chemical research.

This industry, founded on the remarkable discovery and invention of Baron Carl Auer von Welsbach almost thirty years ago, has progressed along a trail blazed by the Chemical Engineer, Baron Auer, a chemist and scientist of world-wide reputation, who having as a lad been engaged in a scientific study of the rare earths, observed the phenomena that suggested to him a new system of gas illumination.

Previous researches of the rare earths by earlier chemists stimulated his desire to work in this field, which he undertook at the beginning for the purpose of contributing to the knowledge of this branch of chemistry, but which culminated in his demonstrating that a vegetable or organic fiber could be perfectly reproduced in mineral form by certain rare earth oxides sufficiently coherent and attenuated to become brilliantly incandescent in a non-luminous gas flame.

By patient and persistent chemical research for a period of years, the Welsbach gas mantle eventually reached a state of perfection which crowned the work of the inventor with commercial success. The spectacular discovery that a mantle made of thoria with a small admixture of ceria would increase the light-giving efficiency of previous mantle compositions more than three-fold, provided the impetus necessary for this purpose.

The thoroughness of the work and the investigations of Baron Auer are indicated by the fact that although the last quarter of a century has brought much enlightenment into the field of rare-earth chemistry, there is, however, today no satisfactory substitute for his basic invention.

Originally the rare earths had never heretofore been produced in great purity or in large quantities, and the science of chemistry and the research of the chemist was called upon to remove many obstacles in this direction before the industry was successfully launched. Many complex problems were undertaken and solved before an efficient manufacturing process, which is, of course, absolutely essential to the economic development of the incandescent gas-light industry, was attained.

It was early found that much depended upon the satisfactory and uniform character of the organic or vegetable fiber which was to be reproduced in mineral form in the incandescent mantle. The deleterious influence of impurities entering the light-giving body through this channel was soon demonstrated, and bleaching and cleaning processes had to be refined and perfected until a product of the required degree of purity was produced. It was soon discovered that the length of fiber or staple of the mantle fabric had much to do with the strength and durability of the finished product. Long staple or Sea Island cotton was in demand for this purpose, but the longer fibered ramie or China-grass was later made use of after it had been finally degummed, bleached and washed, a problem successfully accomplished by chemical research. These developments made possible the inverted or pendant type of incandescent gas burner.

The mantle manufacturer has held before himself for many years certain ideals towards which he has earnestly striven. Among these may be mentioned: strength with elasticity, high and maintained candle power, preservation of color and absence of shrinkage. A realization of these ideals seems finally to have been met in the mantles made from the bundle of homogeneous elastic, spring-like fibers known as artificial silk. Chemical science was engaged for a generation in the solution of this intricate problem, but even after a satisfactory quality of artificial silk had been produced, long years of patient research were needed before the incandescent mantle chemist was able to utilize this material in the preparation of an ideal mantle, and the final successful solution of this problem ranks high among the chemical accomplishments of this industry.

The protective coating, which carries the finished mantle from the factory to the consumer, has always been an item of great importance. At first incandescent mantles were coated by dipping in an alcoholic solution of shellac, which was made slightly flexible upon drying by the addition of a gum, or non-drying oil. The development of the nitrocellulose industry, and the invention of soluble cotton opened up a new field for the mantle maker, and the knowledge gained of the many varieties of nitrocellulose and their numerous solvents, together with the ability to control such characteristics as viscosity and hygroscopic effects, has now made it possible to prepare collodion solutions of almost ideal qualities and adapted to the ever-increasing variety of incandescent mantles.

All of these have been chemical and physical problems demanding research work of the highest order, and to the science represented by the chemist must be credited the present state of efficiency and economy of the incandescent gas light which bears the inventor's name "Welsbach."

GLOUCESTER, NEW JERSEY

## CONTRIBUTIONS OF THE CHEMIST TO THE TEXTILE INDUSTRY

By FRANKLIN W. HOBBS

President Arlington Mills and Past President American Cotton Manufacturers' Association

Chemistry has made many and varied contributions to the textile industries and in the brief space of this article it will be possible to mention, briefly, only a few of the most important.

Among the primitive races the use of colors undoubtedly preceded the use of textiles and it is probable that the earliest fabrics were colored with stains obtained from fruits and plants. We can imagine that by progressive steps it was found that some stains faded or washed out quicker than others and there was a gradual selection of those found best. Then came the discovery of the influence of heat and boiling, followed, perhaps accidentally, by the knowledge that certain salts precipitated some dyes and that cloths impregnated with these salts retained their colors longer. This discovery of mordants was perhaps the first real point of contact between chemistry and textiles. The date is unknown, but we do know that alum and iron salts were used by the ancient Egyptians.

Bleaching was also known to the oldest peoples. It was first known that cloths of linen or cotton became whiter when dried in the sun and sun bleaching became a common practice. Then came the development in the use of soaps and alkalis followed by the discovery of the bleaching property of chlorine. After this came the use of electrolytic chlorine, liquid chlorine and peroxide of hydrogen. The use of chlorine, of course, is not adapted to wool, but in early times the use of sulfur in bleaching wool was known and peroxide of hydrogen also is now used on that fiber.

Improvements in methods of dyeing have gone hand in hand with chemical progress. The introduction of mordants already mentioned widened the range of available colors. Insoluble colored salts such as tannate or iron, chrome yellow and Prussian blue were made use of and the active principles of some of the natural dyes were separated and purified. The reducing action which takes place during fermentation was utilized at a very early date in the dyeing of indigo, and the fermentation vat is still in use.

The greatest advance in the chemistry of dyeing came in the production of Mauve by Perkin in 1856, which was followed by the marvelous development of the coal-tar dyestuff industry. This discovery is said to have led to the investment of $750,000,000 in the coal-tar industry and has revolutionized the production of dyestuffs. Many of these colors are fugitive, but faster colors have been gradually produced and there are now fully one thousand brands on the market from which to choose. Of course many wool colors are not adapted to cotton and *vice versa*. There is an unquestioned superiority in many of the artificial colors over most of the so-called natural dyes.

The effect of synthetic alizarine upon the raising of madder was profound, for, as a result, a whole industry was destroyed. None the less startling was the discovery of synthetic indigo which was achieved after long endeavor and great expenditure of money and affected indigo-growing countries like India very greatly. As is often the case with great discoveries, loss comes to some in the readjustment, but in the end the world, as a whole, gains.

To chemistry and the research of chemists all over the world are due these great advancements in the knowledge and preparation of dyestuffs, and, as a result, a new industry unknown through all the ages has now been developed. In this connection, showing what chemistry has done, it is interesting in passing to note that the "Purple of Tyre," the dye used on royal robes in ancient times and which was obtained a drop at a time by killing small shell fish, has been analyzed and reproduced as a brominated indigo compound. The romance of the ancients has become a chemical formula of the moderns!

One of the greatest discoveries in its effect on the cotton industry was that made in 1850 by John Mercer of the process now known as "Mercerization." By a strange chance, however, he simply found that the treatment made cotton yarns and fabrics stronger and gave a greater affinity for dyes, but he did not notice

that the process when properly carried out under tension produced luster. For more than forty years this process was little used and little appreciated. It was not until about 1895 that the great increase in luster due to mercerizing under tension was appreciated and its commercial advantages realized. Since then the art has gone forward by leaps and bounds, and today the production of mercerized cotton yarns and cloths is enormous, and has had far-reaching effects on cotton textiles. In many ways it marks the greatest advance in recent years in that branch of the textile industries.

Artificial silk is another great contribution chemistry has made to textiles. This was invented by Count de Chardonnet and was first exhibited in Paris in 1889. Development was slow and at first, from a financial point, disastrous, but now the annual production of artificial silk is fully 20,000,000 pounds. There are various processes—collodion, gelatine and viscose. The viscose process now seems to command the field and is developing rapidly in quantity and quality produced. Here is a case where common wood pulp worth a few cents a pound, by a touch of the chemist's art, is changed to a beautiful silky-appearing yarn worth from $2.00 to $3.00 a pound. An entirely new field has been opened up and its development has just begun.

Weaves, fabrics and patterns are numberless, but have reached a point where there is little that is really new or unknown. The greatest advances in textiles in the future must be along chemical lines. Coal-tar dyes, mercerizing, artificial silk—these and many others are already accomplished facts. The next steps rest in your hands and it is to the chemists we must look for the future developments.

78 Chauncy Street, Boston

## CONTRIBUTIONS OF THE CHEMIST TO THE FERTILIZER INDUSTRY

By H. Walker Wallace

Manager General Sales Department, Virginia-Carolina Chemical Company

In considering what the chemist has done for the fertilizer industry we are dealing with a subject intimately connected with the culture of the soil, and while valuable services have been rendered in other directions it must be admitted that the most valuable achievements have been those which have had a direct bearing on agriculture, that noble calling which is the foundation of all industry and the very backbone of the nation itself. Any contribution, therefore, which has advanced the condition of agriculture has indirectly benefited all avenues of trade.

The science of chemistry has played a most important part in building up various industries which are dependent on the products of the soil, but perhaps no service has been of so much value to agriculture as that which has caused the development of the fertilizer industries of the world. The tremendous storehouses of plant food accumulated through the ages have been made useful by the chemist, who has found means of converting them into mixtures which make it possible to produce the larger crops made necessary by the ever-increasing population. Thus the tremendous accumulations of natural phosphates in this country and elsewhere, the large deposits of potash salts in Germany and the nitrate beds of South America have all been converted into useful products. The very air we breathe has been utilized in producing nitrogen compounds in suitable form for plant nutrition. In addition to the various supplies of raw materials furnished in nature, large quantities of refuse substances from the various industries have been collected, treated chemically and utilized in the manufacture of fertilizers.

Seventy-five years ago the fertilizer industry was unknown. Liebig was the first to study the chemical composition of the ashes of plants and to point out the necessity of supplying plants with mineral food; he conceived the idea of dissolving bones with sulfuric acid and thus rendering the phosphoric acid soluble, in which condition it could be more readily utilized by growing plants. This, then, was the real beginning of the manufacture of superphosphate fertilizers.

The treatment of mineral phosphates with sulfuric acid, however, originated with Laws, who took out a patent for the process in 1842 and established a factory, from which time the commercial production really dates.

During the first years development was slow, but in the past thirty years there has been a steady growth until at the present time the manufacture of fertilizers has reached enormous proportions in the eastern part of our country. In the year 1900 there were produced in the United States alone 2,200,000 tons and in 1913 the production had increased to 6,800,969 tons.

In the building up of this large industry what then has been the rôle of the chemist? In a brief statement it is impossible to tell all that the chemist has done, but a few of the important features may be summed up as follows:

1—He discovered the necessity of the industry by studying the composition of soils and plants.

2—It was the chemist who first suggested the production of superphosphate and established its manufacture.

3—The process of manufacture has been gradually improved so that the insoluble phosphoric acid has been reduced from two or three per cent to a fraction of one per cent.

4—He was responsible for the manufacture of sulfuric acid, which is necessary for the production of superphosphate.

5—He has produced a double superphosphate containing from 45 to 50 per cent available phosphoric acid.

6—His researches have made it possible to convert many waste products into valuable plant food constituents, which are utilized in fertilizers.

7—The nitrogen of the air has been combined and converted into forms suitable for plant nutrition.

8—The chemist has worked out processes for saving the nitrogen in flue gases and coke ovens and converting it into sulfate of ammonia.

9—He has worked out formulas and blended the various fertilizer constituents into the compounds best suited for different soils and crops.

Not only has the chemist been of great assistance in working out the initial problems of plant nutrition and the production of suitable fertilizers, but his services are indispensable in the regulations of the operations of the factory. In these days of close competition and rigid government inspection, profits may be easily turned into losses or goods confiscated by the state inspectors because of unsatisfactory analyses. The manufacturer must, therefore, have able and competent chemists to do his work or serious consequences will result.

In fact, the whole manufacture of fertilizers is intimately associated with chemistry and largely dependent on it for its existence. Notwithstanding the large measure of success obtained in the past, there are still new problems to be worked out and the chemist will not have done his part until the science of fertilization is thoroughly understood and he has made "two blades of grass grow where but one grew before."

Richmond, Virginia

## CONTRIBUTIONS OF THE CHEMIST TO THE SODA INDUSTRY

By F. R. Hazard

President The Solvay Process Company

The rôle of the chemist in industrial operations is to answer the question "Why?" Why did the ancient Egyptians use straw in making brick? Until very recently the true answer to this question remained unknown, but with the true spirit of

investigation of the trained scientist, Mr. Acheson has quite recently determined that the action of vegetable acids upon the clay creates a change, probably both physical and chemical, which adds enormously to its tensile strength. Thus one of the secrets of possibly the most ancient of all industries has been finally brought to light and the production of Egyptianized clay has been made possible with as yet unknown benefits.

This instance is but typical of the questions which arise in constantly increasing numbers in the complex industrial operations of our time. The chemist is the enemy of the rule-of-thumb methods. He is not content to accept the superstitions and prejudices which have been handed down in all industry, but seeks to ascertain the causes underlying the effects which, in some cases at least, are produced with a considerable degree of regularity by these rule-of-thumb practices. He is willing, in a truly scientific spirit, to take the known effects and to carefully examine them, seeking constantly the answer to the eternal question "Why?"

It is only within the past twenty-five or thirty years that the chemist has been admitted as an important member to the manufacturing staff in our modern industrial life. It is well within the memory of many of us that the master teaser in a glass factory had many strange and useless additions to the batch, and sometimes even murmured incantations while mixing it, or chose the dark of the moon, or had a rabbit's foot in his pocket, thinking that by these precautions he would obtain good results. At that time too often the managers and owners of the business knew very little about the practical operation. They relied absolutely upon the secret formula brought to their plant by the master teaser, and, in fact, a capable man in this position not infrequently made capital out of his formula and so obtained for himself a more important position at some other plant. In many other industries similar conditions existed; in other words, the manufacture of most of our products was then carried on by the rule-of-thumb method, and the question "Why?" remained unanswered.

Under these circumstances it is easy to see that the advent of the chemist was attended with great difficulties. He was regarded as their natural enemy by superintendents, and was looked upon with distrust by workmen. His experiments were ridiculed and not infrequently were purposely interfered with, so that their results would be without value. Thus, early in his introduction into the industrial field, it became absolutely necessary for the chemist to tell the workmen, the superintendent, the manager or owner, that none of them really knew their business, which unfortunately was the fact, but it is easy to see that it required the greatest amount of tact and diplomacy to make such a statement without giving so violent offense as to make his own position untenable and thereby practically destroy his usefulness in that particular work. It does, in fact, require unusual gifts outside of the scientific field to enter a manufacturing establishment and tell those who are conducting its operations that they do not know their own business, yet this is substantially the fact, even today, in many lines of work. The chemist must, therefore, exercise the patience of Job, he must have the wisdom of the serpent and the gentleness of the dove; he must be persevering and constantly alert to see the first signs which will lead him toward the answer to his question.

What has been accomplished by the chemist in industry during the last few years would require too great a space to catalogue. There is not a single field of industrial enterprise in which he has not made a notable mark. The synthetic production of indigo, followed by all the other developments in the color industry, is only one of the great achievements of the age. Metallurgical chemistry has absolutely revolutionized the manufacture of iron and steel. The cyanide process has made available ores of the precious metals which could not otherwise be economically worked. The chemistry of the animal fats and acids has made possible the production of enormous quantities of glycerine in connection with the manufacture of soap. The so-called chemical industry, including the production of alkalies of all kinds, acids, bleaching powder and the allied products and by-products, has built up an enormous industry which, in fact, lies at the basis of practically all other industries.

The field of the industrial chemist, though already broad and comprehensive, is constantly growing in all directions, just as the ripple on the surface of a pool created by throwing in a stone rapidly spreads over the entire surface. The opportunities before him are by no means exhausted. Every one of the interrelated industries of our modern life has its chemical problems. In each one of them the investigating mind finds many questions, correct answers to which will add much to the profitable operation of each one.

As an illustration of the delicate position of the chemist toward the manufacturer, the following is taken from our own experience: About twenty-five years ago a soap-maker complained that 58 per cent alkali purchased from us was not as good for his purposes as 48 per cent alkali imported from England. After considerable correspondence it developed that his method of ascertaining this peculiar fact was to take, say, 100 lbs. of each quality of alkali, dissolve each by itself in about a barrel of water and then determine the specific gravity of the solution by means of a Twaddle hydrometer. The 48 per cent alkali gave a somewhat greater specific gravity, and he thereupon concluded that it was a superior article. As he was one of our important customers and a somewhat difficult man to deal with, it became necessary to convince him by his own methods that his conclusions were not correct. We prepared samples of several different kinds of alkali, also of common salt and of sulfate of soda, and, using the same hydrometer, we determined the density of each, whereupon it was found that on his theory it was an absolute waste of money for him to purchase alkali of any kind as ordinary commercial sulfate of soda showed a considerably greater specific gravity than any of the other solutions. When confronted with this actual test, made on the same scale and using the same instrument as he had been accustomed to employ, our customer acknowledged himself convinced, and continued for many years thereafter to make his soap by the use of our 58 per cent alkali.

Only last year, to show that the knowledge which a chemist can contribute is still of value, a complaint was made by a glass-maker that the 58 per cent alkali furnished to one of his works was inferior to that furnished at another. Correspondence developed the fact that the workmen at one plant were also employed in handling lime and that the ventilation of the plant was not very good, while the conditions at the other plant were much better. The chief complaint was that the men in the one plant suffered seriously from sores; in fact, some of them were quite disabled. A personal investigation by one of our representatives showed that the unfortunate men were employed first in handling lime and then in unloading alkali, which was in bulk. The weather being quite warm and the exertion by no means easy, these men were establishing upon their own persons miniature caustic soda plants, and the resulting soreness and tenderness of the skin, if neglected, as was too often the case, led to rather serious conditions which required a long time to heal. An elementary knowledge of chemistry would have been sufficient to ascertain the cause of the difficulty.

Although much has been accomplished during the past fifty years, although the chemist has now found his proper place in practically all industrial operations, there still remains an enormous amount of ignorance to be overcome, a fund of ancient superstition to be vanquished, and a field of almost unlimited possibilities to be explored, in which the chemist of the future will find answers without number to the question "Why?"

SYRACUSE, N. Y.

## CONTRIBUTIONS OF THE CHEMIST TO THE LEATHER INDUSTRY

By William H. Teas
President Marion Extract Company

Although one of the most ancient of industries, and involving as it does chemical reactions, the leather industry has, in only comparatively recent years, received the attention of chemists. The record of the accomplishments of the chemist in this industry during the past twenty-five years will comprise most of the advance along chemical lines that has taken place in the industry. The advent of the chemist in the leather industry was induced by desire to effect economies in raw materials; research, and improvement in methods became a secondary effect of the chemist's presence in the tannery, but success in the primary effort for economy was responsible for secondary effects, and for the now very general custom of laboratory control of the tannery.

The leather industry is divided into general divisions of vegetable and mineral tannages, and each of these has been subdivided into many specialized industries developed by the product demanded, and the use of the raw material suited to the product. In general, the tanning agents used, the oils, greases, finishes, etc., have in themselves been the chemists' fields, and in these and in the methods of application the chemists have found their work.

The chemist has indicated improvements in the soaking and preliminary preparation of the raw skins, so that a saving of the costly hide substance has resulted; his work in selecting the proper depilating materials, and in improving methods of their application has resulted in economy and in improved products. Practically all of the progress in deliming hides by the use of special preparations has been accomplished by the chemist; and to him is also due full credit for the results of investigations of the influence of the character of the water supply on the tanning operations. The utilization of by-products in this preliminary stage of tanning is another branch of effort in which the chemist has demonstrated his value.

In vegetable tanning, the chemist has improved the methods of leaching the raw tanning materials so that more of the tannic acid content has been made available; his laboratory work has shown the reasons for many of the rule-of-thumb methods of the practical tanner, and thereby afforded a means of anticipating and correcting conditions which would produce an unsatisfactory product. The standardization of tan-liquors, with the consequent tendency toward uniformity of product, could not have been accomplished without the work of the laboratory. The utilization of spent tan liquors formerly run to the sewer, by purifying and concentrating into a thick extract for mechanical tanning, is also a laboratory development; and the chemist is responsible for the progress so far made in the sewage disposal problems of the tanner.

The chemist has materially aided in the work of replacing the fast diminishing native barks, with combinations in proper proportions of foreign tanning materials, foreign and domestic extracts, so that physical characteristics and quality the leather produced under the new conditions is similar to the old product. The standardization of leather oils, greases and waxes, and the protection of the tanner against adulteration is a matter of course with any laboratory, but the standardization and protection was badly needed in the leather industry, and the accomplishment of the chemist in this line is fully credited. The development of special oils for leather work, especially sulfonated oils, and the application of the oils to remedy certain defects in leather, is due to the chemist; he is also responsible for special combinations of waxes and greases for stuffing leathers according to the requirements of the use to which the leather is put.

The development of the mineral tannages has been due almost entirely to the chemist; the chrome process was first suggested by a chemist and later its development to a commercial success was accomplished by a chemist. Ever since chrome tanning was started in a commercial way, the modifications of process and materials, tending to economy and improvement, have been due to chemists, so that one of the greatest accomplishments of the chemist in the leather industry, has been the process by which most of the light leathers of the world are tanned. The successful lubrication of the fiber of chrome-tanned leather has meant much to the utility and consequent popularity of chrome leather, and by means of saponifiable and so-called "soluble oils" the chemist has materially helped in this important factor.

Other mineral tannages, and tannages by formaldehyde and other aldehydes, have been worked out by chemists and brought to more or less commercial success as a result of laboratory work. Combinations of mineral and vegetable tannages for the production of leathers for certain purposes, are also the work of the chemist. Synthetic tannins, or at least products which give reactions analogous to the natural tannins, have been introduced by chemists, and their commercial value in some lines of the industry has already been demonstrated.

In the manufacture of tanning extracts from raw materials which grow in localities distant from the tannery locations, chemists have played an important part. Clarification processes introduced by them have, in some instances, increased the availability of some tanning materials, which, without clarification, would have a diminished economic value. Credit is also due the chemist for the production of special extracts, which have made possible the saving of time and labor in the production of certain kinds of leather.

In the production of patent and enameled leathers, of fancy leathers, and in the field of dyeing and coloring so important to light leathers, and in the numerous other departments of tanning, not mechanical, which space will not permit of particularizing, the chemist has been and is an important factor in product improvement.

The chemist in the leather industry has had to overcome the prejudice of the practical tanner against tanning theory, and without guiding precedents has been obliged to make his own standards, and develop his own ground work. Recognition of the value of the efforts of the chemists is evidenced in the vast increase in the number of tannery chemists during the past twenty-five years. And still further evidence is the establishment of a tanning school in which chemistry is the most featured branch in the curriculum; and also the definite plans for starting a national research laboratory to be supported by the industry, and to be devoted to research work in the chemistry of tanning.

Marion, Virginia

## CONTRIBUTIONS OF THE CHEMIST TO THE FLOUR INDUSTRY

By John A. Wesener and Geo. L. Teller
Consulting Chemists

Flour may be defined as the fine white meal of the interior of the wheat grain, either by itself or mixed with a small proportion of finely ground wheat bran or wheat germ. Its quality depends upon the kind of wheat from which it is made and upon its freedom from bran and germ, which for the most part in the ordinary process of milling find their way into coarse by-products ordinarily sold as feed for domestic animals.

There are several types of wheat recognized in this country, the most clearly defined groups of which are soft winter wheat, hard winter wheat, spring wheat, durum wheat. There are many gradations between the first two of these classes and sometimes it is difficult to distinguish one from the other: both also include distinctly different types of wheat. The leading types of hard winter wheat are found in Kansas and Nebraska: the leading soft winter wheat section is in the Ohio Valley and

northward with varying types scattered in different sections throughout the country. The flour from soft winter wheat grown on the Pacific Coast is for the most part different from that of soft wheat grown in the Ohio Valley. The chief home of the spring wheat is in Minnesota and the Dakotas, while the natural location for the durum wheat is in the semiarid regions of the northwest, east of the Rockies.

The wheat grain consists of three distinct parts: the outer seed covering or bran, the embryo plant, also called the germ, and the endosperm which contains the store of food to nourish the young plant. This latter, when crushed, produces white flour. Because of this make-up of the grain modern milling processes necessarily make several grades of flour from the same wheat. In milling, the wheat is first broken on rolls with grooves or teeth-like corrugations. These tear the bran apart and break it from the interior of the grain. If this separation could be made complete, the entire endosperm could be crushed into a pure flour of highest quality, and the remainder of the seed could be set aside for stock feed. As it is, some fine particles of bran always adhere to and go with the part that is wanted for flour. Purifying machines help to get rid of this and then the small fragments of flouring material are crushed between smooth or very finely fluted or scratched rolls. Some bran particles which still adhere are also crushed and torn into smaller fragments. The germ is rich in oil so that it holds well together and forms a little flake; this and the coarser bran separated from the middlings in the crushing are held on the top of a sieve made of silk or wire while the finer flour passes through. The crushing of the endosperm must be not so hard as to make it sufficiently fine at one operation for all of it to pass through the sieve or the bran and germ will be too finely powdered and will pass through with the flour. Such of the endosperm as does not pass through the sieve is again crushed by rolls. The processes of sieving and crushing are repeated as often as is necessary and a greater or less quantity of flour is produced at each step. A little flour is always made in the first breaking of the wheat. This is of the softer starchy part of the grain and is not of as high quality as that made from the so-called middlings, which are fragments of the endosperm too large to be called flour. The first middlings are very pure and require little more than crushing to make them into flour. The flour made from these is the highest quality of flour from the wheat: later crushings of the middlings contain more bran and contain a little more of the germ. These change the appearance of the flour and help to make it darker in color. The later crushings also include more of the harder part of the endosperm which is richer in gluten, in oil and in carrotin, which gives the characteristic yellow tint to fresh milled flour.

The several streams of flour which are produced in the mill by these successive crushing and bolting processes are combined according to their characteristics to form the various grades for the market. Flours from the same wheat have in general come to be divided into three grades which are designated patent, clear and low grade, the percentage of these grades differing with the varieties of wheat and milling ideas. Where all of these streams are combined in one grade, it is known as straight, or where all are combined, except a small percentage of the low grade, it is known as a long patent.

With any method of grouping there is a small amount of flour containing a large proportion of fine cuttings of bran and germ designated low grade that it is seldom advisable to combine with any of the other grades as the discoloring effect is out of proportion to its quantity.

There is no set rule for making these divisions and they are governed largely by local circumstances. Strictly speaking, it is very difficult to define just what a patent flour is, and many different qualities of so-called patent flour may be made from the same wheat, depending on how the several portions of flour are combined.

As among the several grades of flour from the same wheats, the patent—that which is whitest and freest from bran particles—will contain the least ash, the least gluten, slightly less fat and the most starch. None of the commercial grades of white flour contain any appreciable quantities of crude fiber or of other indigestible matter. The clear flour and the low grade contain more gluten or more protein, more phosphates and slightly more fat than do the patent or the straight grade from the same wheat. Since among American food products, protein is considered to be more costly than starch, clear and low grade flours should naturally be looked upon as having greater food value than patent flours. When taken by themselves, however, their products when baked are darker in color and bread from the clear and low grades have a stronger flavor which is not relished by all. The clear, when mixed with the patent to make a straight grade, does not show this objectionable flavor in the bread and the objectionable color is not so marked. In commercial bakeries the clear flours are mixed with rye flours in the making of rye bread. The gluten of the wheat flour is necessary to give volume to the rye loaf, for the proteins of the rye flour, while apparently of the same character and chemical composition as those of the wheat flours, do not, when made into a dough, produce the peculiar glutinous mass characteristic of the latter. Contrary to a general opinion, rye bread is not more nutritious than wheat bread for rye flours themselves contain much less protein than do wheat flours. Graham flour or unbolted wheat meal contains more protein, more fat and more mineral matter than the white flours produced from it, but it also contains much more matter which is indigestible.

White flour is pre-eminently the bread stuff of civilized man. With proper handling almost any sound wheat flour can be made into a palatable wholesome bread but there are wide differences in flour, and different flours require very different treatment. Flour is often pronounced poor for bread-making when it simply is not suited for the method used. For centuries bread has been made from wheat flours by fermenting the dough with some form of yeast. This fermentation has several purposes. As used at the present time, with white flour, it makes the bread more attractive, more palatable and more wholesome. This was, perhaps, the first step in the application of chemistry to bread-making, but even up to the present time, the full chemistry of it is not understood and it is less than a half century since the true cause of the fermentation was first pointed out. Fermentation, aside from producing gases to develop porosity of the dough and leaven the bread, plays an important part in softening the gluten so as to permit its proper expansion when put in the oven. It also assists in developing the proper flavor of the bread. The fermentation required to produce the best bread depends upon the flour and should be varied to suit the flour used. Soft wheat flours require little fermentation: hard wheat flours require more; and in all cases a clear flour from any wheat requires more fermentation than patent flour from the same wheat, partly because it contains more gluten and partly because the gluten present is more resistant to the mellowing influences of the fermentation. Soft wheat flours make excellent yeast bread when properly handled. They are not suitable for commercial bread makers because they make a smaller loaf of bread and less loaves to the barrel for the same amount of flour than do the hard winter or the spring wheat flours. Some of those who are familiar with the characteristics of soft winter wheat flours select the clear flour for yeast bread and get better results in all respects, except as to color, in so doing. They are especially adapted for the making of warm biscuit, of crackers and of pastry. This is partly because they contain less gluten and partly because they give products of better color. Hard winter and spring wheat flours are both well suited for yeast bread. They are also used with good results in the making of pastry and table biscuit by those who are familiar with them and therefore

make a sufficiently soft dough and use other ingredients in the proper proportions. Durum wheat flours are exceptionally useful for the making of macaroni, largely because of the deep yellow color; also because of the peculiar toughness of the dough which becomes apparent on drying.

The characteristics which distinguish flour of the soft winter wheats from that of other wheats are a lower gluten content and greater starchiness; a whiter color; a softer gluten and a lower capacity for the absorbing of water in the making of dough. In general, the flours from the hard winter wheats are between those of the soft winter and the spring wheats, in these particulars, but there are some hard winter wheat flours which have more gluten than many of the spring wheat flours and the hard winter wheat flours often have a better water absorption capacity than the spring wheat flours. The durum wheat flours do not differ greatly from the spring wheat flours, either in the water-absorbing capacity or in the amount of gluten which they contain.

Baking powder biscuits have, to a large extent, superseded the old sour milk and saleratus product. Aside from the large sales of the baking powders themselves, the self-rising flour industry, where the baking powder is sold in the flour itself has, in recent years, developed enormous proportions, especially in the south. It has been made possible by the manufacture of low-price baking soda and high-grade acid phosphates. Soft white flours are chosen for self-rising flour and baking powder biscuit, partly because the trade using these articles in the greatest quantities is accustomed to a very white flour and demand it, and partly because the mellower gluten of the soft wheat acts promptly in a limited time with these leavening agents and does not require fermentation with yeast to make it sufficiently tender to offer little resistance to the proper expansion of the dough in baking.

Different wheats yield flours containing different proportions of starch and gluten and flours of different shades of color and of different baking qualities. From the manufacturer's standpoint it is highly important for the miller to keep his product and for the baker to keep his raw material uniform. Of recent years the miller has come to make much use of the chemist in selecting his wheat, and both rely upon him to know the character of the flour.

Normal wheat flouf is not a dead inert matter, but is in many ways an active, changing, living substance. Freshly milled flour from new wheat bakes very differently than does the same flour after it has laid in storage for a few weeks or months. Bakers and millers have long recognized this and have provided for it in the handling of the material. The amount of storage required depends largely upon the length of time after harvest and apparently also upon the condition under which the grain has ripened and the completeness of its maturity at the time of gathering. During this storage, change takes place in the gluten or in some of the other nitrogenous bodies present, and also in the coloring matter. Under some conditions, too, the flour may become drier and thus have increased absorption. It was to overcome the defect of newly milled wheat flours and supply the demand for white flour and white flour products that modern flour bleaching and maturing processes were devised. It has long been known that when flour has been exposed to the air it quickly loses its yellow color and more recently it was found that when certain oxides of nitrogen and some other gaseous agents are mixed in small proportions with the air which comes in contact with the flour, the yellow color disappears almost instantaneously. The chemistry of the process appears to be a direct combination of the agent with the coloring matter, which coloring matter is carrotin: the new product is colorless, while the carrotin itself is yellow. When the agent used is an especially purified anhydrous chlorine, applied in the proper manner in minutely accurate quantities, there are changes other than color brought about in the flour which simulate very closely those changes which flour undergoes in long, favorable storage. Such flours not only produce a whiter bread, but a loaf of better texture and in many cases of greater volume. The gluten of these flours, being mellowed, will not require the extreme fermentation to produce satisfactory results that the same flours when fresh would have required to render their strong, harsh gluten sufficiently elastic not to offer undue resistance to expansion.

Of recent years, especially in England, various chemical salts have been proposed as additives to flour in minute quantities for the purpose of promoting the baking qualities of it. Up to the present time they do not appear to have met with great favor in this country.

Up to the time of the introduction of bleaching, flour making was looked upon as a purely mechanical process. Color as an indication of freedom from impurities became a distinguishing mark of quality and was the impetus for improvement in all departments of milling. Mechanical improvements in this direction, having apparently reached their limits, it was entirely natural that chemistry should step in and furnish the finishing touches. Even though industries manufacturing and using flours have been slower than others to realize the possibilities in this direction it is apparent that much has already been accomplished. We may summarize briefly as follows:

Chemistry assists in selecting and buying the grain; it helps to show the quality of the flour produced. It has supplemented mechanical processes of the mill and accomplished what had long been desired but could not be attained, in the improvement of color and baking qualities of the flour. By the introduction of baking powder products it has made possible many delicacies in the way of pastry and biscuit and has made possible the great self-rising flour industry. It has helped to explain the intricate process of the fermentation of bread dough, has pointed out the way to fit flour for it, and has unlocked doors for investigating problems of bread production, which have, as yet, opened only enough to permit a glimpse of a large space filled with interesting and useful possibilities.

COLUMBUS LABORATORIES, CHICAGO

## CONTRIBUTIONS OF THE CHEMIST TO THE BREWING INDUSTRY

By GASTON D. THEVENOT
Consulting Chemist

Before we endeavor to ascertain what influences the chemist has been able to exert on the development of the brewing industry within the last 25 years, we must realize that brewing is not merely a chemical process in which chemical reactions in connection with mechanical appliances bring about all the changes from the raw material to the finished product, but that biological phenomena also play an important rôle. In fact, the biological side is of as much importance as the chemical one, so that the chemist who devotes his energies to the brewing industry must be just as well versed in the biology of micro-örganisms and bacteriological work as in chemistry itself, besides possessing a thorough knowledge of the practical and mechanical ends of the industry.

The influence of the chemist makes itself felt first in the selection and preparation of the raw materials from which the beer is made.

In the manufacture of malt, marked progress has been made. The old-fashioned methods of steeping the grain and of floor malting have largely been done away with. The introduction of aeration and agitation of the grain during steeping not only permits a thorough cleaning of the material, thus freeing it from the greater number of adhering microörganisms, but also furnishes to the grain some of the oxygen necessary for its ulterior sound germination. Pneumatic malting, which has generally taken the place of floor malting, permits an excellent regulation of those conditions of moisture, temperature and aeration which scientific investigations have found to be

essential for the manufacture of a high-grade product. Lately the germination of the barley, at least temporarily, in an atmosphere of carbonic acid gas generated by its own germination has attracted considerable attention, as it supplies a high-grade malt with a considerable reduction of the loss of valuable substances otherwise incidental to respiration during germination.

Starch being the most important ingredient of barley malt, inasmuch as it furnishes most of the extractive matter as well as the alcohol of the finished beer, it was tried at quite an early date to substitute barley malt, at least partly, by materials richer in valuable starch and, if possible, of a lower cost. Only in the last decades, however, has the introduction of malt adjuncts become practically universal, in this country at least, and rice and various corn products are largely employed in conjunction with malt. The greatest progress has been made in the manufacture of corn products, as they are now made of a very high grade of purity, some practically free from oil, others prepared with great skill in such a way that the cooking process which was formerly necessary can be dispensed with and the material used directly in the mashtun together with the malt without any further treatment at the hands of the brewer. The great purity of these products permits of the manufacture of an extremely clean-tasting beer of special character which appeals greatly to the American consumer and which admirably suits the conditions under which beer is consumed in the United States.

Neglected for a good many years, the influences of the brewing water has of late been made again the subject of a thorough study and the effect of the different mineral ingredients of natural waters on malt, yeast, and beer has been closely investigated. Some of these investigations have led to quite remarkable results which have prompted chemists to treat brewing waters in various ways in order to either remove such mineral constituents as have an unfavorable effect on the character of the beer or add to them those ingredients in which they are lacking and which tend to improve the quality of the product.

An enormous amount of energy has been expended by the chemist on the explanation and scientific control of the mashing process and great strides have been made in this field.

The hydrolysis of the complex starch molecule and the nature of the various cleavage products formed have been made the subject of careful study; painstaking experiments have been carried out, new formulas evolved, and while our knowledge today of the action of diastase on starch is not final we yet have a clear insight into the hydrolysis of starch and are well able to regulate mashing conditions so as to obtain any desired degree of inversion and consequently to produce a beer of any desired composition.

The proteid side of the mashing process has not been neglected. On the contrary, it received all the more attention when it had been recognized what great importance the proteids possess for the nutrition of the yeast, the foam-keeping capacity, stability and brilliancy of the finished beer. Experimental investigations have demonstrated what special groups of proteids or their cleavage products furnish food for the yeast, what groups cause the formation of a creamy and lasting foam, and what proteids are responsible for the appearance of a haze or a turbidity in the finished product. The temperatures and conditions of acidity controlling the changes of the complex proteid molecule under the action of the enzyme peptase have likewise been studied thoroughly so that the brewer, armed with the knowledge which the chemist has provided for him, is well able to regulate his mashing operations and the subsequent treatment of the beer in storage.

Colloidal chemistry has begun to play an important part in all these investigations and with its aid several difficulties have been overcome which for years had baffled all endeavors of the brewery chemist. Thus it has been possible with the aid of lupulin in colloidal state and peptic enzymes to prevent the appearance of a proteid turbidity in pasteurized beer, even when the latter is kept at the freezing point for a long time or is actually frozen. This is of the greatest importance to the brewer in view of the fact that the American consumer desires above all an absolutely clear and brilliant beer which will retain this desirable appearance even when chilled to the extremely low temperatures at which beer is generally consumed in this country.

The progress made in the fermentation of the beer during the last decades has been of the first magnitude. First of all must be mentioned Hansen's remarkable discovery of the existence of the types of yeast which produce various sicknesses in beer, their isolation, and the study of the conditions under which they thrive, how they differ from the useful or culture yeast, and how their presence in beer may be obviated by the introduction of pure culture yeast propagated from one single cell Not since the days of Pasteur's wonderful publications has the study of microörganisms been furthered to such an extent as by Hansen's classical investigations which have not only benefited the brewing industry but form the foundation on which rests all future study of microörganisms in general.

As every type of yeast behaves differently during fermentation and produces a beer of different character, the brewer is enabled to select the type best suited to his requirements, to propagate it from a single cell and absolutely free from wild yeasts or other foreign microörganisms, and to retain the character of his beer at all times.

The study of the activity of the yeast during fermentation has also received great attention and the discovery of the enzyme zymase as the agent causing the splitting of sugar into alcohol and carbonic acid has for all times disposed of the various fermentation theories which had been set forth for a hundred years or more. The study of other enzymes has not been neglected and their specific actions as well as their enormous influences in all malting and brewing operations have been firmly established.

Considerable attention is also due the investigations on the decomposition of albuminous matter during fermentation, it having been proven that, contrary to older theories, many by-products of fermentation, aromatic ethers and higher alcohols, such as amylic alcohol, are not cleavage products of sugar but of proteids. The discovery of the formation of the latter alcohol, while of comparatively little importance to the brewer, is no doubt of great value for other industries.

It is of prime importance that beer, through all of its stages of manufacture, be kept as free from contamination as possible, and the sterilization of brewery vessels or all implements with which beer comes in contact therefore received proper attention. A number of very efficient disinfectants have been invented for the purpose. The introduction of ozone as a sterilizer of the air in the brewery cellars and of the water employed for cleaning purposes is one of the latest developments in this field.

As far as the finished product is concerned, its clarification and sterilization have been given great attention. The important rôle which the proteids play in regard to the stability and brilliancy of the beer has been mentioned before. It was part of these investigations to determine what proteids were responsible for a more or less turbid appearance of beer and what means had to be employed to either restrict or prevent their formation during mashing or to eliminate them during the final stages of manufacture. It has been stated that this question has been successfully solved. Mechanical means of clarifying beer by freeing it from most of its suspended yeast cells by means of filtration through cellulose material have been greatly perfected and lately a filtration process has been introduced which removes all yeast cells or other microörganisms

present by forcing the product through porous stone cylinders and which produces an absolutely sterile beer, capable of keeping perfectly unchanged for an almost unlimited period of time. The object of the latter process is really to do away with pasteurization which checks the development of microörganisms in the finished beer in the bottle by heating. The conditions yielding the most satisfactory results in preserving beer by pasteurization have likewise been studied and the methods greatly improved.

The large quantities of spent or waste material derived from brewing operations have, for a long time, attracted the interest of the chemist. The question of the disposal of spent grains was most easily solved and for a long number of years these spent grains have formed a valuable cattle feed. Their value for this purpose has been considerably increased since drying of the wet grains is resorted to, thus resulting in a stable article which can be kept in perfect condition for a long time and which is even suitable and actually used for export.

The enormous quantities of carbonic acid gas escaping during fermentation, which amount to several hundred thousand tons per year in all of the breweries of the United States combined, were next given attention. Part of this gas is now, after suitable washing, compressed and sold in liquid form, while another part is utilized on the brewery premises for charging the fermented beer with the gas required to impart to it the necessary life and to insure a sufficient head of foam. The latter process, the carbonating of beer, has been largely introduced and has resulted in a very great saving to the breweries in which the system is installed.

The third waste product which has attracted the attention of the chemist is the yeast, of which very large quantities are discarded and run to waste after each fermentation. Analysis showed that yeast is extremely rich in valuable proteids and phosphates, and many chemists have endeavored and quite a number have succeeded in manufacturing from the waste yeast an extract which in taste and nutritive qualities is at least equal to meat extract. By others highly valuable cattle feed has been prepared from yeast and it is to be expected that in a relatively short time almost all of the yeast now going to waste will be diverted into useful channels.

In the above paragraphs the achievements of the chemist in his relation to brewery operations could merely be touched upon. As in all sanely conducted manufacturing enterprises, it has been and is the chemist's ideal to get at the bottom of, and explain in a strictly scientific way, the principles underlying all phases of the entire operation and to evolve means of cheapening the manufacture of the final product. At the same time I wish to emphasize that it is the aim of the brewery chemist to assist in producing a sound and healthful article in which the factors of purity and quality are of paramount importance and rank first before all other considerations.

## CONTRIBUTIONS OF THE CHEMIST TO THE PRESERVED FOODS INDUSTRY

By R. I. Bentley

Vice-President and General Manager California Fruit Canners' Association

A little over a century ago Appert, a French chemist, was awarded a prize by his government for discovering a process for preserving foods without the use of preservatives. Appert's process of hermetical sealing is the same in principle as that in use today by food preservers the world over.

The industry has grown to such wonderful proportions that the annual output runs into billions of packages and nearly every known variety of meat, fish, vegetable and fruit—to say nothing of various sundries—is preserved in tin or glass. Statistics show that New York City expends $150,000,000 annually for preserved foods—as much as that city spends for milk, bread and eggs combined for the same period. This gives some conception of the volume of the business and the extent and variety of the field that it covers.

A chemist having made the industry possible, it would be presumed that chemists would have more or less to do with the preserving of foods from that time on—but in the early days of the industry, in our country at any rate, preservers of foods had little or no scientific knowledge. Their business for the most part was done in a very small way. There was an air of mystery about the processes and each preserver very jealously guarded the methods which he had acquired by experience, or by purchase from some one who had the experience. Under such conditions the keeping quality was the primary consideration in the mind of the preserver—if the flavor or appearance received any consideration, it was merely secondary.

It is a question whether, up to 20 years ago, it ever occurred to a preserver of foods that he could make use of a chemist or bacteriologist in his business. It is a question also, if it had occurred to him, whether he could have found a man, excepting at very large centers, who could have assisted him to any material extent. It is also a question whether, without special knowledge of the industry, a chemist could accomplish much until some insight and knowledge of the business was acquired. If the chemist and bacteriologist gave any attention to manufacturers prior to 20 years ago, they confined their attention to industries other than that of the food preserver. The food preserver, however, having now started to avail himself of their services, is making up for lost time.

Reference will be made to the application of bacteriology to the industry as well as to that of chemistry. The two sciences are so closely related and interwoven in the preservation of foods that it is difficult to discuss the one without referring to the other. If an apology is necessary, your attention is called to the fact that the presentation of this subject is not by one of your profession.

It is impossible within the limits of this paper to go very much into detail, or to present any statistics for your consideration. In this general discussion, therefore, the application of chemistry and bacteriology for the benefit of the industry will be mentioned, and illustrations of such application will be given.

Chemistry has enabled the food preserver to get the best materials suited to his use. A very simple illustration is that of salt—used to a large extent in the preservation of vegetables. Formerly, the preserver considered it a matter of economy to use the cheapest grade of salt that could be purchased. The chemist has shown him that some salt on the market contains injurious materials and that its use affects both the quality and appearance of products. Chemistry having already determined what grade of salt is best suited to his use, on its delivery the chemist determines whether the preserver has received what was selected. In the item of solder also, chemistry has enabled the preserver to get those proportions of metals which are best suited to his use, and on delivery the chemist tells him whether he has received what he ordered.

The application of bacteriology has enabled the preserver to scientifically determine the best methods of processing. The bacteriologist has ascertained the forms of organisms which cause trouble and by means of cultures of the same and inoculation experiments he has determined definitely what times and what temperatures are necessary for sterilization in order to preserve the different products.

The preservers of corn probably had the first experience with bacteriology as applied to the industry, for they had more or less trouble with what was termed "sour corn." Ordinarily corn that was not properly processed would develop what the trade terms "swells;" *i. e.*, gases would be formed to such an extent that the heads of the tin cans would swell out—hence the name "swell,"—and ultimately burst; but in the "sours"

no gases were formed and the preserver was completely at sea. While the corn men had experienced this in a limited way, it had not been of sufficient importance to warrant them going to any great expense in the matter of research—but one season it developed in such large proportions in the case of one packer that investigation was started. About the same time some of the California preservers experienced the same difficulty with their asparagus. The California people were fortunate in getting hold of the same bacteriologist who was investigating the matter for the corn people and at the same time the matter was put in the hands of a bacteriologist in California. What seemed almost uncanny to the California asparagus packers at that time was the fact that two bacteriologists working entirely independently of each other arrived at the same conclusions as to the methods of processing the goods in order to obviate the difficulty.

Application of the laws of chemistry and bacteriology has also enabled the preserver to improve the quality of his product. The preserver, before he was shown a scientific method of processing, whenever he had any trouble with his goods—no matter from what cause—subjected the same to heat for a longer period of time, with the result that the quality suffered. The bacteriologist having informed him of the time beyond which it was unnecessary to go, he now knows that if he has trouble he must look elsewhere for it. This has greatly improved the quality and flavor of his products.

Among the applications of chemistry that have given the food preserver an improvement in the quality of his products may be mentioned improvement in the color of some varieties of fruit, such as berries, by the enameling of the inside of the can; also the examination of the water supply of the food preserver and the elimination of the objectionable elements in the water or the securing of a new supply. The almost complete elimination of iron in the machinery which comes in contact with the canner's products is due to the chemist pointing out the fact that the source of darkening or discoloration of the products was caused by the affinity of iron for tannin.

The application of bacteriology has enabled the preserver to detect promptly possible spoilage and remedy it before any material damage is done. It is a common practice with most preservers to have their products examined frequently; for instance, in the manufacture of catsup, tomato pulp is examined daily; the bacteriologist determines whether this product is right or not before it has gone beyond the initial stage of manufacture.

Chemistry has enabled the preserver to arrive at more economical methods of manufacture, particularly in the saving of labor and eliminating or reducing waste. Many fruits and vegetables are made ready for canning by immersing them for a few seconds in a solution of caustic soda, after which the fruits or vegetables are subjected to the action of fresh water sprays. In this manner the peeling is removed at a great saving in waste and labor without affecting the flavor of the fruit and vegetables so treated. By this method riper, and consequently better-flavored fruit can be handled than by the hand method of peeling. This method is now used almost exclusively on some varieties and is far more cleanly and sanitary than the old.

The application of chemistry has enabled the preserver to improve the conditions under which he operates. The supervision of the boiler water supply of the cannery has resulted in the reduction of costs of generating steam by lessening the amount of fuel, and has lessened depreciation of plant by the elimination of boiler scale and consequent shortening of the life of the boiler. The modern canner does not attempt to feed his boiler with water that has not been declared fit by a chemist.

Chemistry has enabled the preserver of food products to utilize some of his waste materials. There are some fruits, for instance, that have to be treated to a preliminary manufacturing process. Much waste results from this method of manufacture, but the chemist has enabled the food preserver to utilize some of this waste, and what was previously a source of expense has now become a source of revenue.

The most notable application of chemistry in the matter of utilizing the by-products of a food preserver is that of the pineapple waste in the Hawaiian factories. More than 50 per cent of the pineapples received by the preserver were waste, the disposition of which was a heavy item in his expense account. A firm of chemists has worked out processes and methods for the recovery of the sugar values in this waste and proposes to furnish a syrup to the preserver, thereby almost entirely eliminating the use of cane sugar. These chemists have produced the syrup in the laboratory for the preserver on a small commercial scale. The syrup produced experimentally has been satisfactory both from a chemical standpoint and to the preserver as well. They have now about completed the erection of a small plant of a capacity of 50 tons of waste per day. Aside from the sugar value of the waste, it is expected that other products which will have considerable commercial value will also be recovered. If the larger commercial plant proves as successful as the experiment justifies the promoters in expecting, it will be very profitable both to the preservers and the chemists originating the process. It may be of interest to you to know some of the details of the business transaction between the chemists and the preservers. The chemists secured optional contracts from some of the largest producers of the waste in the Hawaiian Islands before even conducting their preliminary experiments, thus safeguarding the interests of the firm during the experimental period. If the small plant referred to is successful then it becomes binding upon this firm to erect a plant of sufficient capacity to take all of the waste of the preservers with whom contracts have been made, process the same and sell the sugar syrup back to the preserver at the equivalent of the market price for cane sugar. Each preserver shares in 50 per cent of the net profits as represented by his proportion of the waste furnished. The Hawaiian pineapple preservers will undoubtedly require the equivalent of $500,000 worth of cane sugar in 1915. It is expected that the recovery plant will return to each preserver syrup recovered from his waste equal to 90 per cent of his requirements.

It is said that the preserver of meats has the utilization of waste and by-products down to such a fine point that he turns everything but the squeal of the slaughtered animal into profit. The preserver of fruit and vegetable products does not even approach such a position, for there are thousands upon thousands of tons of waste that are a source of expense which by the application of chemistry will be made ultimately to bring in a revenue.

While there has been something of accomplishment in this direction, it is not entirely the fault of the food preserver that it has not been more extensive. Many a good idea has been partially developed by chemists and submitted to manufacturers, and owing to the chemist's lack of practical knowledge of the food preserver's business, and owing to the manufacturer's lack of technical knowledge of chemistry, failure has resulted. When a manufacturer has one or more failures which have been a source of considerable expense to him in the way of equipment, etc., he is not inclined to continue experimenting. On the other hand, no class of manufacturers is more progressive and more likely to put money into research work than food preservers—but they must have a few successes along with the failures.

Every new idea should be worked out first in the laboratory and then on a small commercial scale, so that the expense in case of failure will not be large—and even if the experiment is ultimately a success it is best to hold down the expense and perfect the process before trying it out on a large scale. If chemists would work on these lines with manufacturers, we are satisfied that the application of chemistry would accomplish great things,

both for the chemist and the manufacturer. Under such conditions the preserver of fruit and vegetable products will, by the application of chemistry, be able to utilize all waste and even retain and preserve the bloom on the fruit and the spicy odor of it as well—and thus beat out the meat packer, who admits losing the squeal.

San Francisco, California

## CONTRIBUTIONS OF THE CHEMIST TO THE POTABLE WATER INDUSTRY

By Wm. P. Mason

Professor of Chemistry Rensselaer Polytechnic Institute

Less than a generation ago, the chemist approached the question of "Potable Water" with a confidence born of his ignorance, and he issued his pronouncements after an examination less thorough than that required to determine the fitness of a water for boiler uses.

E. Frankland and J. A. Wanklyn in England, and W. R. Nichols in America recognized that something more was needed than a knowledge of "total solids," "mineral matter" and "loss on ignition" before an opinion could be formulated as to the potability of the sample, and to them are largely due the beginnings of that advance in the technique of water examination which has taken such strides in our day.

It was perhaps to have been expected that, in their enthusiasm over their improved analytical processes, the water chemists should make the blunder, into which the bacteriologists fell at a later day, of demanding more from their recent discoveries than could with reason be asked. Thus we find Wanklyn dogmatizing upon the infallibility of the "albuminoid ammonia" process and insisting upon the reliability of a fixed standard for all waters, which measure should divide the good from the bad with accuracy.

Slowly, however, there crept into the minds of chemists the conviction that general standards could not be maintained, as waters were too various for their application; and therefrom developed the tendency towards that breadth of view in the matter of interpretation of analytical results which has led to a recognition of the great importance of what is now termed the "Sanitary Survey."

Considering that any one of the sundry items reported in an ordinary water analysis, is in itself harmless, and, therefore, is scrutinized only because of the possible bad company it might keep, it was soon admitted that an unusually high reading might be accounted for through some perfectly innocent cause in water from one locality and, therefore, justify a favorable report, while the same data from water derived elsewhere might determine condemnation of the sample.

The dictum is not new but it is as true as when first uttered that "no opinion should be risked as to the quality of a water from an unknown source."

It is even possible to add this further word, that, although we need all the light that chemistry, bacteriology and microscopy can throw upon the question as to the suitability of a water supply, nevertheless if but a single branch of inquiry be available the "Sanitary Survey" is the one to be chosen.

While declining to be bound by the hard and fast "standards of purity" advocated in the past, chemists have nevertheless done faithful work towards the establishment of suitable "comparates" where such records can be of service.

For instance, those chemists who undertook a determination of the "normal chlorine" of Massachusetts and Connecticut, and who gathered the data for plotting the "iso-chlors" of those states, certainly added much towards making an interpretation of analytical results more reliable.

Analytical averages for gound waters are now separated from those of surface supplies; the measure of "hardness" is so defined that the non-chemical laundry-man or boiler-user can easily secure the information he needs; and, further, the public is informed as to how much iron would likely be objected to by the average community.

"Turbidity" and "color" are no longer described in words but are reported in definite "parts per million," as are the other items of the analysis, to the great advantage of the manager of the city filter, whose duty it is to watch the work done by the purification plant for which he is responsible.

The day is passed when a municipal filter is expected to run itself, except during its period of occasional cleaning. A chemist and bacteriologist will now be found continually on duty, ready to detect faulty operation on the part of the plant and prepared to apply those remedies which experience has shown to be proper under the circumstances.

"Pin-point coagulation" and its relation to water temperature is one of the disturbances of a mechanical filter that the chemist in charge must watch, for as the late autumn approaches, and the thermometer reads forty or less, the flocks of aluminum hydroxide decrease in size and tend more and more to pass through the sand bed.

Without a trained man in charge, aluminum compounds are likely to pass the filter at any time, for it is an easy matter to carelessly allow an overdose of alum to reach the filtered water; but the detection of too great an addition of coagulant is one of the simplest jobs the attending chemist has to do and it requires small effort on his part to keep down the alum bill.

When "bleach" is needed, as so often is the case, its strength in "available chlorine" must be determined, not only that the management may know the quality of the goods for which payment is made but also that a proper "dose" may be added to the water. Enough must be turned into the supply to do the work demanded, but an overdose should be avoided lest its disagreeable taste be complained of by the consumers. Who but the chemist in charge is to fix the proper value for the dose of "bleach" and who else can suggest a remedy if the right quantity should accidentally be exceeded?

It would not seem a very complex matter to supply properly purified water to a few people, but when this procedure is to be undertaken upon a large scale, the duties of the chemist in charge of the work become most varied. He has to examine and report not only upon the water product itself but also upon all the odds and ends of supplies and equipments that enter the establishment. Such a chemist must of necessity be a bacteriologist, and it would be of advantage to him should he be an electrician, mechanical engineer, biologist and general sanitarian as well.

So it is seen that the old rivalries between the chemist and the bacteriologist in the field of water supply have been outgrown and extinguished in that fusion of activities which produced the present water purveyor. There is yet much of the chemist in his makeup because there is much that is chemical in the detail of his daily work. Without bacteriology, he admittedly could not go far, because with that branch of his mental equipment he detects the present danger lurking in the water under investigation, but it is to chemistry he must turn in order to inquire as to the future and to estimate the probability of a yet distant danger following upon present safety. No better example of what is meant could be given than to cite a very recent instance falling within the writer's experience.

Two wells, each fifty feet in diameter, were sunk eighteen feet deep in a sandy soil, within a half mile of each other.

They were intended for use "in tandem" upon the same water service. One of these was, by bacteriological examination, shown to be grossly contaminated, a showing which was confirmed by both chemical analysis and the sanitary survey; the water from the other well appeared to be singularly good from the bacteriological standpoint but the chemical analysis indicated very material "past pollution" and the sanitary survey

located the cause for such indication. The sandy soil had filtered out and removed all offending organisms but the soluble material which accompanied them had passed on and revealed a threatening danger. Of course, the objection to the water was, not what it contained at the time of observation, but what it would be likely to contain in the future should the protective barriers of nature be overworked or broken down.

Without the chemical side of the investigation no comprehensive report could have been rendered in this case.

And so, in short, chemistry takes its position on the prophetic side of water examination, and it is aided, not supplanted, by the science of the bacteriologist.

The latter's work has to do with showing things as they now exist, while the chemist's field reaches back into the past and throws as well no uncertain light into the future.

TROY, NEW YORK

## CONTRIBUTIONS OF THE CHEMIST TO THE CELLULOID AND NITROCELLULOSE INDUSTRY

By R. C. SCHÜPPHAUS
Consulting Chemist

When we bear in mind that the discovery of nitrocellulose was due to chemical research, we perceive at once that the development of industries based on this discovery must be indissolubly linked with the patient work of the chemist. It need hardly be dwelt upon that the hopes built on the availability of nitrocellulose as a successor to gunpowder were realized only forty years later. Yet the new material quickly found its place in the arts of peace, first as photographic and surgical collodion. The employment of nitrocellulose as the base or an ingredient of explosives, either propelling or shattering agents, is beyond the scope of this article and will not be discussed. However, it must not be forgotten that the work done by chemists in this field, both for war offices and private manufacturers, was of great assistance to the workers in other directions and that the results achieved by this second line of investigators paved the way for the manufacture of gelatinated explosive nitrocellulose compounds, the modern powders and explosives. All the applications of nitrocellulose in the arts are based on the fact that the structure of its various forms may be broken down by the action of suitable solvents. The discoverer of nitrocellulose was already in possession of its colloid solution. The differences between soluble and insoluble varieties (in certain solvents) were quickly recognized, and representatives of four great groups of solvents were known at the very dawn of the nitrocellulose industries, *viz.*:

1—Alcohols : Methyl and ethyl alcohols
2—Esters : Methyl and ethyl acetates.
3—Ketones : Acetone.
4—Mixed solvents : Ethyl alcohol and ethyl ether.

With these fundamental facts to start from there began a long line of chemical activity. Among the industries developed, the manufacture of pyroxylin plastics occupies the first place, and the other developments, such as the production of photographic films, artificial leather, pyroxylin varnishes and even artificial silk made from collodion may be regarded as offshoots from this branch. The activity of the chemist in this industry is twofold, covering research and control of operations. It was necessary to investigate and select the best raw materials, devise methods for their purification and to solve the problem of the production of a nitrocellulose of even composition on a large scale. The various industries require pyroxylin of different characteristics, such as nitrogen content, solubility in specified solvents and viscosity of such solutions. These conditions were worked out in the factories, and the work done in their laboratories would fill volumes. Needless to say that the influence of proportion of acid to cellulose, the composition of the acid bath, temperature and time factors were known to the chemists in these industries long before the laboratories of scientific institutions took these matters up. Important discoveries concerning the connection between solubility, viscosity and mode of production were made and put to practical use. The methods of analysis of the acids and their mixtures as well as of the nitrocellulose and its finished compounds were brought to the greatest refinement and developed to a state which permitted the quick attainment of results that technical operations call for. The determination of oxalic acid in the nitrating bath, for instance, which the latest literature lays much stress on, has been a routine operation for a long period in well-conducted factories. Other problems sprang from the demand for perfectly transparent materials, requiring special methods of washing and stabilizing the nitrated cellulose. In the designing of the most efficient apparatus for the manufacture of the ever-growing quantities of nitrocellulose the chemist took a prominent part. The urgent call for an economical method of regenerating the weakened acid bath was met by the simple and elegant process of adding fuming sulfuric acid to the fortifying mixture which enables a skilled operator to avoid any accumulation of spent acids with all its drawbacks. The best way of removing the larger part of water from the washed nitrocellulose consists in displacing the water by alcohol. While the problems presented appear at first glance purely physical, yet their solution required the alert coöperation of the chemist. So much for the basic material.

In the industry of pyroxylin plastics the original Spill solvent of 1869, commercial grain alcohol and camphor, still reigns supreme. In the intervening years many expedients have been tried, owing to the fiscal policies of various countries in regard to alcohol, and wood alcohol and fusel oil or its separate constituents have found wide application. The other groups of solvents were advantageously extended by the introduction of the esters of the alcohols of fusel oil and of polyatomic alcohols, of ethers of higher alcohols and phenols, of aromatic nitroderivatives and other compounds. These solvents are, however, of more importance in the allied industries. With the rising price of camphor, which is nearly treble of what it was thirty years ago, the old attempts to produce the material from cheaper products were stimulated, and today large factories exist for its manufacture, thus putting a check on unreasonable advances. The same cause led to the elaboration of methods of recovering camphor from scrap materials that cannot be utilized in other ways. The feverish searching for a camphor substitute has been less successful though large classes of solid solvents of pyroxylin were discovered. A few of them, belonging to the group of acid derivatives of aromatic amins, find a limited application for special purposes. Chemical investigation has led to a revision of the old mixing formulas for the manufacture of pyroxylin plastics, and the old empirical standards have been abandoned. The chemist is continually called upon for advice regarding the application of coloring matters and other materials for obtaining special effects.

The allied industries are based on the same principles. In the manufacture of photographic films, varnishes and artificial silk from pyroxylin flowing solutions are prepared. Artificial silk made from dissolved nitrocellulose and subsequently (preferably) denitrated is being superseded by threads made from cellulose brought into solution by other means.

There is not a factory of pyroxylin compounds of any importance in existence today that has not its busy staff of analytical, managing and research chemists.

175 PEARL STREET, NEW YORK

## CONTRIBUTIONS OF THE CHEMIST TO THE GLASS INDUSTRY

By A. A. HOUGHTON
Vice-President Corning Glass Works

The first experiments dealing with the chemical composition of glass of which we have record were directed toward producing

glasses for optical purposes. To give an achromatic image the crown glass lens of a microscope or telescope should have with low refractive index not only the same total dispersion, but also the same partial dispersion in all parts of the spectrum as the flint.

The glasses originally available for optical purposes were made up of only five oxides—silica, potash, soda, lime, and lead oxide—and the crown and flint pairs obtained by means of this limited list of constituents gave a strong secondary chromatic aberration, owing to the different distribution of dispersion in the crown and flint.

Fraunhofer, working with the glassmaker Guinand, by varying the composition of the common glasses, succeeded in materially reducing the chromatic aberration. The glasses were never produced in quantity, however, and there probably was some practical difficulty which prevented their use.

In 1829, the well-known chemist Döbereiner of Jena introduced barium and strontium into glass and probably made other experiments along the same line. A letter to Döbereiner from the poet Goethe, whose interest in optical problems is well known, shows that Goethe made an attempt to establish in Jena a scientific glass laboratory under Döbereiner's instruction.

Harcourt, the English clergyman chemist, in 1834, was the first to experiment systematically on the introduction of new substances into glass; his purpose was to determine the relation between chemical composition and optical properties. He was the inventor of the first experimental furnace for high temperature work, consisting essentially of a small platinum crucible rotating in a hydrogen flame. He discovered that boric oxide and phosphoric oxide will combine with almost any other oxide to form a glass. Harcourt, in a series of experiments extending over 35 years, introduced into glasses in important quantities twenty elements in addition to those already in use. No immediate practical result came from Harcourt's work owing partly to lack of homogeneity of his glasses and partly to the fact that when polished they were quickly tarnished by the moisture of the air.

Otto Schott was the son of a Westphalian window-glass manufacturer. Although his first experiments in glass melting, made while a student of chemistry, were not for optical purposes, yet he early came into contact with Prof. Ernst Abbe who was in serious quest of better glasses for optical instruments. About this time (1880) Schott was planning to undertake on a manufacturing scale the production of new glasses for scientific purposes, but Abbe convinced him that the laboratory method would yield results more quickly. Rather, however, than take up the systematic and slow investigation of all possible combinations of silicates as proposed by Abbe, Schott, guided by his chemist's instinct and his knowledge of the optical properties of the natural minerals, went at once to the substances which appeared to him most likely to furnish glasses of unusual characteristics and submitted to Abbe for examination boric oxide and metaphosphoric acid in glass form. This was little less than a stroke of genius, for to the present day it is boric oxide more than any other one constituent which makes possible the glasses of special properties for use in optical instruments, thermometers, lamp chimneys, laboratory ware, etc.

In January, 1882, a laboratory for glass melting was established at Jena supported by Abbe, Schott, and the Zeiss optical firm. By 1883 the Zeiss works had made up with the new borate and phosphate glasses microscopes in which the disturbing secondary spectrum had entirely disappeared. It is to these microscopes designed by Abbe for glasses made by Schott that modern biology owes its extraordinary development.

In 1884, Schott took a step as a business man which perhaps contributed as largely to the development of the glass industry as anything that he accomplished as a chemist. Together with Abbe and the Zeiss brothers he invested 60,000 Marks in a factory for the melting of the new glasses, which, up to that time, had been made on a small scale only. The Prussian Government, urged by scientific men interested in optics and thermometry, contributed another 60,000 Marks. The enterprise promised little in financial return, for the amount of glass required for optical instruments is from the glass-maker's point of view absurdly small.

After optical glass, the first development in the new factory was a thermometer glass. When a thermometer cools after use above room temperature the mercury reservoir returns only very slowly to its original volume, and at the temperature of melting ice the thread will therefore stand at a lower point on the scale than originally. With ordinary glasses this depression of the zero point after heating to 100° amounts to about 0.7°; after use at higher temperatures the error is much greater. The chemist Weber had found that a potash glass free from soda showed less than the usual depression of the zero point, and Schott proved that either a potash glass or a soda glass gives better results in this respect than a glass containing both alkalis. Schott finally developed glasses which practically eliminated the error. These were the well-known Jena normal glass, $19^{III}$, and Jena borosilicate glass, $59^{III}$. The $59^{III}$ has the further advantage of requiring a high temperature for softening, so that with it thermometers can be made reading to 500° C. or higher.

The borosilicate glasses have low coefficients of expansion, and their use for lamp chimneys, especially in lamps with the incandescent gas mantle, has probably been the most profitable commercial application of the new glasses. Here also incidental advantages resulted from the use of the new material, for it was found that the low-expansion glasses could be shaped and perforated more freely than the old, and chimneys of more efficient design have followed.

It is hardly necessary to remind chemists of the revolution in laboratory glassware brought about by Schott's development of a glass practically insoluble in reagents and at the same time capable of use directly over the flame without wire-gauze protection. This was in itself no small achievement.

The manufacture of Schott's compound glass for boiler water gauge tubes is based on the same principle as the process of tempering glass by sudden cooling in hot oil. In both cases the glass is made mechanically strong by the presence of a surface layer under compression. Glass tubing as ordinarily made, without annealing, takes on compression strain on the outer surface and tensile strain on the inner surface. The outer layer cools first and then tends to prevent the normal contraction of the more slowly cooling inner layer. The inner layer is held by the outer in a state of tension, while the outer layer in turn is drawn by the inner into a state of compression. By lining the tube with a glass of lower expansion, which on cooling obviously reaches its normal contraction with less change of volume, Schott not only eliminates the tensile strain and the resulting weakness of the inner surface but actually introduces compression strain caused by the inner surface cooling somewhat more rapidly than the adjacent layers within the wall of the tube. The result is not entirely unlike that produced by shrinking the jacket on a large gun. The compound gauge glasses thus produced excelled all others made at that time in resistance to pressure, to sudden temperature change, and to the solvent action of water and steam.

To Schott we owe also the Uviol glass for transmitting ultraviolet light. This has been of service in therapeutics and in astronomy; the number of stars revealed by the photographic plate is actually increased 50 per cent by use of a telescope-objective of Uviol glass.

Among the properties investigated at Jena in relation to chemical composition are the following:

| | | |
|---|---|---|
| Specific Heat | Solubility | Specific Gravity |
| Thermal Conductivity | Hygroscopicity | Tensile Strength |
| Thermal Expansion | Refraction | Compression Strength |
| Dielectric Constant | Dispersion | Modulus of Elasticity |
| Electromagnetic Dispersion | | Hardness |
| Electromagnetic Rotation of Plane of Polarization | | |
| Absorption (Transmission) of Radiation Both Within and Without the Visible Spectrum | Diathermancy<br>Ultraviolet Transmission<br>X-ray Transmission and Fluorescence | |

The physical measurements were made in collaboration with the Physics professors of the Jena University and their students. In the glassworks on the chemical side Schott has had the assistance of such men as Herschkowitz, Schaller and Zschimmer, all of whom have contributed to the literature of glassmaking. It is to Zschimmer's work on "The Glass Industry in Jena" that we are indebted for many of the facts here presented.

Other names to be mentioned in connection with glass development are Henrivaux at St. Gobain, famed for plate-glass; Bontemps, maker of optical glass at Choisey-le-Roi and later at Birmingham with Chance; the Guinands, the eldest of whom originated the stirring process for optical glass; Feil, Mantois, Verneuil, Benrath, Powell, Chance, Harris, Siemens; and to the list might be added others equally deserving.

America's contributions to the development of the glass industry, chiefly in methods of working and handling the molten glass, are epoch-making in character; along more strictly chemical lines creditable work has been done, as instanced by the Tiffany or Aurene glass, the selenium red, and others. Aside from optical glass, on which a beginning is being made, the glasses produced in this country probably are fully equal in quality and variety to those produced abroad; and in some respects America is forging ahead.

CORNING, NEW YORK

## CONTRIBUTIONS OF THE CHEMIST TO THE PULP AND PAPER INDUSTRY

By F. L. MOORE

President American Paper and Pulp Association

The manufacture of pulp and paper is an industry based largely on chemical reactions and processes and as such has been largely dependent upon the efforts of chemists for its maintenance and advancement. Chemists of former days are responsible for inventions to which paper making literally owes its existence in its present form, and our modern chemists are essential factors in the every-day operation of this industry. It is not too much to say that the development of modern paper making and the enormous extensions of the use of paper in recent times have been due for the most part to the introduction of the three chemical processes by which wood fiber has been made available as a general substitute for rags.

The sulfite process, by which wood is reduced to paper pulp by digestion in acid bisulfite solutions, was invented by a Philadelphia chemist, B. C. Tilghman, in 1867. Tilghman was also the inventor of the sandblast and of the important autoclave process for the manufacture of glycerin. Although his attempts to manufacture sulfite fiber upon a commercial scale failed and were abandoned because of the many serious technical difficulties encountered, his patents nevertheless disclosed a remarkably clear and comprehensive understanding of the principles involved. The process was later taken up in Sweden by Ekman and in Germany by Mitscherlich, both of whom were chemists, and by other inventors in England and elsewhere, by whom it was developed along somewhat divergent lines. It returned to the United States in 1883 when the mill of the Richmond Paper Company was built at Rumford, Rhode Island, to operate under the Ekman modification of the process, with a nominal capacity of 10 tons per day. Arthur D. Little, who served for many years as official chemist of the American Paper and Pulp Association, began his professional work as chemist to this plant. From this modest beginning, the sulfite industry of the United States has developed at present to a daily production of over 5,000 tons, and the process has revolutionized many departments of paper manufacture. Needless to say its efficient operation requires constant chemical supervision and control.

Another important chemical wood process, the soda process, by which the wood is reduced to pulp by digestion in a strong solution of caustic soda, became possible only after the discoveries and engineering triumphs of a long series of chemists from Le Blanc down through Muspratt, Weldon and Tennant, had supplied the world with cheap caustic and carbonated alkali.

The soda process itself as applied to the manufacture of wood pulp is, like the sulfite process, of American origin, having been invented by Watt and Burgess, in 1853, and developed at Manayunk, near Philadelphia. At first, and for many years, the process was operated with no attempt at recovery of the soda liquors. The process has been able to hold its own only because of the development, largely by chemists, of the processes of soda recovery. Similarly, in case of the sulfite process, many chemists have attacked the far more difficult problem of utilizing the waste sulfite liquors but thus far only with moderate success. It is, nevertheless, to chemists that we must look for the solution of this important problem.

The sulfate process for chemical wood pulp, an interesting modification of the soda process, was developed by the chemist Dahl at Danzig about 1883. It has become of great industrial importance during the last few years through its application to the manufacture of the now well known Kraft wrapping paper, the introduction of which from Sweden has already exercised a profound influence upon the whole wrapping paper industry.

The great names of Le Blanc, Weldon, Solvay and Mond stand for the highest type of the chemical engineer, and to them and the long line of their associates and successors the paper trade, like many other industries, is indebted for the cheap alkali and cheap bleaching powder, without which it could hardly exist today. It is only necessary to contrast the old methods of treating rags by retting and grass bleaching, with the modern methods of pressure cooking and rapid bleaching, to realize how many of the foundation stones of paper making have been set in place by chemists.

A further step in advance is the production of electrolytic bleach and alkali which has become a matter of routine in many paper mills as the result of the discoveries of Watt in 1851, and the later work of chemists like Le Sueur, Hargraves, Castner, Townsend and many others.

Among the less fundamental, but nevertheless highly important advances in the art of paper making, which are directly attributable to the chemist, is the introduction of coal tar colors. Practically all of the colors now employed in paper making are the products of the chemical laboratory, the work of an army of German chemists having supplied us with the whole wonderful range of coal tar colors, many of which are more permanent than the natural dye-stuffs which they displace.

To chemists also we are indebted for the discovery of the useful properties of rosin in rendering paper resistant to ink and water and for the modern methods of rosin size production, for processes for producing casein for paper coating and for rendering it insoluble by the action of formaldehyde, for the discovery of soluble starch so largely used for top sizing, for processes of water purification and those for the manufacture of alum, especially of the high-grade alum, the cheap production of which has been made possible by the Bayer process for the manufacture of pure alumina.

Enough has been said to indicate the vastly important service which the chemist has rendered in the development of the pulp and paper industry. The chemist of today is no less vital to the industry's operation and advancement. Under the stress of modern competition, pulp and paper manufacturers are forced

to turn to the chemist with constantly increasing frequency for the testing of supplies, for the control of processes, many of which are essentially chemical in nature, and for the elimination of wastes. The testing of paper, which yearly assumes increasing importance, is entirely in the hands of the chemist, and the chemist is in large part responsible for the startling expansion in the use of paper which has taken place in the last two decades.

## CONTRIBUTIONS OF THE CHEMIST TO THE INDUSTRIAL DEVELOPMENT OF THE UNITED STATES—A RECORD OF ACHIEVEMENT[1]

By Bernhard C. Hesse

Since the outbreak of the European War, the American public has been led, adroitly or otherwise, to believe that industrial chemistry, that is, the industrial activity of the chemist, is limited to coal-tar dyes and that nothing should be regarded as industrial chemistry that does not deal with the manufacture of these dyes. Nothing could be further from the truth.

While it is true that the manufacture of coal-tar dyes forms an important branch of industrial chemistry, or of chemical industry, whichever you will, it by no means forms the whole of it or even a preponderating part of it.

From the economic point of view, economic effect and economic result is the measure to apply in determining economic importance and not the intellectual or scientific labor involved in the creation of that result.

From a strictly economic point of view coal-tar dyes can hardly be said to be vital or essential and by that I mean, that we can get along without them and not suffer great hardship, personal or otherwise; anything of less need than that can hardly be called an economic necessity.

### THE CHEMIST AND HIS WORK

The American public has seemingly given too little consideration to those industries of this country that make use of chemical knowledge and experience in the manufacture or utilization of products and yet these are the ones that compose chemical industry or industrial chemistry.

For the present, permit me to give in a few words the substance of the impressive series of papers presented at the meetings of this forenoon and this afternoon, and, as this presentation is being made, please have in mind the question as to whether you would prefer to have the United States able to produce all of its requirements of coal-tar dyes and *not* able to produce any of the various things which I am about to mention.

According to this symposium there are at least nineteen American industries in which the chemist has been of great help, either in founding the industry, in developing it, or in refining the methods of control or of manufacture, thus rendering profit more certain, costs less high and output uniform in standard amount and quality.

The substitution of accurate, dependable and non-failing methods of operation for "rule-of-thumb" and "helter-skelter" methods must appeal to every manufacturer as a decided advancement and a valuable contribution

### NINETEEN AMERICAN CHEMICAL INDUSTRIES

In presenting to you these various contributions of the chemist, I by no means wish to be understood as in any wise minimizing or reducing the contributions made to the final result by others, such as merchants, bankers, engineers, bacteriologists, electricians, power-men and the like; all that I wish to emphasize is that the chemist *did* make a contribution, and to that extent he is entitled to credit and acknowledgment.

The chemist has made the WINE INDUSTRY reasonably independent of climatic conditions; he has enabled it to produce substantially the same wine, year in and year out, no matter what the weather; he has reduced the spoilage from 25 per cent to 0.46 per cent of the total; he has increased the shipping radius of the goods and has made preservatives unnecessary.

In the COPPER INDUSTRY he has learned and has taught how to make operations so constant and so continuous that in the manufacture of blister copper valuations are less than $1.00 apart on every $10,000 worth of product and in refined copper the valuations of the product do not differ by more than $1.00 in every $50,000 worth of product. The quality of output is maintained constant within microscopic differences.

Without the chemist the CORN PRODUCTS INDUSTRY would never have arisen and in 1914 this industry consumed as much corn as was grown in that year by the nine states of Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut, New York, New Jersey and Delaware combined; this amount is equal to the entire production of the State of North Carolina and about 80 per cent of the production of each of the States of Georgia, Michigan and Wisconsin; the chemist has produced over 100 useful commercial products from corn, which, without him, would never have been produced.

In the ASPHALT INDUSTRY the chemist has taught how to lay a road surface that will always be good, and he has learned and taught how to construct a suitable road surface for different conditions of service.

In the COTTONSEED OIL INDUSTRY, the chemist standardized methods of production, reduced losses, increased yields, made new use of wastes and by-products and has added somewhere between $10 and $12 to the value of each bale of cotton grown.

In the CEMENT INDUSTRY, the chemist has ascertained new ingredients, has utilized theretofore waste products for this purpose, has reduced the waste heaps of many industries and made them his starting material; he has standardized methods of manufacture, introduced methods of chemical control and has insured constancy and permanency of quality and quantity of output.

In the SUGAR INDUSTRY, the chemist has been active for so long a time that "the memory of man runneth not to the contrary." The sugar industry without the chemist is unthinkable.

The WELSBACH MANTLE is distinctly a chemist's invention and its successful and economical manufacture depends largely upon chemical methods. It would be difficult to give a just estimate of the economic effect of this device upon illumination, so great and valuable is it.

In the TEXTILE INDUSTRY, he has substituted uniform, rational, well thought-out and simple methods of treatment of all the various textile fabrics and fibers where mystery, empiricism, "rule-of-thumb" and their accompanying uncertainties reigned.

In the FERTILIZER INDUSTRY, it was the chemist who learned and who taught how to make our immense beds of phosphate rock useful and serviceable to man in the enrichment of the soil; he has taught how to make waste products of other industries useful and available for fertilization and he has taught how to make the gas works contribute to the fertility of the soil.

In the SODA INDUSTRY, the chemist can successfully claim that he founded it, developed it, and brought it to its present state of perfection and utility, but not without the help of other technical men; the fundamental ideas were and are chemical.

In the LEATHER INDUSTRY, the chemist has given us all of the modern methods of mineral tanning and without them the modern leather industry is unthinkable. In the case of vegetable-tanned leather he has also stepped in, standardized the quality of incoming material and of outgoing product.

In the FLOUR INDUSTRY the chemist has learned and taught how to select the proper grain for specific purposes, to standardize the product and how to make flour available for certain specific culinary and food purposes.

In the BREWING INDUSTRY, the chemist has standardized the methods of determining the quality of incoming material and of

[1] Public Address at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

outgoing products, and has assisted in the development of a product of a quality far beyond that obtaining prior to his entry into that industry.

In the PRESERVATION OF FOODS, the chemist made the fundamental discoveries; up to twenty years ago, however, he took little or no part in the commercial operations, but now is almost indispensable to commercial success.

In the WATER SUPPLY OF CITIES, the chemist has put certainty in the place of uncertainty; he has learned and has shown how, by chemical methods of treatment and control, raw water of varying quality can be made to yield potable water of substantially uniform composition and quality.

The CELLULOID INDUSTRY, and the NITRO-CELLULOSE INDUSTRY owe their very existence and much of their development to the chemist.

In the GLASS INDUSTRY the chemist has learned and taught how to prepare glasses suitable for the widest ranges of uses and to control the quality and quantity of the output.

In the PULP AND PAPER INDUSTRY the chemist made the fundamental observations, inventions and operations and today he is in control of all the operations of the plant itself; to the chemist also is due the cheap production of many of the materials entering into this industry as well as the increased and expanding market for the product itself.

### THE STATISTICAL POSITION

For the census year of 1909 the wage-earners and the value of manufactured products and the value added by manufacture in twelve of these industries and in the manufacture of chemicals is given in Table I*a*.

### AMERICAN INDUSTRIES *vs.* COAL-TAR DYES

A most liberal estimate of the market value of the world's entire production of coal-tar dyes places it under $100,000,000;

| TABLE I*a* | Wage-earners | Product value | Value added by manufacture |
|---|---|---|---|
| Wine | 1,911 | $ 13,120,846 | $ 6,495,313 |
| Copper | 15,628 | 378,805,974 | 45,274,336 |
| Fertilizer | 18,310 | 103,960,213 | 34,438,293 |
| Textiles | 44,046 | 83,556,432 | 48,295,131 |
| Canned and preserved foods | 59,968 | 157,101,201 | 55,278,142 |
| Cotton-seed oil | 17,071 | 147,867,894 | 28,034,419 |
| Cement | 26,775 | 63,205,455 | 33,861,664 |
| Sugar | 20,730 | 327,371,780 | 52,523,806 |
| Brewing | 54,579 | 374,730,096 | 278,134,460 |
| Leather | 62,202 | 327,874,187 | 79,595,254 |
| Glass | 68,911 | 92,095,203 | 59,975,704 |
| Paper and wood pulp | 75,978 | 267,656,964 | 102,214,623 |
| Chemicals (strictly) | 23,714 | 117,688,887 | 53,567,351 |
| TOTALS | 529,823 | $2,455,035,132 | $897,688,496 |
| TABLE I*b* | | | |
| Iron and steel | 278,505 | $1,377,151,817 | $399,013,072 |
| Petroleum refining | 13,929 | 236,997,659 | 37,724,257 |
| Lead smelting and refining | 7,424 | 167,405,650 | 15,442,628 |
| Illuminating and heating gas | 37,215 | 166,814,371 | 114,386,257 |
| Confectionery | 44,638 | 134,795,913 | 53,645,140 |
| Paint and varnish | 14,240 | 124,889,422 | 45,873,867 |
| Soap | 12,999 | 111,357,777 | 39,178,359 |
| Carpets and rugs | 33,307 | 71,188,152 | 31,625,148 |
| Explosives | 6,274 | 40,139,061 | 17,328,113 |
| Zinc smelting and refining | 6,655 | 34,205,894 | 8,975,893 |
| Turpentine and rosin | 39,511 | 25,295,017 | 20,384,174 |
| Oil cloth and linoleum | 5,201 | 23,339,022 | 7,788,921 |
| Chocolate and cocoa | 2,826 | 22,390,222 | 8,867,162 |
| Baking powder and yeast | 2,155 | 20,774,588 | 11,436,603 |
| Dyestuffs and extracts | 2,397 | 15,954,574 | 6,270,923 |
| Blacking, cleansing and polishing preparations | 2,417 | 14,679,120 | 7,716,728 |
| Wood distillation other than turpentine | 2,721 | 9,736,998 | 3,861,147 |
| Oleomargarine | 606 | 8,147,629 | 1,650,997 |
| TOTALS | 513,020 | $2,605,262,886 | $829,052,389 |
| TOTAL FOR 31 CHEMICAL INDUSTRIES | 1,042,843 | $5,060,298,015 | $1,726,740,885 |
| TOTAL FOR ALL INDUSTRIES | 6,615,046 | $20,672,051,870 | $8,529,260,992 |

the entire consumption in the United States is less than $15,000,000, duty included, and this amounts to about 15 cents per person per year.

Now, which would you rather have, these thirteen industries with their $2,500,000,000 worth of manufactured product or the coal-tar dye industry with its $100,000,000 of product? The number of persons employed in these above thirteen industries is in excess of 500,000; the entire world's supply of coal-tar dyes is made by fewer than 40,000 people. Which would you rather have?

These thirteen industries employ 8 per cent of all wage-earners in manufacturing enterprises in the United States, produce 12 per cent of the total value of manufactured product and 10.5 per cent of the total value added by manufacture. In other words, the chemist engaged in these thirteen pursuits plays an important, if not indispensable part in the lives of 8 per cent of our wage-earners and affects 12 per cent of our manufacture values and 10.5 per cent of our values added by manufacture. But the total number of chemists makes up only about 0.01 per cent of the population of the United States.

### NO NATION CAN DO EVERYTHING ITSELF

Of course, it may be said that having made all these other things, there is no excuse why the American should not make coal-tar dyes in addition. Perhaps so; but nations, like individuals, cannot each have or do everything. If each nation could do everything equally as well as every other nation, there would be no occasion whatever for international business. As this world is constituted, each nation does that which it can do the best and trades off the product for what some other nation can do better than it, and both sides are satisfied and make a profit; this is the same as the relationship between individuals. The shoemaker can make shoes better than he can bake bread; he makes shoes and exchanges part of his income with the baker for bread which the baker has made.

If American chemists can operate these industries better than or as good as other nations, it is no real ground for criticism that they cannot do everything better than any other nation, no more than the shoemaker is to be criticized because he cannot make as good a suit of clothes as can the tailor. If you want the shoemaker to be able to make a suit of clothes as well as the tailor you must provide him with the opportunity to learn how to tailor and take care of him while he is learning, and no doubt his suit of clothes will cost him more than it would cost an established tailor to turn out the same kind of a suit of clothes, and you must again help your shoemaker while he is trying to market his suit of clothes against the established tailor.

### EIGHTEEN ADDITIONAL AMERICAN CHEMICAL INDUSTRIES

The above nineteen American industries referred to by no means comprise all the American industries in which the chemist can be of help and of assistance. Many more are open.

A search through the census for 1909 discloses the eighteen additional industries listed in Table I*b* which make use of chemists in the control of their operations.

In these eighteen additional industries the chemist affects 8 per cent of our wage-earners, 12.6 per cent of our manufacture values and 9.7 per cent of our values added by manufacture. For these thirty-one industries, then, the 0.01 per cent of chemists of our population directly affect 16 per cent of our wage-earners, 24.6 per cent of our manufacture values and 20.2 per cent of our values added by manufacture.

This, therefore, is a measure of the influence of the chemist upon the industrial development of the United States; however gratifying this result is, it is nevertheless true that many other industries could employ chemical control to great advantage, if they only would, and many establishments under the above cited industries could, if they would, make use of chemical control. There is plenty of work left for the chemist to do in these industries to keep him fully and profitably engaged. This being so, why should he not continue to direct his energies to improving those things that he can already do, rather than attempt new and exotic things which others can do better than he?

### THE FOREIGN BUSINESS

So much for our internal relations. How about our international relations? To answer this question I will use the official classification of the German Government as to what constitutes

products of and for chemical industry and also the same Government's corresponding figures for 1913.

No two countries, speaking through their statistical departments, have the same working definition of chemical industry. None of the official classifications is as comprehensive as is the official German classification. So far as the exchange of products and commodities involved in chemical pursuits is concerned, the German classification shows a total of 442 items of which 229 are involved in international trade between Germany and the United States. According to these figures and this classification, the United States imported from Germany in 1913, $60,860,880, and exported to Germany $156,036,090, or a total business of $216,896,970, with a balance in favor of the United States of $95,175,210. I have selected from this 1913 list of items of business between Germany and this country those whose gross is $400,000 per annum or over (Table II).

It is interesting to note that we sell Germany more lard than Germany sells us of potash and aniline and other coal-tar dyes put together; that we sell Germany half again as much

TABLE II—U. S. CHEMICAL TRADE WITH GERMANY (1913)

| U. S. imports from Germany | Value in U. S. money | U. S. exports to Germany |
|---|---|---|
| | $75,000,000 | 1 Copper |
| | 26,700,000 | 2 Lard |
| 1 Potash salts | 18,819,000 | |
| | 12,690,000 | 3 Refined petroleum |
| 2 Aniline and other coal-tar dyes | 7,290,000 | |
| | 4,970,000 | 4 Phosphate rock |
| | 4,880,000 | 5 Oleomargarine |
| | 4,585,000 | 6 Turpentine rosin |
| | 4,460,000 | 7 Mineral lubricants |
| | 3,840,000 | 8 Spirits turpentine |
| 3 Caoutchouc | 2,582,000 | |
| | 2,220,000 | 9 Crude benzine |
| | 2,171,000 | 10 Beef tallow (prime) |
| | 1,744,000 | 11 Nickel and nickel coin |
| 4 Straw, esparto and other fibers; paper stock | 1,649,000 | |
| | 1,550,000 | 12 Cotton-seed oil |
| 5 Alizarin and anthracene dyes | 1,463,000 | |
| | 1,421,000 | 13 Pig lead and scrap |
| 6 Indigo | 1,319,000 | |
| | 1,231,000 | 14 Crude and hard paraffin |
| | 1,162,000 | 15 Acetate of lime |
| 7 Platinum and allied metals | 1,120,000 | |
| 8 Hops | 952,000 | |
| 9 Miscellaneous volatile oils | 941,000 | |
| | 903,000 | 16 Tin and tin scrap |
| 10 Tin and tin scrap | 900,000 | |
| 11 Potassium and sodium cyanide | 845,000 | |
| 12 Chrome, tungsten, etc. | 784,000 | |
| 13 Superphosphates | 766,000 | |
| | 724,000 | 17 Crude wood alcohol |
| 14 Beet sugar, refined | 716,000 | |
| | 695,000 | 18 Carbides |
| | 673,000 | 19 Miscellaneous volatile oils |
| 15 Alkaloids exc. quinine | 672,000 | |
| 16 Toilet and tooth powders | 658,000 | |
| | | 20 Heavy benzine and patent naphtha |
| | 656,000 | |
| 17 Lime-nitrogen, etc. | 635,000 | |
| 18 Potash carbonate | 632,000 | |
| | 617,000 | 21 Lubricants of fats and oils |
| | 579,000 | 22 Beef and mutton tallow |
| 19 Ferro-Al, Cr, Mn and Ni | 567,000 | |
| 20 Potassium magnesium sulfate | 509,000 | |
| 21 Gold ores | 506,000 | |
| | 506,000 | 23 Copper alloys |
| 22 Beet sugar, raw | 492,000 | |
| 23 Aniline oil and salt | 476,000 | |
| 24 Bronze and metal colors | 473,000 | |
| 25 Glue | 471,000 | |
| 26 Aluminum plates and metal | 454,000 | |
| 27 Quinine and its salts | 436,000 | |
| | 422,000 | 24 Portland cement |
| 28 Terpineol and allied synthetics | 409,000 | |
| 29 Gelatin | 403,000 | |

refined petroleum as it sells us aniline and other coal-tar dyes; that we sell Germany practically the same amount of pig and scrap lead as Germany sells us of alizarin and anthracene dyes; that we sell Germany almost as much paraffine as Germany sells us of indigo; and so on through the list.

### RELATIVE QUALITIES OF IMPORTS AND EXPORTS

Of course, it will be contended that the things that we sell Germany are, from a chemical point of view, less refined, *i. e.*, involve less hard chemical intellectual work than do our imports from Germany. But, is most of the potash, which is practically mined from the ground in Germany, any more of a refined product than the phosphate rock we sell them? Does it not involve quite as much chemical ingenuity to produce good illuminating oil from petroleum as it does to produce many of the coal-tar dyes? There is no question that the general position above outlined is correct, namely, that our products, as a whole, are less refined than those that we get, as a whole, from Germany, but is that not true practically throughout our entire export and import business? Are not the textiles we export of a lower grade than those we import? Are not our leather products less refined than those we buy? And so on down the list. That being so, why pick out the chemist as a special mark for criticism when he is at least up to the average of his surroundings?

In 1913 the total foreign business of the United States amounted to $4,277,348,909, and the excess of exports of all kinds over imports of all kinds amounted to $691,271,949.

The trade in chemicals and products of and for chemical industry between the United States and Germany in 1913 furnished 5 per cent of that total of international business and provided 13.8 per cent of the balance of trade.

### THE INFLUENCE OF THE CHEMIST

The symposium of papers presented today constitutes a record of proud achievement, of solid accomplishment in nineteen different branches of American industrial activity, to which advance the application of chemical knowledge, chemical principles, and chemical experience by American chemists, has contributed a noble share and an effective part. It is perhaps true that much of that progress would have come without the American chemist, but it is equally true that under those conditions the advance would have been much slower and also much of what has been accomplished would never have happened at all without the faithful, enthusiastic and alert coöperation of the American chemists on the job. With such a record, the American chemist can hold up his head with pride and self-confidence, firm in the belief, and warranted in his conviction that he has done a man's work, in a man's way, that he has not been an idler, nor a sloth, nor a drone, but that he has been one of the busiest of busy workers, with a keen eye and an alert intellect, always searching for an opportunity for the betterment of his industry, and for improvement of the conditions of his fellow man.

### GERMAN SUPREMACY

That the chemist has not done more is by no means due to any unwillingness. It is due in the largest part to the apathetic attitude of those in charge of the management of many of our industrial enterprises requiring chemical knowledge in their exploitation. Many of these men in responsible positions do not have a chemical education even along the lines in which they are financially active. In those cases chemical novelties and chemical problems are not passed upon, on their merits, by chemists or by men with a chemical point of view, but by merchants, by lawyers and by bankers, men who, by their very training, are not capable of taking the chemist's point of view, of having the chemist's sense of proportion, and are unwilling to take a chemist's chance in a chemist's way. Therein lies, perhaps more than in any other one thing, the reason for Germany's supremacy in most of the branches of chemical industry. That also is the reason for the success of a great many of our own huge transportation, electrical and chemical enterprises. The business is run by men who know it from the technical point of view. Railroads are run by men who know the railroads from the operating and construction point of view; electrical enterprises by men who know the business from the electrical engineer's point of view, and they make their enterprises take their business chances in a transportation way, and in an electrical way. Practically all of our chemical enterprises that have

been managed in the same manner have also been successful, but there is still great room for improvement, and just as soon as that improvement is accomplished, just so soon, and no sooner, will there be less and less talk about the incompetency of the American chemist. German chemical enterprises are run and managed by chemists.

Some years ago I was thrown in company with a very successful meat packer, and a very successful metallurgist; the packer asked me when chemists would make glycerin synthetically and make it cheap as the price of glycerin was getting to be altogether too high; the metallurgist asked me, rather impatiently, what elements make up glycerin; somewhat dazed, I replied, "Carbon, hydrogen and oxygen." Thereupon the metallurgist said to the packer, "Why, carbon is coal, hydrogen and oxygen are water, both are plentiful and cheap; I do not see why these chemists cannot mix coal and water and produce glycerin." I felt that my life was altogether too short to attempt to educate those two very successful men to a proper appreciation of the difficulties of converting coal and water into glycerin. This metallurgist's answer to the packer might with equal truth have referred to such dissimilar things as wood alcohol, grain alcohol, vinegar, olive oil, castor oil, whale oil, starch, camphor, cane sugar, beet sugar, grape sugar, carbolic acid, alizarin, and host upon host of similarly different things. I do not know whether that packer, when he got home, told his chemist to take a hunk of coal and drop it into a bucket of water, and make glycerin. I hope for the chemist's sake, that he did not give him that task.

### THE RESPONSIBILITY OF MANAGERS

If there is such a misconception of the chemistry underlying their own products of manufacture on the part of many of our manufacturers, as this meat packer displayed, and if the general chemical viewpoint of the managers of many of our chemical industries is as confused and unfounded as was the view of this metallurgist, then it is no wonder that American chemical enterprises are behind some other countries; the real wonder is that we have any chemical industry at all. Nor is there any dearth in this country of properly trained chemists. There are almost ten thousand of them now in the United States, and they are being turned out by our technical and other schools with great regularity and with increasing volume every year. The fault is not with the American chemist, nor with his ability, nor his willingness; the fault lies principally and almost wholly with those in charge of many of our industrial enterprises, who fail absolutely in a chemical understanding of their own products and are devoid of any sympathetic contact with chemistry and with chemical points of view and therefore are incapable of, and unable to appreciate the value of chemical work or to have a wholesome understanding of the snares, the pit-falls, and the tedium of chemical research.

### CHEMISTS IN MANAGERIAL POSITIONS

This plea for the wider introduction of chemists in positions of managerial responsibility is, however, not to be interpreted into a statement that any kind of a chemist can do any kind of a chemical job. Just because a man can swing a scythe and cut wheat rapidly is no reason why he should be entrusted with the job of giving a man a shave; therefore, if you have a cotton oil problem, do not give it to a man whose specialty and training is in iron and steel only. The non-chemical managers of chemical enterprises will have their hands full picking out the right chemist for the right job and training promising chemical material for managerial positions. To do this successfully is quite an undertaking and will not be accomplished without many trials and many failures. Why should there not be failures? Not every man who is sent out on the road makes a successful traveling salesman, nor is every man put in as a superintendent a success as a superintendent.

In selecting your chemist for a responsible position, you must look out that you do not get a square peg for a round hole, just as you would when engaging a man for any other position, but the trouble seems to be with many of those who have engaged chemists, that they have not appreciated that there are chemists and chemists; they seem to have some sort of an idea that there is a magic about what a chemist does. Now, there is no magic at all. It is all plain, hard work, that calls for a lot of intellectual effort, and above all, the application of common sense, which as every one knows, is a very rare article.

### THE RESPONSIBILITY OF THE PUBLIC

With this record of solid achievement placed before you today, together with what I have just said, I hope that the conviction will finally break through, and will penetrate the public mind as well as the minds of those in charge of many of our industrial establishments, that if the American chemist is not doing as much as the public expect him to do, it is because the public through its industrial enterprises has deliberately declined to give him a chance. With this wonderful record of fruitful endeavor is the American chemist to have his chance? The answer to that question is largely in the hands of the American public.

However, the public will have to acquire in some dependable way an appreciation of what the chemist's work stands for and really is. There are numerous difficulties in the way. By its very nature, the work of the chemist is more or less concealed from public inspection. If you have a particularly well tanned piece of leather, the lay-person thinks no further than that it is a pretty good job, and is utterly unable to appreciate the large amount of work that has been necessary to produce or to create the way of making that particularly good piece of leather. There is nothing so conspicuous about the chemist's work as there is, for example, about the bridge builder's work, or about the work of a man who erects a skyscraper. The chemist's work, as a whole, does not fill the eye nor appeal to the imagination; and not filling the eye, and not appealing to the imagination there is really no practical method of valuation easily accessible to the ordinary individual; not only is the ordinary individual incapable of such a valuation, but even men high in industrial pursuits have not that particular intellectual vision which permits them to appreciate the real significance behind any given chemical product. The only exception hereto seems to be coal-tar dyes.

The reason for this exception is not hard to find. Could anything appeal more to the imagination than the conversion of such a disgusting, sickly mess as coal tar into brilliant colors that rival and excel every tint and shade in nature?

### THE RESPONSIBILITY OF THE CHEMIST

However, the chemist must not attempt to absolve himself from all responsibility for the prevailing lack of appreciation or skepticism among capitalists and bankers of the value of chemical work in industrial operations. While competent chemists and chemical engineers by their very effective work have wrung from reluctant financial men proper acknowledgment of the value of chemical examination, control and management of enterprises requiring such, yet the work has not gone far enough, and it is not at all unusual for financial men to support with might and main enterprises which any qualified chemist or chemical engineer could and probably did tell them were foredoomed; also it must not be forgotten that qualified chemists and chemical engineers, like other professional advisers, have gone astray in their calculations and have supported enterprises which ultimately failed. The mining, electrical and railroad engineers finally succeeded in obtaining their present influential position among the industrial councils of this country and with the brilliant success of the chemical engineers of Germany in the same direction it is not too much to hope that ultimately

the American chemist and chemical engineer will come into his own. When he does, there will be far fewer exploitations than heretofore of the wild and fantastic schemes of chemical enterprise now so easily financed by the gullible portion of our investing public and fewer and fewer failures of chemical enterprises undertaken in good faith and serious mood.

Therefore, let every chemist in advising on chemical operations prominently bear in mind that failure to give correct advice not only reacts upon him but upon each and every member of the chemical profession and merely helps to postpone the day when the chemist will come into his proper position among the makers of the nation.

### CONGRESS AND CHEMICAL INDUSTRY

Like every other industry, all the branches of chemical industry are dependent for their ultimate success upon economic conditions. They must be able to sell at a price greater than their costs. It is not enough to have the material, the men, and the "know how;" you must have the market as well. However, the attitude of consumers of chemicals in this country has habitually been opposed to the creation in this country of conditions favorable to the manufacture of chemicals.

The following quotation from an address in 1910, by Dr. W. H. Nichols,[1] presents this aspect of the problem completely.

"If a comparison were made between the chemical industry of this country and that of other countries, it would be found that the industry in this country in most respects is fully on a par with that of any other country, and in some respects is well in the lead. It is a public notion that our industry is coddled by the tariff, and is thereby based upon a somewhat insecure foundation. Like many other public notions, this is not true. It will be seen by casual examination of the imports that there are a number of chemicals which are not made in this country at all, and a number of others which are made only to a moderate extent. This is not due as much to lack of enterprise of the chemical manufacturers as the fact that the tariff is distinctly unfavorable to the manufacture of many chemicals which are produced in Europe on a large scale and whose manufacturers use this country as a 'dumping ground.' In our tariff all chemicals, unfortunately, are enumerated in Schedule 'A.' It has been the history of several revisions of the tariff that these revisions have been approached with a firm intention on the part of our legislators to lower the tariff, and they have begun on Schedule 'A' with a great deal of enthusiasm. The rates of duty of this Schedule have been steadily reduced, and many articles placed upon the free list before the log-rolling, which is popularly supposed to form such an important part of all tariff inquiry, has begun to get in its work; hence the chemical industry has met with constantly lower tariff rates, while the materials which it has to use have often been left in a position unfavorable to chemical manufacturers. In the interest of fair play, it is to be hoped that when the tariff shall again be revised our legislators will begin at the other end of that document.

"I think it may be stated safely that the chemical manufacturers of this country do not ask and have not asked any favors of the people which would result in any way in a fictitious advance in the values of their output. It is also fair to state that the chemical manufacturers of this country, while entirely friendly to one another, are in no way connected by agreements or 'pools.' While there may be exceptions to this of which I am not aware, I think this can be put down as a general statement and I am sure it will be believed by all consumers of chemicals who come in contact with the active salesmen of the numerous companies."

It is, therefore, only fair to say that the American chemist and chemical manufacturer has throughout made the most of his opportunities, has made his fair contribution to the country's need and growth and has taken a fair and proper share in the internal and international business of the United States. The people of the United States, speaking through Congress, have repeatedly told the American chemist and the American chemical manufacturer "so far and no farther will we help you." The chemist and manufacturer have done all that can be accomplished under those circumstances; if they could not attract capital to all the enterprises they desired to found it was for the reason that capital could be more profitably employed otherwise and money has the stubborn habit of going where it can obtain the biggest return—long waits and uncertain results have no attractions for it.

### CONGRESS HOSTILE TO AMERICAN DYE INDUSTRY

The law makers of the United States knew that coal-tar dyes were made almost wholly in Germany; they knew that those dyes were essential to the ordinary growth and conduct of enterprises in this country, not themselves chemical enterprises but which produced large values of goods annually and employed many people; they knew that attempts had been made for over thirty years to produce those dyes in this country and they knew that they had persistently and deliberately declined to bring about economic conditions which those who were in position to know told them were essential to the establishment of an independent coal-tar industry in this country; they knew that whatever coal-tar dyes were produced in the United States were produced merely by assembling dye-parts which they knew were imported almost wholly from Germany and which they knew could not be profitably made in the United States; finally they knew that if for any reason whatever these dyes could not be obtained from Germany the production of large values of goods and the employment of many people in this country would be interfered with, and very likely seriously interfered with.

### THE EFFECT OF THE EUROPEAN WAR

However, hardly had the European war broken out than our daily press, well knowing what our law makers had deliberately and knowingly done, covered the American chemist and the American chemical manufacturer with an avalanche of harsh and unjust criticism for not doing that which our law makers knowingly and persistently had made impossible.

### CRITICISM BY THE PRESS

The burden of these criticisms is that American chemists should make those dyes because they are vital and essential to, for example, the textile industries. But the American chemist has persistently said that he cannot afford to make those dyes at prices at which they can be laid down in this country by foreign, particularly German, makers and he therefore does not make them.

The dye users are not prohibited from entering into, or taking part in the manufacture of dyes; they have the same privilege as others of investing their own or other people's money in that business, and if, as they say, these dyes are so essential to their commercial life, any loss sustained by them in the manufacture of dyestuffs could legitimately be regarded as an insurance premium towards continued and uninterrupted business and operation. If that sum be too great to be looked upon as an insurance premium by those supposed to be vitally interested in the having of coal-tar dyes, it certainly is too great a sum for the manufacturer of chemicals to lose or to transfer from an otherwise profitable business into something that is of no real profit or importance to him, from a business point of view.

In an article headed "Dyestuffs Discussion Is Growing Acrimonious," the *Journal of Commerce* of January 29, 1915, says, "* * * * little credence is given to statements that emanate from men with German patronymics." In order to forestall any criticism, I will say that my first name, my middle name and my last name are all and each German and I am of German extraction. At the time I was born in Michigan, my father

[1] *J. Soc. Chem. Ind.*, **29** (1910), 1443.

was a naturalized citizen of the United States; my mother was a Michigan-born woman. I received all my scholastic education in the United States—five years at the University of Michigan and three years at the University of Chicago. From the latter I went directly into the employ of the largest coal-tar dye factory in the world, at its German plant, and remained in its employ for nine years and five months, traveling between New York and the plant as occasion required; for the last nine years and three months I have had my office in New York, and while I have there done some work for German houses, the total income received from them in any form, direct or indirect, during that entire period does not amount to half the salary of a rather inferior office boy. I am sure that this will relieve me of any suspicion of being a German spy or of being in the pay of German interests. I am as American as they make them.

Broadly considered, the criticisms of the press may be grouped as follows:

I—The present shortage of dyes and inaccessibility of German producers to the American market offers an unusual opportunity for the manufacture of coal-tar dyes in this country.

II—The chemical manufacturers of this country should make those coal-tar dyes.

### NO SHORTAGE OF DYES

With regard to the first of these it is very pertinent to ask: "*Is* there a shortage?" An open- and fair-minded perusal of the textile trade papers, and of the textile sections of daily trade papers from about the middle of August, 1914, to date, leaves the question as to an actual shortage very much open to doubt, with the chances for a negative answer very favorable.

On pages 11 to 13 are selections from a large number of clippings which throw considerable light on that question.

It is only reasonable to believe that such perusal is very likely to result in the following summary of the situation: At the outbreak of the war our cotton mills were loaded up with cotton that cost them from 13 to 15 cents per pound; shortly after the outbreak of the war the price of cotton dropped until it soon reached a level of about 6 cents; *buyers* of colored cottons insisted upon prices for the manufactured goods based upon the then current prices of cotton; *sellers* of cotton goods insisted that the shortage of dyes was sufficient warrant for holding out for prices for colored cotton higher than the current prices of cotton would seem to justify; the buyers would not buy and the sellers would not reduce the prices. In the meantime dyestuff shipments which were curtailed in some of the months, increased, and for the year of 1914 the receipts of dyestuffs, *i. e.*, alizarin, etc., dyes, coal-tar dyes, indigo and anilin salts are $633,616 under 1913; that is, the totals for 1913 were $10,065,012 and for 1914, $9,431,396; in other words 1914 was 93.4 per cent of 1913. In 1912 the corresponding total was $10,386,703; *i. e.*, 1913 was only 96.9 per cent of 1912 or $321,691 short of 1912. No one complained in 1913 that this shortage as against 1912 was due to the American chemist. The answer, therefore, is that there was *not* any serious shortage of dyestuffs. With that answer also falls the principal condition upon which the press of this country based its insistent demand for immediate dyestuff manufacture in this country.

In this connection it is of interest to note what Mr. William G. Garcelon, secretary of the Arkwright Club of Boston, which includes the treasurers' of cotton mills, said on January 13, 1915, to the Committee on Patents, House of Representatives:

"I presume there are mills all over the country who are suffering from a shortage of dyestuffs. The reports that I have are that the dyestuff men are struggling very hard to look after their customers, and they are succeeding, I think, for the most part. The difficulty perhaps goes deeper than the dyestuff question, because the mills cannot sell their goods. But if they could sell their goods here in this country or anywhere else they might buy more dyestuffs than they do.

"There is another problem, of course, that interests them, and that is the cotton market, a year's supply of cotton having been bought at somewhere between 13 and 15 cents, and on account of the war the price of cotton dropping to 6 and 7 cents, and the mills finding themselves stocked with high-priced cotton and the buyers demanding goods at the basis of 6 cent cotton. It is not, of course, a profitable situation for the mill people. The mills of New England, with exceptions where specialties are involved or where there are large contracts ahead, are not busy. Most of them are running on four and five days' time and curtailing at every possible opportunity, because of business conditions..... It (the Paige Bill) has been discussed, but if you had been in the manufacturing of cotton goods during the last three or four months and had been trying to work at the cotton end of it, and trying to work at the dyestuff end of it, and trying to work out your practice based on cotton which was bought at 15 cents, and which you could now buy at 6 cents, and had all the troubles—I will say this, that it would probably have been much better for the cotton mills of New England if cotton had remained at 12 or 13 or 14 or 15 cents, because we bought our cotton at 13 to 15 cents, and now the purchasers are trying to buy our goods on a basis of 6-cent cotton, and we are in a hole because of that."

### THE UNITED STATES MUST BE INDEPENDENT

Collaterally to this supposed dyestuff shortage our press urged that American industries should be independent of Europe for such vital materials as dyestuffs. Probably on some sort of reasoning, such as that employed by Lord Moulton, *viz.*, that one dollar's worth of dyestuffs is necessary to the production of $100 worth of manufactured product. Granting that dyestuffs are really so important and that such an important constituent of a manufactured product should be manufactured in this country, brings us up to a discussion of the second question.

The dividends declared and paid by the German dyestuff factories in 1912 are in the neighborhood of 10 per cent on the annual turn-over. For the purpose of discussion, let us assume it is 25 per cent and let us assume that the man who makes this $100's worth of manufactured product makes 10 per cent or $10 profit on that. The textile maker, therefore, makes $10 where the dyestuff maker can make 25 cents, or more likely 10 cents if he can manufacture as cheaply as can the German. The American dyestuff and chemical manufacturer is not and has never been attracted by that possible 25 cents profit. The textile maker is spending that dollar anyhow to somebody; the American dyestuff and chemical maker does not care to make that dollar's worth of commodity. It is of no consequence to him in his business; he is making a living some other way, but the textile maker says it is a matter of life and death to him to get those dyestuffs.

### THE DYE USERS MUST MAKE THE DYES

An obvious question at this point is that if the dyes are so vital to the textile makers, and the American dye makers will not make them, why do not the textile makers invest their money in a dyestuff plant and charge up any losses that they may sustain thereby as insurance premium to insure the sale of their goods and the profit therefrom resulting, just as they make their own soap, if need be? There is no ethical nor professional reason against their so investing their money.

Even if the textile maker, under those conditions would just break even, he would still be a gainer; but the American dyestuff and chemical maker, would, under those conditions, be a loser, because he would be unable to return dividends to his stockholders, who have the very unfortunate habit of insisting upon dividends. If it cost the textile maker $1.50 to make a dollar's worth of dye, he would be out fifty cents; that is, he would have paid a 5 cent insurance premium to make sure of a 95 cent profit; if the dyestuff and chemical maker were obliged to sell a thing

that costs him $1.50 at one dollar, the sheriff would very soon have possession of his property.

Granting, therefore, that the stability of our textile and allied industries demand that these materials be produced in this country, it also follows that the financial burden and risk connected with the manufacture of the dyes should fall upon them. To this responsibility I have yet to see from the dye users of this country any adequate or sufficient answer.

If it be the part of wisdom for textile makers not to enter upon the manufacture of dyestuffs in this country, even though dyestuffs are a matter of life and death for them industrially, then where is the wisdom in the chemical manufacturers of this country, who are making satisfactory money in other fields, risking millions of dollars of real money and years of effort and labor in an attempt to make 25 per cent at the very outside, when it would be money in the pockets of the textile makers to invest their capital in the very same venture and be ahead of the game, even if they lose 50 cents on every dollar's worth of dye produced?

I have no doubt in my own mind that the stockholders and the bondholders in our various chemical enterprises would resist any such venture on the part of their respective properties.

Throughout, since the beginning of the war, it seems that the sellers of colored cotton goods have been indulging in the cry of "wolf" many times more than once too often, and the buyers of cotton goods have not believed them; if the buyers of cotton goods, knowing the sellers of cotton goods better than the manufacturers of chemicals do, will not believe those sellers, what reason have the chemical manufacturers to believe the sellers, or, upon representations of those sellers alone, to invest huge sums of money and vast effort in an attempt to help the sellers?

### PATRIOTISM AND BUSINESS

One answer that seems to be uppermost is that the chemical manufacturers should have a sufficient sense of patriotism to lose their money, and the money of their stockholders, in order to help out the textile makers. On this point the *Journal of Commerce* of October 5, 1914, says: "There are some merchants who think motives of patriotism should prevent large purchases of foreign goods at this time, but there is not as much patriotism in business as one liked to hope for and the cold fact of the situation is that constant appeals are made by the holders of foreign merchandise for an opportunity to unload here."

If patriotism will not induce buyers of cotton goods or sellers of cotton goods to pay more for goods made in the United States than for those made elsewhere, then why should patriotism cause the chemical manufacturers of this country to go ahead deliberately with a project in which they are sure to lose money?

### WHY AMERICAN DYE MAKERS CANNOT COMPETE

But the answer to that is, "Sure to lose money, why?" and the answer to that question is a very long story, but it can be summed up as follows: The total world's consumption of coal-tar dyes of all kinds, the year round, and the world over is considerably below $100,000,000; ever since 1879, chemical and dyestuff manufacturers in this country have been attempting to get that business, or a portion of it, away from Germany; not only that, but the chemical manufacturers in Austria, Belgium, France, Great Britain, Italy, Russia and Switzerland have been engaged in the same effort, and all of them have failed; there is no real reason to look for glittering and immediate success now.

At the end of the year 1912 the world owed Germany $51,545,326 for dyes. Switzerland was second with a credit against the world of $3,794,898. Great Britain was the home of the coal-tar industry, but the Germans took it. At the end of 1912 Great Britain owed Germany $6,275,775 for this class of goods.

For the fiscal year ending June 30, 1912, German dyestuff factories declared and paid dividends of 21.74 per cent on their capital stock; for the fiscal year ending June 30, 1913, they declared and paid dividends of 24.96 per cent on their capital stock; in both years the dyestuff makers' dividends were fully 10 points ahead of the nearest income-producing division of the entire German chemical industry. In other words, the German dye industry is getting stronger all the time, not only relatively, but actually as well, for her competitors are becoming more and more dependent upon her; this is shown by the fact that Great Britain and France were hit more quickly and more acutely by the failure to obtain dyestuffs and dyestuff materials from Germany on account of the war, than was this country, in spite of the fact that both countries have branch factories of German dyestuff works within their borders. It must also be remembered that in the early history of the coal-tar dye business, France was an important factor, not only in the invention of dyes, but in their manufacture, but it, too, has had to yield to Germany.

### THE INDIFFERENCE OF THE DYE USERS

Now the American chemical manufacturer is urged to transplant to this country as much of the German coal-tar dye industry as is needed to satisfy the wants of this country. To transplant the whole of it means that the American chemist must learn how to produce on a commercial scale, at low prices and in high quality, over 1200 different chemical products, each distinct from the other, each calling for separate manufacture and close and careful supervision of each step. The textile makers could make the problem a great deal easier for the American chemical manufacturer by making up a statement of the chemical nature of all dyes that they use, the amount used annually of each, and the average prices at which they have been purchasing them. Should it then turn out that the American textile makers could be satisfied with, say 400 out of the 900 dyes, it might very well be that 200 of the 300 intermediate products would be sufficient, and that would reduce the difficulty of the dye manufacturers' problem by 50 per cent. This is not an unreasonable expectation since seven colors have been able to do substantially all the tinctorial work of the 86 different colors used in food coloring prior to their prohibition by our Federal and State Governments. The textile makers decline absolutely to coöperate even to this slight extent.

Surely compared with the demand on the part of the textile makers that the chemical manufacturers invest not less than $5,000,000 and spend a year or two, or even more, in making the 900 different dyes and the required intermediates, the request on the behalf of chemical makers that the dye users furnish some dependable statement as to the actual consumption, both as to kind and amount, and the prices thereof, is a very, very vanishing quantity. The textile makers and other dyestuff users could prepare such a list at a total cost to them of less than $1000. If the users of dyestuffs are so reluctant about this small expenditure of money and trouble in order to simplify the dye maker's problem by over 50 per cent, representing millions of dollars of real money, the conclusion does not seem to be wholly unjustified that these users of dyestuffs have cried out long before they were even hurt, and that the extent to which they are hurt is not worth $1,000, for the purpose of ascertaining how conditions can be remedied. It is difficult, for me, at any rate, to believe that since the users of dyestuffs in this country will not go to that slight expense, they are very seriously hurt, if they are hurt at all.

### THE PUBLIC AND THE DYE-INDUSTRY

Now the public at large has a right to know what it would mean to them to have $10,000,000 worth of dyestuffs produced in this country; roughly it would cost over $5,000,000 of capital and would not, at the very outside, employ to exceed 7000 people all told, in all divisions of manufacture, sale and distribution of the dyes and the necessary chemicals therefor, and

would result in a diminution of our import business by only 0.4 per cent.

I say in all seriousness that this agitation on the part of our press, and this public clamoring that the chemical makers of this country should at once make coal-tar dyes in this country, is very much of a tempest in a tea-pot, and I believe that the presentation just given, is ample justification for anyone's taking the position of "Doubting Thomas." I, at any rate, have come to the conclusion that if coal-tar dyestuffs *must* be made in this country, the users of the coal-tar dyestuffs are the ones who should foot the bill for the venture; they should go out and get the money, and they should stand the losses that are bound to result, since they are in a position to absorb those losses without substantial harm to themselves. Failing that, the public at large must foot the bill.

The *Wall Street Journal* of December 28, 1914, says: "Users of dyestuffs in quantity are more or less indignant over the fact that manufacturers in this country are dependent upon other countries, and Germany particularly for the dye supply. They ask: 'Why haven't our chemical companies experimented sufficiently to produce synthetic dyes, pharmaceuticals products, essential oils and synthetic perfumes, in the production of which Germany seems to have had almost a monopoly?'

"The users of dyestuffs say that the General Chemical Company, with its cash resources and its extra cash and stock dividends yearly, and other companies in a similar position, ought to have had sufficient initiative to use a portion of their large profits in experimental work, which would have permitted us to manufacture synthetic dyes without recourse to other countries and would not have permitted American manufacturers to suffer severely when imports were checked by the war. They state that the interests of manufacturers of the country should have been placed ahead of large immediate profits and unusual dividend returns to stockholders." This, in my opinion, is a childish statement.

On January 7, 1915, the *Indianapolis News* said: "If the chemical and dye manufacturers are too timid to seize what appears to many to be an exceptional industry they cannot be forced to do so." It is a great relief to know that the chemical manufacturer must not spend his money and cannot be forced to spend his money as someone else may dictate.

### SMOKE DOES NOT MAKE DYES

The daily press did not discover the coal-tar dye industry, nor did the daily press first bring the information of the existence of a coal-tar dye industry to this country. Some of the information upon which the *Indianapolis News* bases its view, that many regard this as an exceptional industry, is probably of the same order of accuracy as that contained in an article by George H. Cushing, in the November issue of the *Technical World Magazine*. On page 335, Mr. Cushing has a picture of the smoke stack of a power house, from which a cloud of smoke emanates. Under this cloud of smoke he has written "Throwing away products we buy from Germany; all of the aniline dyes are by-products of coal; Pittsburgh, Cincinnati, Chicago and Cleveland belch great vats of gorgeous colors into the air daily, and then send all the way to Germany to buy a supply." The *Literary Digest* for Nov. 7, 1914, prints the same remarkable news with approval.

Mr. Cushing, the editors of the *Technical World Magazine* and the editors of the *Literary Digest*, seem all of them to have forgotten the distinction between combustion and distillation. For those in a position such as theirs to attempt to represent to the American public that you can make dyestuffs from the smoke issuing from a chimney is the rankest kind of nonsense, and cannot be properly termed anything else but trash; it cannot be justified on any pertinent ground whatever.

It would probably astound these gentlemen to learn that one single coal-tar dye plant throws away the smoke from 22 chimneys every day and never makes an ounce of dye from the 800 tons of coal they burn daily, but sends fully 250 miles away to get coal tar and coal products for making dyes; nevertheless, such is the fact.

Any elementary text book on chemistry describes and insists upon the difference between combustion for power purposes and distillation for tar production purposes, yet these wonderful discoverers of new truths airily wave such fundamental distinctions aside, and mean to tell the American chemist that all that needs to be done is to put a fly-net over a chimney and get dyestuffs; because such trash is the foundation of the view of many that the dyestuff business is an unusual opportunity for American manufacturers, the *Indianapolis News* says the chemical and dye manufacturers in this country are timid, and the *New York Times* of September 5th, says they need more "spunk." Anyone who knows the facts, knows that the American manufacturer is wise in keeping out of any attempt to get into the entire dyestuff business. The chemists and chemical manufacturers of the entire world, outside of Germany, have been unable to take the dyestuff business away from Germany. In fact, they have been progressively losing to Germany. Millions of dollars have been expended in an effort to take this business. If the American chemical manufacturer declines to get into an undertaking of that sort and with that antecedent history, it is wholly unreasonable to accuse him of timidity.

Those who publish our daily papers are in the printing business, yet these publishers do not do all kinds of printing; otherwise they would print all of the $1,500,000 worth of lithographed labels that come into this country, principally from Germany, every year. Are the owners of our daily papers too timid and too devoid of spunk to print lithographed labels? It seems to many that there is an exceptional industry. I presume that the owners of the daily papers would feel rather ruffled if someone were to come up to them and tell them, as a piece of real news, that this country imports $1,500,000 worth of lithographed labels a year. If so, why should the chemists of this country patiently listen to such alleged exceptional industries as the daily press seems to believe that it has discovered?

### ENGLAND REQUIRES PROTECTION

The *Indianapolis News* in the same issue opposes any protective tariff on dyestuffs on the ground among others that "The demand for independent manufacture of needed chemicals and dyestuffs has met with response in England—and England supports a policy of free trade." Now, as a matter of fact the response obtained in England is negative—almost absolutely negative. The dye users decline to contribute to a dyestuff-making venture, they decline to contract for any future deliveries, they decline to commit themselves in any way whatever to the support of any such policy, even though the British Government offers to raise one-half of the needed capital which was quoted at $15,000,000 (afterward reduced to $10,000,000); the British Government stands ready to contribute $7,500,000, or $5,000,000, and yet the users will not raise an equal sum. Why? The answer is that they insist upon protection; they want a protective tariff so high that when the war is over Germany can never sell in Great Britain. Russia is reported as attempting the same thing but so far without success.

### GERMANY INDEPENDENT

The *Boston Evening Transcript* of December 21, 1914, says the following: "It is not a question of raw material, because we send to Germany more than one-half of what she uses in keeping us at her mercy. Her dyestuff industry has fattened upon our culpable indifference to the interests of our own people." The facts are that the United States *never did* supply Germany with any part of its coal-tar raw material. The facts, further, are that, as far back as 1905, Germany was utterly and absolutely independent of any nation on earth for any of its coal-tar

raw materials. That was true for 1912 and for 1913, and there is no reason to believe that it is not true for the years intervening between 1905 and 1912. Germany made herself thus independent in the middle of the nineties.

The remedy that some of these newspapers and other equally ill-informed persons suggest is to alter the policy of our patent laws by introducing requirements for compulsory working. That is, by thus radically altering our policy, we are at once going to get a coal-tar dye industry.

THE BRITISH WORKING CLAUSE

France, in the early days of the coal-tar dye industry, was an important factor in the invention and in the manufacture of dyes; the same with Great Britain; France has always had a drastic working clause; in 1907, the British working clause was brought about at the insistent agitation of dyestuff makers of Great Britain, and they promised, in effect, to the British public that if that working clause were enacted into statute, an independent British coal-tar dye industry would spring up at once. After the law had been in operation six years and a half and Great Britain could no longer deal with Germany, what was the result? Was Great Britain able to supply its own needs of coal-tar dyes? Certainly not. Was France? Certainly not. Now since neither of these countries was able to supply its dyestuff needs, when it could no longer trade with Germany, was the working clause the cause of that condition? If not, what was? Certainly the working clause did not prevent that condition from arising. If the British working clause, the last, and presumably the best of the 56 measures now in force attempting compulsory working, absolutely and utterly failed to produce in six and a half years a coal-tar dye industry, when it had at that time five coal-tar dye factories of its own—each of them at one time or another making some of their own intermediate products and some of them at times even exporting to Germany—if those five British dye works *plus* the new British working clause could not produce the $6,000,000 worth of dyes a year that Great Britain imported in 1912, and make themselves independent of Germany, on what grounds and by what course of reasoning has anybody the right to assume that if we were to put the British working clause bodily on our statute book, we would create a large coal-tar dye industry, at once, or within *any reasonable* time?

In a paper entitled "Compulsory Working of Patents" written by Oliver Imray and Hugh Fletcher Moulton, both of London, and read before the International Association for the Protection of Industrial Property at its Convention in London in June, 1912, they sum up the effect of the British working clause as follows: "The results attained are, therefore, infinitesimally small compared with the large number of existing patents (100,000) even after deducting from this number those patents which may be considered of minor importance, and this in itself is an absolute proof of what a small call there was for this very serious and drastic alteration of the law, an alteration practically admitted by all countries from many years' actual experience to be a mistake."

At the meeting of the Imperial Industries Club of Great Britain, April 1, 1914, the compulsory working of patents was discussed. No one speaking in favor of the 1907 British Act named any specific cases of any new industries being brought to Great Britain thereby. Those speaking against the Act referred to case after case where foreigners revoked the British patents and then dumped foreign-made goods on the British market. Lord Moulton said of this British Act: "It is no use arguing about legislation of that kind. It is self-condemned."

Those who have spoken favorably of this British Act with but one or two exceptions have colored their statements; for example, one new plant was represented as employing 1600 people—it employed 37; another represented at 600 employees, employed 60. There are no official figures as to the real effect of this Act; the only figures are those of real estate agents having land and factories for sale; under those circumstances their fall from truth is understandable, but it does not heighten their credibility.

While the debate was on as to this British working clause the rosiest predictions were made, and I remember distinctly that it was promised that $500,000,000 of new capital would be brought into Great Britain on account of this working clause, and that hundreds of thousands of British would receive fresh employment.

Shortly after the enactment of the British working clause there was a considerable scramble among non-British corporations for opportunities to work in England, and that was looked upon as a great confirmation of the wonderful efficiency of that particular Act.

After two years of full operation, and under date of March 23, 1911, the *London Times* says: "Some fifty firms have commenced or are about to commence work under the Act, and the new factories involved a total outlay of some $4,000,000. It is hoped that employment will in this connection be found for 7,000 additional men, and that the wages paid to them will total something like $4,000 per week. Among the new industries are metallic filament, electric lamps, cinematograph films, aniline dyes, mercerized cotton, foods and medicines, oxygen, clay glaze. The foreign firms principally represented are German and American." That is, $4,000,000 came in instead of $500,000,000. For 50 firms that makes an average outlay of $80,000 per firm; this is probably four times the truth, at that. Under date of Sept. 26, 1914, the *Textile Manufacturers Journal* quotes as follows, on page 6, from the *Textile Mercury* of Manchester, England: "OPENINGS FOR NEW INDUSTRIES—A few years ago every one was full of hope of the foundation of new industries in our midst. The occasion was the passing of the Patents Act of 1907, which, for awhile, appeared to threaten the validity of foreign-held British patents. Municipalities, dock, railway and estate companies saw what they took to be an opportunity, and they went about to meet it. They issued books and advertisements in furtherance of the claims of their situations in order to catch the eye of capitalists who might entertain the idea of opening English works. For reasons into which it is unnecessary to enter, the result from these efforts was somewhat disappointing. The act did not lead to the establishment of any large number of new factories on British ground, but the facts that the anticipations existed and efforts were made deserve to be remembered at the present." Whatever the cause, the fact is that England today cannot make and does not make her own supply of dyestuffs.

Furthermore, it must be remembered that on July 13, 1832, the President of the United States approved an Act compelling all foreigners to work their patents in the United States under penalty of automatic cancellation. That Act was repealed July 4, 1836; it died at the tender age of three years, eleven months, and twenty-two days. If it was bad policy for us then, and experience proved it to be, why should it be good policy for us in 1915 to try the same thing over again? It has not worked in any of the 56 countries that have tried it. Why should it be successful after so many failures under present conditions, and why should it be successful when the old conditions, under which it invariably failed, return?

Another thing that must not be lost sight of is that when we put such an Act upon our statute books we expose ourselves to retaliatory measures, and retaliation may take place just as Germany and France retaliated upon Great Britain for the working clause of 1907.

From the *London Times* of March 23, 1911, just quoted, it appears that Germany was not the only country hit, but that we suffered with it.

The transplantation of the coal-tar dye industry to the United

States is not a question of patent protection; it is nothing but an economic question, a plain matter of dollars and cents; those products can be made in this country if persons will buy those products at a fair margin of profit over the cost of domestic production, and since we know in advance that the cost of production here will be above cost of production elsewhere, plus any prevailing import duty, why should we go to the costly venture of spending millions of dollars to prove the obvious?

As a matter of fact, the whole world's coal-tar dye consumption is about enough to make a decent-sized business for one country. Ordinarily it is best to do the world's work where it can be done best and to transport the products from their place of manufacture to their place of consumption. If it be necessary, for other reasons, that these products should be made elsewhere under conditions economically less favorable, then those who want those products made at such economically unfavorable place should bear the burden, but that is precisely what the dye users do not want to do; they want someone else to foot the bill.

### KEEPING TWO MILLION PEOPLE AT WORK

The textile makers say that if they do not get those dyes, 2,000,000 people in this country will be thrown out of work, and in order to prevent that, the chemical manufacturers of this country must go down into their pockets for millions of dollars. Now, who brought those 2,000,000 people into the textile business? Who has the moral responsibility of keeping those 2,000,000 people employed? Is it too much to ask the textile maker to give up, say 5 per cent of his profits to keep his word and live up to his moral obligations, or should the chemists of this country furnish millions of dollars to enable the textile makers to keep their word with the making of which the chemical manufacturer is in no wise concerned? Is it patriotic to decline to give up 5 per cent of your profit in order to keep 2,000,000 people at work, for which 2,000,000 people you are morally, directly, responsible? Is it unpatriotic to decline to furnish millions of dollars to aid in the keeping of a promise with which you had nothing whatever to do, and from whose keeping you have nothing whatever to gain?

From an economic, a moral, or a patriotic point of view, the responsibility for and the financial burden of making coal-tar dyes in this country rests squarely and solely upon the users of dyestuffs, and in no wise, whatever, rests upon the chemists or the makers of chemicals in this country.

### CONCLUSION

To bring the matter up squarely before you let me recapitulate: The 10,000 chemists in the United States are engaged in pursuits which affect over 1,000,000 wage-earners, produce over $5,000,000,000 worth of manufactured products and add $1,725,000,000 of value by manufacture each year; the business in products of and for chemical industry between the United States and Germany alone in 1913 provided 5 per cent of our total foreign business and 13.8 per cent of our balance of trade for that year. Please bear in mind that I am not by any means attempting to claim all the credit for this for the chemist; all that I ask is that his claims to recognition for intelligent, active and effective collaboration in bringing about those stupendous results be not thrown aside as worthless and that he shall not be made the target of unjust criticism because in 1914 there was a shortage of about $600,000 or 7 per cent in coal-tar dyes and because cotton dropped from 15 cents to 6 cents.

Much more could be said of the chemist and his contribution to the effective every-day labor of this work-a-day world but time and space forbid. I am sure that this short sketch of the chemist's activities, his hopes, his aims and his work will serve to create a wider interest in him and will result in according to him the credit to which he is entitled, namely, that he pulls more than his own weight in our nation's boat.

### SELECTED QUOTATIONS BEARING ON DYE SHORTAGE FROM DAILY PAPERS AUG. 15, 1914 TO FEB. 20, 1915

1—Aug. 15, Textile Manufacturers' Journal: In the meantime it is highly improbable that there is cause for any hysteria on the part of consumers.

2—Sept. 3, New York Sun: Alarming statements were made at the meeting (of representatives of the National Association of Hosiery and Underwear Manufacturers) regarding the shortage of dyes. Assurance was given by local (Philadelphia) agencies of German dye makers, that dyes are coming down the Rhine, but other jobbers reported that the dyes were not coming to America.

3—Sept. 4, Daily Trade Record: Wrote one concern, "We will leave it to you to see that we get dyestuffs as ordered. The question of price is not disturbing us in the least."

4—Sept. 19, New York Evening Post: There has been little difficulty experienced in securing dyes to carry through for several months.

5—Sept. 20, New York Times: A calmer survey of the conditions resulting from the war has removed some of the earlier apprehensions. The scare on the subject of dyestuffs, for instance, has spent its force now that supplies from abroad are coming in with some regularity, and it has been shown that there was no such scarcity of the materials in this country as not a few were led to believe.

6—Sept. 21, Journal of Commerce: The situation in regard to dyestuffs is still disquieting. The prices on certain colors have gone up and other colors have been withdrawn from the market entirely.

7—Sept. 24, Journal of Commerce: It seems difficult to make the truth about dyestuffs known to buyers of cotton goods. Political and business factors of an unusual character are at work to becloud the truth and all users of colors and all sellers of colored goods complain of the harm that is being done..... It is possible to publish on the very best of authority that leading finishers, printers and dyers regard the dyestuffs outlook seriously..... Unless a distinct change occurs in the next three weeks (*i. e.*, by Oct. 14th) some large printing establishments will be forced to close a substantial part of their works.

8—Oct. 1, Journal of Commerce: We have contracts with many of the leading dyestuff concerns and have found, with one or two exceptions, that they have taken no advantage of the present situation, have lived up to their contracts and in many cases have secured dyes and chemicals at no advance in price for mills, with whom in the past they have done no business, so that the former might continue manufacturing.

9—Oct. 2, Journal of Commerce: In colored cotton lines prices rule steady because the dyestuffs scarcity is a real factor and supplies of dyestuffs are being exhausted from week to week. ... the representatives of the largest textile finishing plants in the market declare that the situation is growing worse with them every week. ... There is noted at the same time unwillingness on the part of buyers to regard color scarcity as a serious matter, and manufacturers say they can only await developments in silence.

10—Oct. 4, New York Times: ... unless the tie-up of dye importations is broken by next February the textile and printing trades will be in a desperate way.

11—Oct. 8, New York Times: That dyestuffs in considerable quantities are moving inland through this port without examination and appraisal by the local custom officials was learned yesterday on the best of authority.

12—Oct. 14, Journal of Commerce: The cautious production of printers and other large users of colors in textiles is finally assuming proportions that command the attention of buyers of goods, as well as manufacturers of gray cloths. Printers will not produce goods on their own account, and thus tie up coloring matter that may be more profitably used in other directions if present prospects for limited supplies of dyestuffs continues. This fact is being thought over by some buyers, and those who were in the market were less disposed to pooh-pooh the attitude of sellers of goods of this class.

13—Oct. 17, Textile Manufacturers' Journal: Prints, both staple and fancy, are being held at stiff prices on the ground of higher-priced dyes which counterbalance lower cotton. ... The end of indigo for denims is in sight ....

14—Oct. 17, Textile Manufacturers' Journal: ... all the major industries using the products of his (dyestuffs and chemicals) house were now evidently impressed with the fact that the supply on hand and that due to arrive in the shipments expected would take care of their running needs, and that buyers from these industries no longer were eager to secure as much coloring matter and chemicals as they could in fear of a sudden cutting off of all supplies.

15—Oct. 22, Journal of Commerce: The hopes of dyestuff users are centered now on what will be brought into this country by the two ships reported as ready at Rotterdam for anything the German Government will permit to come through. ... There are some dyes filtering in all the time, but generally speaking the position of large dyeing and finishing concerns is just what it was a month ago with possibly this difference: The volume of new business offered to dyers and finishers is diminishing, hence it is possible to say that the supplies of dyes on hand may last a little longer

than was estimated two months ago, when goods were being rushed to finishers in anticipation of a dyestuffs shortage.

16—Oct. 24, Journal of Commerce: ... the prices asked for dyestuff and other chemical supplies are so high that the normal gain from cheap cotton is being almost wholly offset.

17—Oct. 24, Textile Manufacturers' Journal: Shipments received to date have in most instances enabled local houses to supply customers with their usual quantities of dyes and chemicals without materially decreasing stocks on hand in this country at the beginning of the war.

18—Oct. 28, Journal of Commerce: Some large mills have already ceased producing certain lines pending the securing of additional dyes, and other mills have shut down a part of their machinery to conserve the limited supplies of dyes on hand. Buyers still refuse to take the dyestuff shortage as a serious matter which is likely to affect merchandizing. .... According to the most reliable mill advices, the time is near at hand when additional dyestuff supplies will have to come from abroad, or a very general curtailment of the colored goods trading will be seen.

19—Oct. 29, Journal of Commerce: Many large plants have not enough dye on hand to supply them for three weeks if they are to go on using the stuff in normal volume. They will shut down on the production of colored goods unless they receive dyes before the first of December. ... How to make buyers see the situation as manufacturers see it is a question, but it will probably be the case as in other times, that scarcity will be acknowledged only when prices begin to rise and not when they are maintained at any given level. Prices on standard prints, ginghams, denims, tickings and other staple colored cottons have not been revised, save that here and there some manufacturer wants business to move stock goods, to secure cash for the purchase of cotton, or to provide enough business to use up the dye on hand.

20—Oct. 30, Journal of Commerce: There does not seem to be any ground for hoping that colored goods will be revised to the same relative levels seen in uncolored goods, as the costs of dyes and chemicals have risen out of all proportion to other values. ... where colored lines are wanted, business in a great many cases will have to be accepted subject to conditions in dye-stocks when the orders are taken up at the mills.

21—Oct. 1914, Textile World Record (p. 154): MEETING THE DYESTUFF FAMINE IN ENGLAND. How to obtain a sufficiency of dyestuffs in view of the situation of German trade is almost as acute a problem for England as for America (p. 158). SHORTAGE OF DYES IN ENGLAND. We may start this article with the statement that there is no shortage of dyes.

22—Nov. 5, Journal of Commerce: Mill agents are unable to receive assurances from mills that dyestuffs will be plentiful for the early part of the year and they are still very guarded in their commitments. In several instances orders for certain colored goods are being declined. Thus far this condition has not influenced buyers to any extent.

23—Nov. 6, N. Y. Commercial: Handlers of well-known brands of dress ginghams are getting more business than they were, and report that the dyestuff situation is slowly improving ....

24—Nov. 8, N. Y. Times: Whatever uncertainty there was regarding the procuring of all kinds of dyestuffs in sufficient quantity and at regular intervals has now been dissipated. With the removal of the doubt, also, has vanished any real pretense for much, if any, increase in price for the materials above the normal.

25—Nov. 10, Journal of Commerce: It is certain that most of the leading manufacturers of colored goods will ask no questions as to prices if they can be assured of supplies, as the time is at hand when many looms will be idle unless dyestuffs supplies come to hand.

26—Nov. 11, Journal of Commerce: Some mills making colored cotton goods are instructing agents to sell when they can at the best prices obtainable in order to keep stocks down. While dyestuffs are scarce and high the mills recognize that buyers are not much influenced by the dyestuffs situation....

27—Nov. 11, Daily Trade Record: Many finishers reported their supply of colors would carry them only until the first of the year, others until February. No one reported that the colors would carry them past April.

28—Nov. 13, New York American: Paterson silk manufacturers declare that at present there are dyes in sufficient quantity to last the silk, cotton and woolen industries in this country a long time.

29—Nov. 14, Daily Trade Record: Experts in textile dyeing, with special reference to silk, are recalling predictions at the opening of the war, that no textile mill or dye-shop would have to close because of a shortage of dyes, and are asserting that they were undoubtedly accurate in their prophecy. And now, as one of them said yesterday, the danger is almost past.

30—Nov. 14, Journal of Commerce: Within a month it will appear to buyers of colored goods that the dyestuffs problem is a very serious matter, as some large producers of colored goods have already reached the point where they must shut down if dyestuffs in large quantities do not come forward before the first of December.

31—Nov. 16, Journal of Commerce: Investigation as to the importance of dye-materials from various European ports into this port during the month of October discloses the interesting fact that despite the reported scarcity of dyestuffs alleged to be due to the blocking of the German ports, there was brought into New York a greater number of packages, having a slightly higher value than was brought in during the corresponding month of last year when war conditions did not prevail.

32—Nov. 17, Boston Post: At the beginning of the present European war the cry went up that dyes, which are purchased chiefly in Germany, would be unprocurable and that the textile industry would be seriously injured. But the cloud in this direction has for the moment passed, and in all probability before another has time to gather, the exigency will be provided for.

33—Nov. 19, Journal of Commerce: Uneasiness is shown by some buyers because prices on prints, ginghams and percales are not revised downward. If selling agents were not being held back by the fact that mills will not guarantee deliveries until the color and dyestuffs question is more settled, they would revise prices at once. .... It seems useless to agents to try to impress buyers with the fact that some of the largest textile users of dyestuffs are on the verge of closing and have already shut off the production of several important colored lines. The only impression they expect to see effective is the one that will be made when goods ordered are not delivered because dyes cannot be had for making them.

34—Nov. 22, New York Sun: According to mill men in this section (Boston) of the country the dyestuff situation is today more serious than at any time since the European war started. This afternoon the Pacific Mills at Lawrence employing 2000 hands, was forced to shut down for at least a week on account of a lack of dyestuffs. ... the prospects of adequate supplies of dyeing material are poorer now than at any time in months.

35—Nov. 23, Providence Evening Tribune: "BOSTON, Nov. 23—It will surprise most people to learn that the dyestuff situation is today more serious than at any previous time.....

The dyestuff subject is ultra-technical and presents ramifications almost baffling of expression in every-day description. But it seems there has been a 'nigger in the wood-pile' in this dyestuff situation all along which the public has practically never heard about."

36—Nov. 24, Journal of Commerce: In the cotton goods division it is no longer doubted that large mills using dyestaffs are confronted with the necessity of shutting down in order to conserve the limited supplies of dyes on hand. That some plants would be kept running if orders were coming in normally is admitted by agents, but in the absence of normal orders idleness in the factories has become a necessity, which comes now instead of later, when dyes are actually exhausted.

37—Nov. 25, New York Times: There has been a marked improvement in the demand for colored cotton goods on the part of the wholesalers in the last few days, and, as a result, the anticipated price revision on these goods have become realities. For example, it is now possible to get a Southern 4.30-yard Chambray fully a cent a yard under the figure which prevailed in September 1, while staple ginghams of Southern make have been dropped a half a cent a yard in the last sixty days. A drop of about a half a cent a yard has also been recorded in Southern denims. Eastern priees are firmer, but it is figured that downward revisions of them are not far off.

38—Nov. 26, New York American: Just at present he (a leading shirt manufacturer) said printers are at a loss as to how to cope with the shortage of dyestuff, which is growing larger each day. In the past week or two, several of the largest mills shut down on this account while a number of others radically reduced their running time.

39—Nov. 28, Textile Manufacturers' Journal: The shortage of indigo is one of the notable features of the present dyestuffs situation.

40—Nov. 30, Journal of Commerce: Many of the large mills making colored goods have less than a six weeks' supply of colors, while many cloths have already been withdrawn from the market because duplicates cannot be produced until certain dyes come in. These facts have been so often repeated that buyers disregard them as of no consequence and will probably so continue to regard them until an actual demand for goods cannot be met.

41—Dec. 2, Journal of Commerce: The dyestuffs situation so far as hosiery is concerned ... is as critical at present as it has been since the war began, despite some views to the contrary.

42—Dec. 2, Wall Street Journal: A textile authority says to the Boston News Bureau: "The dyestuffs situation is undoubtedly growing worse daily. There is nothing in sight or on the way to relieve the situation. Some mills have more dyestuffs than others, but unless a sudden exportation of German dyes starts and starts right away there will be a gradual withdrawal from the market of line after line of staple goods. The greatest shortage at present is in blacks, indigoes and fast colors. Substitutions are being made where possible and with some success. But there is a limit to what can be done in this direction. If conditions continue without a break it is a matter of weeks and not months before the consuming public will find an acute shortage of standard colored goods."

43—Dec. 4, Journal of Commerce: It is understood that the mills can be kept in operation for about sixty days. If no further dyes suitable for cotton goods of this class (denims) come in, the large plants must shut down.

44—Dec. 8, Daily Trade Record: An important textile authority is quoted as follows: "The first real flag of distress has been hoisted in the dyestuff situation. This has been the withdrawal from the market of all lines of denims manufactured by the two largest denim mills of the country. These mills state that present orders will exhaust their supplies of dyestuffs and they have no means of replenishing. These two great mills have about two months' work ahead and will then probably have to shut down.

"The average retailer in this country appears to have a very faint comprehension of the critical situation in dyestuffs. He was told the story of the danger of cutting off of supplies at the very outbreak of the war. He was urged by the selling agents of the mills to stock up with this line and that of colored goods on the theory that there would be a famine in prints and other colored lines within a few weeks' time. But these jobbers and retailers have found themselves steadily able for four months, to buy all they wanted, and they have naturally assumed that this tale of woe was simply another device of clever salesmen to tempt them into placing large forward orders.

"And the curious fact is that in many lines of colored goods today, the very dyes of which the mills are most acutely short, are represented by manufactured stocks of goods on hand of which they have the largest supply. This fact will tend to postpone still further the general recognition of the dye famine which the mills are forcing."

45—Dec. 9, Daily Trade Record: At a meeting of the Dyestuffs Committee of the National Association of Finishers of Cotton Fabrics, held prior to the general meeting of the association, at the Arkwright Club yesterday, the proposed convention of users and producers of dyestuffs was discussed, and it was decided for the present that the matter would not be pushed. The committee is well aware of the serious shortage of dyestuffs, but does not feel that the shoe has yet pinched hard enough to bring it home to consumers. The responses to the circular letter sent out by Secretary Danner, to users and producers of dyestuffs, asking if they favored sending delegates to a general convention, were disappointing to the committee, and showed that the time was not opportune for a general convention.

46—Dec. 9, Daily Trade Record: The Glenlyon Dye Works, of Saylesville, R. I., are reported to have resumed the use of colors which were withdrawn several months ago, when the dyestuffs shortage first became acute. The Glenlyon is said to be in a position to put out its full line of yarn dyes again. J. G. Whitaker, manager of the Glenlyon works, is quoted as saying that the supply of fast dyes which the concern now has should last from four to six months, according to the demand of the trade.... There has been a heavy curtailment among colored goods manufacturers, both in the East and South, for some weeks past. This curtailment is still in evidence. It has been due partially to lack of orders for goods and partially to the shortage of dyestuffs. Manufacturers and finishers do not hesitate to say that if there was a normal demand for goods, the supplies for dyestuffs on hand would be cleaned up within a few weeks.

47—Dec. 10, Journal of Commerce: If they (the buyers) really show a need for goods and will place orders on which mills can predicate plans of future operations to the extent of stocks or dyestuffs on hand, it is thought quite possible that agents will make a revision that will meet immediate conditions. .... The fact that the largest printers are operating less than half their machinery is its own answer to the crisis in the dyestuffs situation with them. There are some of the large jobbing house buyers who are now very anxious concerning certain colored goods they will need for Spring. During the past week agents have had reason to know that buyers no longer regard the dyestuffs shortage as something to joke about.

48—Dec. 12, 1914, Textile Manufacturers' Journal: STOCKS STEADILY DEPLETED. SUPPLY OF COLORS WANTED GROWS CONSTANTLY SMALLER. ..... DYESTUFF SUPPLY SMALL. CONSUMERS NOT OPTIMISTIC ABOUT FUTURE DEVELOPMENTS.

49—Dec. 30, New York Times: WILL DYES HOLD OUT? Factors in the piece goods market are rather puzzled over what the dyestuff shortage will mean during the coming heavyweight season. The tremendous amount of dyes required in filling the contracts let out here for army cloths will seriously deplete the small stocks of dyes on hand.

50—Jan. 9, Textile Manufacturers' Journal: The situation in some of our dyestuffs is desperate. There is no gainsaying it, and it behooves us to look the facts in the face and not squander time, which we could put to much better uses, in vain regrets and recriminations that our supply houses had not foreseen contingencies as they have happened and provided an unlimited stock of the colors which we need.

It is to be expected that American dyestuffs makers will largely benefit by these circumstances; but, on the other hand, it is doubtful whether they will have the courage of enlarging to such an enormous extent as to be able to meet the European deficit, since they must figure upon the probability that when peace is again established the Europeans will make every effort to regain the profitable American field.

BLEACHING SUBSTITUTE FOR DYEING.—This leaves a clear-cut issue before us textile manufacturers: What we have not got we cannot make use of, and our commission merchants and jobbers and stores cannot sell. The public will then be forced to content itself with undyed goods, but this does not mean the raw, woven or knitted fibers, which would be too unsightly for wear. We can beautify them immensely by bleaching, and this will be the solution of our problem and the salvation of our textile industries. As long as we have white goods to wear we shall always be able to clothe ourselves in good taste.

51—Jan. 20, Journal of Commerce: Theodore Boettger, of the United Piece Dye Works of Lodi, N. J., the largest dyers of textile in the piece, told the members of the Jobbers' Association of Dress Fabric Buyers yesterday afternoon, who were holding their annual convention at the Waldorf-Astoria, that the scarcity of dyestuffs on account of the war, was not serious, although a scarcity really exists. The buyers of dress goods, Mr. Boettger said, could go ahead and conduct their business without interruption. At any rate, he said, they could let the dyers do the worrying.

52—Feb. 20, Textile Manufacturers' Journal: So far little if any machinery has had to shut down on account of inability to obtain dyes, but any reserve stock, either in manufacturers' or importers' warehouses, has absolutely disappeared.

90 William Street, New York City

# COMPULSORY WORKING OF PATENTS IN THE UNITED STATES, GERMANY AND GREAT BRITAIN[1]

By BERNHARD C. HESSE

The United States Patent Act of July 13, 1832, for compulsory working of patents reads as follows:

"AN ACT CONCERNING THE ISSUING OF PATENTS TO ALIENS, FOR USEFUL DISCOVERIES AND INVENTIONS"

"Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled, That the privileges granted to the aliens described in the first section of the Act, to extend the privilege of obtaining patents for useful discoveries and inventions to certain persons therein mentioned, and to enlarge and define the penalties for violating the rights of patentees, approved April seventeenth, eighteen hundred, be extended in like manner to every alien who, at the time of petitioning for a patent, shall be resident in the United States, and shall have declared his intention, according to law, to become a citizen thereof: *Provided*, That every patent granted by virtue of this Act and the privileges thereto appertaining, shall cease and determine and become absolutely void without resort to any legal process to annul or cancel the same in case of a failure on the part of any patentee, for the space of one year from the issuing thereof, to introduce into public use in the United States the invention or improvement for which the patent shall be issued; or in case the same for any period of six months after such introduction shall not continue to be publicly used and applied in the United States, or in case of failure to become a citizen of the United States, agreeably to notice given at the earliest period within which he shall be entitled to become a citizen of the United States."

That part of this Act preceding the *proviso* was introduced into the House of Representatives January 6, 1832; then it went to the Senate and there the *proviso* was added; then accepted by the House and finally approved by the President.

This Act was repealed July 4, 1836. No such compulsory provision has since been placed on our statute books.

Precisely why this Act should have been passed and then repealed is not now determinable since a thorough search through the records of Congress does not disclose any debate nor any committee report; my information is that in those days Senate

[1] Received March 1, 1915

proceedings were secret and records were not kept; detailed committee reports on patents do not begin until 1837; the House record merely notes introduction, the acts of reading and of passing.

GERMAN WORKING CLAUSE

Dr. C. Wiegand, of Berlin, in a paper entitled "Compulsory Working and Compulsory Licenses" published at p. 188 of the "Transactions of the International Association for the Protection of Industrial Property," for the meeting of June, 1912, says of the German Compulsory Working Act of June 6, 1911: "Under the provisions of the previously existing law a patent could be revoked, if the invention was not worked to a sufficient degree within the country, or at any rate everything done to secure this working. Opposition to this unconditional compulsory working was made by numerous manufacturers and lawyers, and as established by the arguments in support of the Law of June 6, 1911, it was shown that the system of compulsory working in itself led to an uneconomical splitting up of the source of production and that consequently the abolition of compulsory working was to be desired. The Imperial Government adopted this view in principle, but pointed out that so long as other important manufacturing countries, in which the German industries and German applicants for patents had important interests, retained their compulsory working provisions or introduced them afresh, a general abolition of compulsory working in Germany was not to be recommended. On the other hand, in all cases where another State was ready to accord the same benefit to German inventors, compulsory working should be abolished as against this State by treaty.

"There exist between Germany on the one hand and the United States, Switzerland and Italy on the other hand, treaties by which the subjects or citizens of these States, either generally or under particular conditions, are not subjected to the compulsory working provisions. The German Government, which in this matter sees eye to eye with the greater part of the German industry, is anxious to proceed further on the same lines and to abolish compulsory working by treaty with other important industrial countries."

The relevant and essential text of the German working clause of June 6, 1911, is given, in translation, as follows by Dr. Wiegand (*Loc. cit.*): "If the patentee refuses to another the permission to use the invention when offered remuneration and guarantee, the right to use the invention can be accorded (compulsory license) to the other person, if the grant of this permission is demanded in the public interest.' The right to use the invention can be granted with limitations and be made dependent upon conditions.

"The patent can be revoked provided State treaties do not prevent this if the invention is exclusively or mainly worked outside the German Empire or the Protectorates. The assignment of the patent to another is without effect if it has only the object of avoiding revocation.

"Before the expiration of three years after the publication of grant of the patent, no decision can be rendered against the patentee."

BRITISH WORKING CLAUSE

In 1907 the British Parliament enacted a compulsory working clause. The following excerpts from the *Journal of the Royal Society of Arts* for 1908 and onwards show how the effects of that enactment were regarded.

*Vol. 56, p. 143* (Jan. 3, 1908): "The new patent law requiring the production of patented articles in English works is having the anticipated effect in bringing German color manufacturers to this country."

*Vol. 56, pp. 283–4* (Jan. 31, 1908): "It is seldom that an Act of Parliament has such an immediate and beneficial effect as that which seems likely to follow upon the coming into operation of the New Patent Act. Many foreign patentees are already negotiating with British manufacturers to carry out in the United Kingdom their British patents. Others have taken land for the purpose of erecting works in order themselves to work their British manufacturers. .....

"A well-known American company which holds British patents for the manufacture of safety razors, hitherto made solely in the States, have secured land in Sheffield, and expect to employ 500 hands as soon as their works are completed. Many other foreign manufacturers holding British patents, which they have hitherto worked solely abroad, are following their example. There is not the slightest doubt, writes Mr. Ivan Levinstein, in an interesting letter directing attention to what the new Act has already brought about, that the advent of these foreign manufacturers will mean additional employment for workers—the operative classes, highly trained engineers and chemists—and give a new impetus to British enterprise. Unlike its predecessor, the new Act is clearly worded, and leaves no loopholes for escape from its salutary and much-needed provisions."

*Vol. 56, pp. 924–5* (Sept. 4, 1908): "This Act, the Patents and Designs Act, became operative on August 28th. Its principal clause runs as follows: 'At any time, not less than one year after the passing of this Act, any person may apply to the Comptroller for the revocation of the patent, on the ground that the patented article or process is manufactured or carried on exclusively or mainly outside the United Kingdom.' In future, foreign manufacturers, if they wish their patents to remain valid in Great Britain, will have to make the goods they sell within the United Kingdom. Otherwise their patents may be copied or infringed at will. Germany and the United States are particularly hit by the new enactment, and they are meeting the altered conditions by (1) building factories of their own in England; (2) acquiring premises already built for the purpose of carrying on their business; (3) arranging with British manufacturers to lay down plant and coöperate in the production of the special articles which are the subject of the patent. Already some thirty foreign firms—many of them conducting operations on a large scale—have begun, or are about to begin operations in this country, most of them choosing the North of England as the scene of their operations. It is said that as a rule the foreign manufacturer is providing a factory many times larger than is really necessary for the construction of his patented article, his explanation being that he cannot run works in England on patents alone, and he intends therefore to manufacture in this country goods that have hitherto been imported ready-made. So far as can be seen at present the Act must profit British labor. It is said in some quarters that these manufacturers, at any rate the German ones, will be worked by foreign staffs, but this is not the case at present with Messrs. Meister, Lucius, and Bruening (Limited) of Germany, a company with a capital of £11,000,000, which has just erected a new chemical factory at Ellesmere Port. Here all the workers employed are English, with the exception of a few German overseers. The working of the Act will be watched with keen and anxious attention, for British manufacturers are beginning to realize that foreign competition is about to invade their own particular territory, and that there will be a fair but strenuous fight on British soil for British custom. That is not a prospect that can be viewed altogether with anxiety when the perfection of German organization is remembered. The German things to be manufactured in England will be mostly aniline dyes, pottery, plant for gas making, rifles, plated goods, electrical contrivances, furnaces, sanitary appliances; the American, typewriters, safety razors, phonograph records, shoes, telephones, and wire roofing."

*Vol. 56, p. 952* (Sept. 18, 1908): "It is seldom that an Act of Parliament works quite as its authors and supporters hoped and expected. The Trade Marks Act is one of the most striking illustrations of this truth. It may be that the New Patents Act will be another. It may bring the foreign competitor to even

closer grips than at present with our manufacturers, and it may lead the inventor to resort more frequently to the secret process.

"Independent discovery is now the only risk menacing a monopoly based on secret working, and the risk of independent discovery is usually not great; it is at least much smaller than that consequent upon betrayal or accident. It is quite possible, therefore, that one of the results of the Patent and Designs Act, 1907, will be largely to increase the number of inventions worked as secret processes."

*Vol. 57, p. 212* (Jan. 29, 1909): "There has been some recent correspondence in the *Times* as to the probable effect of the revocation of certain patents on the ground of their not having been worked in the United Kingdom. The section was intended to encourage British industries, and was indeed welcomed as a Protectionist measure by the opponents of Free Trade. It is now urged that its probable result will be to encourage the manufacture of the patented article abroad and its importation into this country, it being improbable that manufacturers here will find it pays to produce it if the manufacture is unprotected by a patent. Thus the clause may now conscientiously be approved by Free Traders. Attention has also been drawn to the remarks made by the Comptroller, who, in delivering his judgment expressed the opinion that it was to the general advantage that the trade should be freed and the importer enabled to obtain the foreign manufactured goods readily. This doctrine, if carried to its legitimate conclusion, would seem to justify the abolition of patents entirely, and the revocation, not of an occasional patent, but of the Statute of Monopolies itself."

*Vol. 57, p. 340* (March 6, 1909): "The great advantages to this country attendant upon the passing of the Patents and Designs Act, 1907, have not, so far, been sufficiently appreciated by manufacturers and merchants in the United Kingdom."

*Vol. 58, p. 473* (March 18, 1910): "The expectation that the Patents Act of three years ago would result in foreign firms acquiring land and erecting buildings in this country to a considerable extent has already been verified. The Act came into force on January 1, 1908, and since then foreign firms have acquired land in England to the value of £188,650, and they have spent £290,750 in the erection of buildings and the housing of their work-people, and a further sum of £410,972 on plant, machinery and equipment. Thus in two years the Act has caused foreign firms to spend £890,372 in this country. Mr. Farmer, of Messrs. Leopold Farmer and Sons, who has given special attention to the subject, says that the Americans, Germans, Dutchmen, Frenchmen and Swedes have taken part in this commercial invasion, and he estimates that over forty firms are represented. Among them are manufacturers of matches, electrical apparatus, chemicals, pottery, pencils, mercerized cotton goods, musical instruments, roofing felt, incandescent gas mantles and rubber goods, all compelled by the Patent Act to make their goods in this country, to buy land, build factories, employ home labor, and pay rates and taxes. The works are scattered all over the country. They are in the metropolitan area, Middlesex, Kent, and Essex. In Cheshire several firms have established works on the Mersey; others are at Leicester bootmaking; others again at Warrington, Wolverhampton, in South Wales and Yorkshire. According to official figures some 8,000 people are employed as the result of the Act, mostly men, and the local authorities will benefit in the shape of rates substantially."

The accuracy and dependability of these statements is probably not very great. For instance, the combined capital of three German dye companies is given at 260,000,000 Marks and of two others at 160,000,000 Marks or 420,000,000 Marks for these 5 German dye companies. On June 30, 1912 the 21 German dye plants, inclusive of these five, had a combined total capital of 146,800,000 Marks. That is, the *Journal of the Royal Society of Arts* attributes three times as much capital to 5 plants as all 21 had together almost 4 years later; the German dye-companies have progressively increased their combined capital stock and have not decreased it.

The following tabulation shows four different estimates of fresh capital invested in Great Britain as a result of this Act:

| | Pall Mall Gazette | London Daily Mail, Nov. 5, 1909 | Jour. Royal Society of Arts, 1910 | London Times (a) March 23, 1911 p. 21 |
|---|---|---|---|---|
| Land | $ 500,000 | $ 585,000 | $ 943,250 | . . . |
| Buildings | 1,000,000 | 535,000 | 1,453,750 | ..... |
| Plant and equipment | 1,000,000 | 435,000 | 2,054,860 | . . . |
| Totals | $2,500,000 | $1,555,000 | $4,451,860 | $4,000,000 |
| Number of firms | ..... | ..... | 40+ | 50 |
| Number of work-people | ..... | ..... | 8000 | 7000 |

(a) Based upon reply-to questions in the House of Commons at the close of 1909, made by the President of the Board of Trade; there are no official figures; official estimates alone are available.

In spite of much searching in Washington and New York I have been so far unable to locate any item-by-item statement for any of these lists. No doubt such lists exist but so far they have succeeded in escaping me.

I quote from private letters to me (B. C. H.) from England by a friend of over nineteen years' standing and dated February 8 and 12, 1915, after, for obvious reasons, having made certain indicated omissions and corresponding textual changes:

"Questions have been asked in Parliament once or twice, and I followed the answers with interest but they were purposely very vague, and gave no real information, but put the effect of the working clauses as great as possible in a vague way.

"A firm of estate agents, Farmer and Company, who did do a little business in selling land or a factory to people coming over here to work patents made the most of the Act and wrote to the papers with reference to it, thereby getting a free advertisement. They published tables, showing the effect of the Act, which were grossly misleading; for instance one factory appeared four times in the list with the nominal capital so that the capital was quadrupled. Again the number of work-people to be employed by it was estimated at 400, and this given four times made 1,600, instead of 37. Precisely the same sort of thing was done with reference to any other factory as to which I know anything. I cannot say whether the list was more accurate about factories of which I know nothing, but in any case these lists were absolutely worthless. The way in which this factory was given four times was this. It was given at first under the proper name—Chemical Works. Then it was given as a factory to be erected by Company A, a factory to be erected by Company B, and a factory to be erected by Company C. (Note: A, B and C companies *together* erected this *one* plant.)

"The ———— factory was similarly treated. The effect of the working clauses in the last New Patent Act has been infinitesimally small from the point of view of bringing about new manufacture in this country, and the employment of labor. In no case has the Act resulted in any manufacture in the coal-tar dye industry continuing in this country after the patent has lapsed; for instance, while ———— was patented over here it was made in large quantities, yet the last English-made———— was sold two or three months before the patent lapsed, and so it has been with everything else. It is impossible to produce any permanent results by these working clauses. Again, a number of patents have been revoked under the new Act. In no case has this resulted in the manufactures being effected in England. The inventor has lost his patent but there has been no manufacture resulting over here.....

"I have now heard from London where I spent a few hours the day before yesterday, with reference to the compulsory working clauses. The Controller at the Patent Office assures me that there has been no official publication at all with reference to the effect of compulsory working.....

"The ———— Chemical Works bought 24 acres of land at

£1,000 the acre, but they did this with the absolute conviction that five acres would be amply sufficient for a factory merely to work the patents. Indeed, with five acres the coefficient of safety was three.

"The factory of the ———— Company at ———— is similarly very much larger than is necessary for working the patents. The site covers, I believe, 25 acres. I am not sure of the exact size of the site. They use, I should estimate, three acres."

According to the *Journal of Commerce* of November 4, 1914, the Farbwerke Hoechst plant in England employed fifty or sixty workmen at that time; statements have been made by supporters of this clause that these works employed 600 workmen.

On April 1, 1914, the Imperial Industries Club of Great Britain had a real in-the-family and heart-to-heart discussion of this Act and its effects. The complete report of that discussion is given below with acknowledgments to The Imperial Industries Club, whose official pamphlet has provided this material.

Since this Act was passed for the benefit of Great Britain's chemical industry and particularly with the hope and expectation of creating in Great Britain a real coal-tar dye industry and has failed of its object, a careful study of this discussion at this time must appeal to every American chemist and maker of chemicals.

90 William Street, New York

## SYMPOSIUM ON COMPULSORY WORKING OF PATENTS AND DESIGNS IN ENGLAND[1]

By The Imperial Industries Club

THE CHAIRMAN: *My Lord Moulton and Gentlemen*—We have received letters of regret from the following, who are not able to attend this evening: Sir John S. Randles, M.P.; the Hon. Sir John Astbury; Lord Parker; Ivan Levinstein, Esq.; C. T. Needham, Esq., M.P.; the Right Hon. Lord Southwark; F. Whitley Thompson, Esq.; G. J. Stanley, Esq., of the Board of Trade; Harry Nuttall, Esq., M.P.; A. J. Hobson, Esq.; Ex-Master Cutler, of Sheffield; and from Sir Joseph Lawrence, a member of this Club and an old friend of ours here, the following telegram has been received. Sir Joseph says: "I deeply regret cannot join you. If present I should stoutly maintain compulsory working benefits this country by creating more opportunities for employment and I strongly support this policy and would strengthen it by Parliamentary means. Please read this to your meeting."

Gentlemen, I think that that is a very good opening for the subject which we are about to discuss and which I think you will all agree will prove a very interesting one. We are a comparatively small party this evening; but I think we are all interested more or less in the subject which we are going to debate. We are fortunate in having around this table gentlemen who are professionally, officially, and commercially interested in patent questions, and we are to have an opportunity of hearing, I hope, expressions of opinion which will voice both sides of the question. Because *at this Club we do not like things to be altogether one-sided.* Our purpose in meeting here is to try to thresh out matters in a friendly and convivial sort of way, and therefore we rejoice when the opener has some little opposition, so that those of us who do not take part in the debate are able perhaps to act as a jury of decision.

I am privileged to call upon Mr. Walter Reid, Chairman of the Institute of Inventors, to be good enough to open the discussion.

MR. WALTER F. REID, F.I.C., F.C.S.: *My Lord Moulton, Mr. President, and Gentlemen*—The reason I have been called upon to open this discussion has been stated by the Chairman, namely, because I happen to hold the office of Chairman of the Institute of Inventors; but I should wish for your sakes that you had somebody who is better able to place the arguments on behalf of inventors before you than I can do myself. I am very glad indeed to have the assistance of my old friend Sir Joseph Lawrence, because I was with him on the deputation to Mr. Lloyd George which resulted in the Patents Act that is now the subject of discussion, and that some of us, at any rate, wish to alter. Previous to that I had also taken part in a deputation to Mr. Gerald Balfour, when he was at the Board of Trade, when we also got an alteration of the Patents Act. I do not know whether anybody was satisfied with that alteration, but I have not heard of many, and that Act was very soon altered. I think, when we are on that subject, it is not quite right to say that Mr. Lloyd George on that occasion gave one of the first and most conspicuous instances of Protection to British industry. He really did nothing of the kind; he placed us on a Free Trade basis with other nations, because undoubtedly—I will not go into the figures on this question—at that time the bulk of the other nations, the most important ones, who were competing with us industrially and commercially, had compulsory working as one of the conditions of granting a patent in their countries. We for a very long time had no compulsory working: we had allowed foreign inventors here to acquire monopolies in certain branches of industry, and they had made use of those monopolies in a way which those who were acquainted with the details of the subject could no longer permit Great Britain to labor under the disadvantage of. On the occasion when we had the last deputation to Mr. Lloyd George a number of cases and details were given of industries that had suffered in Great Britain because foreigners had been granted monopolies here and had not worked the patents in this country, but, having the monopoly, they could demand from our own people prices which they at home could not obtain. A very familiar case was that of the alizarine industry, where our manufacturers here who had to use such dyes were paying about half-a-crown and the practical real value of the material was about sevenpence. Of course, our manufacturers were suffering there under a great disability as regards foreign competition because they required that dye; it was a dye which was necessary, and the wool dyers in Bradford and elsewhere had those excessive prices to pay whereas their German competitors had not.

Now, I think, if we consider that, it is a clear case where the British industry is handicapped and unfairly handicapped; and I would ask you to bear in mind that the first and original idea of a patent was a monopoly for the introduction of an industry into this country, and it was only at a later stage that the inventor was given a monopoly for the produce of his brains. Nobody will deny that an inventor ought to have something for inventing a thing; otherwise we should have no inventors in this country; they would go elsewhere. But I do think, myself, and, so far as I have been able to learn, and I think I am in as good a

[1] Report of the proceedings at the April dinner of the Club held at DeKeyser's Royal Hotel, Victoria Embankment, E. C., London, on April 1, 1914, with the President, Ald. Sir George Wyatt Truscott, Bart., J. P., in the chair. Among those present were the following: The Right Hon. Lord Moulton of Bank; W. Temple Franks, Esq., C. B.; Sir George Croydon Marks, M.P.; Sir R. Ellis Cunliffe, M.A.; Col. Sir John E. Bingham, Bart., V.D., J.P.; Sir Roper Parkington, D.L., J.P.; A. J. Walter, Esq., K.C.; James Hunter Gray, Esq.; H. A. Colefax, Esq., K.C.; G. Henry Wright, Esq.; C. E. Town, Esq.; Stanley Machin, Esq.; H. Hatfield, Esq., I.S.O.; Wm. Martin, Esq., LL.D.; Alex. Siemens, Esq.; Oliver Imray, Esq.; Alfred O. Goodrich, Esq.; Dr. Ernest J. Schuster; George Barker, Esq.; C. Freeman Murray, Esq.; The Hon. Hugh Fletcher Moulton; Laurence Rostron, Esq.; C. Urquhart Fisher, Esq., L.C.C.; J. King Stewart, Esq.; John Cutler, Esq., K.C.; J. M. Forbes, Esq.; Achille Bazire, Esq.; R. B. Dunwoody, Esq.; Louis Sinclair, Esq.; Francis E. Truscott, Esq.; James Webster, Esq.; W. Holmes Reddan, Esq.; R. A. Wallis, Esq.; Percy Richardson, Esq.; W. A. Vernon, Esq.; Dr. A. E. Rose; J. K. Foord, Esq.; C. Beatty, Esq.; Kenelm H. H. Smith, Esq.; Walter F. Reid, Esq., F.I.C., F.C.S.; Douglas Leechman, Esq.; E. T. Ayerst Hooker, Esq.; E. E. Pakeman, Esq.; Geo. E. Pearson, Esq., F.C.S.; G. M. Whiley, Esq.; J. D. Marshall, Esq.; Ernest J. Mitchell, Esq.; Edward Harrison, Esq.; A. J. Martin, Esq.; M. P. Shepherd, Esq., A.C.A.; Henry Cooke, Esq.; J. H. Evans-Jackson, Esq.; J. N. Evans-Jackson, Esq.; Wm. J. Tennant, Esq., M.I.M.E.; H. Wade, Esq.; Jacob Heilborn, Esq.; Geo. Kettle, Esq.; P. Blair Tayler, Esq.; Percy Izod, Esq.; E. H. Harberd, Esq.; J. H. Jack, Esq.; and J. E. Evans-Jackson, Esq. (*Hon. Secretary*).

position as anybody to learn the opinions of inventors generally, they are under the impression that it is an unfair thing to British inventors that a foreign inventor should come here and acquire a monopoly and not do what the British inventor in most cases has to do from the very nature of the subject, namely, work the invention. I think that we, as an Imperial Industries Club, ought to see to it that the British inventor is not, at any rate, worse off than the foreign inventor. He cannot in many cases at any rate,—in some he can, but in many cases he cannot—acquire foreign patents abroad in the same way that a foreigner can acquire a patent here, because there is compulsory working.

Now, no doubt some of those who will follow me may say that compulsory working is a mere matter of form and so on; but, if you have a powerful firm who insist upon that form and put the law in motion, then the British inventor who has a patent abroad may very likely lose that patent in some countries—not in all of them.

There are other points with regard to the working in this country that I think we as an Imperial Industries Club ought to consider. With regard, for instance, to munitions of war, on that deputation to Mr. Lloyd George we pointed out that at that particular time great industries were being founded by which the nitrogen of the atmosphere was being condensed, or concentrated as it were, into the essential material for the manufacture of smokeless powder. I particularly pointed that out. I said: Now there is an industry being created which, if it is not worked in this country, will leave us in time of war without the possibility of carrying on the work ourselves. An industry of that kind cannot be founded in a few weeks, and, consequently, unless the industries had been previously established in this country we should be in the position that if war broke out the saltpeter, which is an absolutely necessary ingredient for all explosives, would be contraband of war and we should not be able to obtain a supply, whereas our competitors, or our enemies perhaps, would be able to do so from the atmosphere. From establishing those industries they would be able to produce as much nitric acid as they required and we should be left without it. That, apparently, appealed to the Government at that time, and compulsory working was then established.

Now, it has not given us altogether what we want. I will not go into the legal argument. Mr. Justice Parker, whose name is a household word among inventors and well known in this room, has interpreted the law in a certain way. We had previously not interpreted it in that way. I do not propose to go into that, because my friend, Mr. Douglas Leechman, who is the Chairman of the Parliamentary Committee of our Institute, has made a special study of that, and if you wish he will give you chapter and verse for everything in connection with the legal aspect of the question. But what I wish to impress upon the members of this Club is that the matter is to some extent an Imperial one. It is one in which we ought to consider those of our kith and kin more, I think, than foreigners who come here, and whom we welcome, by the by. I would not for a moment say that we do not welcome them, for a very large number of our industries in Great Britain have been introduced and developed by foreigners, and I should be the very last one to say that we should not welcome foreigners in every way, but I do say this, that we ought not to give them a monopoly which can in any way injure our own people.

Now, as a consequence of that Act during the time when, if I may use the word, it was active, several firms abroad came and established factories in this country and (without again going into minute details which would probably be rather tedious to you, but I have a very considerable number of figures on that question) a number of factories have undoubtedly been established and industries have been established under the pressure of the Act as we interpreted it. It is not enough to say that one firm or another has put up a factory in England, and they are not doing much, that they have done it just simply as a blind, and so on; that is not so much the question; those who are behind the scenes know very well that a number of patents have been introduced into this country under royalty to British firms that would not otherwise have been introduced. When an industry is introduced into this country, whatever it may be, there is employment for British capital, there is employment for British workmen and the industry becomes established in this country and after the lapse of the patent the industry becomes an English one.

I would mention incidentally that the British Empire now is to some extent, I will not say in the melting pot, but we are going through troublous times with regard to the British Empire. We have self-governing Colonies, and the bond that links our self-governing Colonies to us is one of gossamer, and we can only keep together by the most careful interchange of opinions and of commercial interests especially. When I say that we have seven of the High Commissioners or the Agents-General of our self-governing Dominions as Members of the Institute of Inventors, I think you will see that we deal with the matter from the Imperial point of view, and that is particularly the point of view I should like to impress upon you this evening. There are a great number of things that one might mention that really cause an Englishman to blush because we are so dependent upon foreigners for things which are absolutely necessary for our existence as a nation. Of course, we know very well the history of the Whitehead torpedo. Our own Government would not take it up and it had to go to Austria to be started and then our Government bought it at an inflated price afterwards. That is a very well-known instance. I myself have had an instance. I started the industry of smokeless powder. I could not get our people to look at it here because they said the sights of all the rifles in the Army would have to be altered. The French did not look at it from that point of view quite; they saw a little bit further and they started the industry. Then our people came in afterwards, a second, perhaps a good second; but the less we say about cordite when it was first made I think the better. I think it a shame for Englishmen that they do not and our Government does not push ourselves to the forefront of nations. They can do it and why should they not? Then, again, you may not know it, but the glass required for optical purposes in our Army and Navy is German glass. For instance, the periscopes of the submarines are made from German glass. If we happened to have a war with Germany they would not give us their glasses.

MR. J. E. EVANS-JACKSON: That glass is not the subject of a patent.

MR. WALTER REID: Yes, I think so.

MR. J. E. EVANS-JACKSON: No, certainly not.

MR. WALTER REID: At any rate, any improvement upon it here would be to the advantage of this country. I happen to know something about that particular subject, because I am a member of a committee that studies this special subject; Sir William Crookes is also a member and we have very distinguished scientific men on it, and it struck us as being a great anomaly, and it struck me personally as being rather a shame that we should be dependent upon a foreign country for these things. If, as our genial Secretary says, there is no patent now at the present time, I would point out to him that the glass that was developed by Schott of Jena was developed financially and in every way only through the assistance of the German Government. Whether they give a money subvention for carrying out these experiments or whether they grant a patent, the whole thing is a development of the industry of the country, and if any foreigner were to come over here and were to get a patent monopoly for a new kind of glass he could hold up the whole industry if he liked in time of war. As a matter of fact, we are dependent

for that glass upon the Germans, and that is the point I wish to make here: the Germans developed that industry through the assistance of their Government. There are many other things where our existence as a nation, I will not say is dependent upon, but may be, at any rate, interfered with.

I am reminded that the time is getting short for my opening remarks. I have a number of other matters, but I should like to refer just briefly to the commercial aspect of the question. The patents that are worked in this country may be of very great value indeed. If there are foreign patents which are not revoked or worked in this country they may stand in the way. I happen to be a director of a company that holds a very large number of patents; I think they are put down at about £140,000 in our balance sheet, and they are of considerable value from the point of view of master patents; they control a certain industry. If we had a foreigner come over here and get a patent that would stand in our way British capital would lose. It is a thing that affects commercial men even more than inventors.

Then, again, I would remark to you with regard to the working of a patent that it is extremely difficult—and this is a point with regard to which probably those who succeed me in speaking will say that the onus should lie upon the objector—to prove that a patentee does not work. That is a most difficult thing to prove. I know the legal gentlemen are in favor of that because that seems to be the general practice in the law, but it is not a practice without exception; there are many exceptions. I would point out here that it is almost impossible for a stranger to find out what is going on in any factory. We have an instance where a gentleman told us that he had tried for a year, he employed detectives and he found that the patent was worked; he found a tub in a kitchen; that was all he found and all he was able to find. If it is so difficult as to be almost impossible for an Englishman to find out what his foreign competitors are doing in this country, then I think the purpose of the Act will altogether fail. If the onus lies upon the objector to prove everything that the foreigner is doing I think it is quite impossible. With those few words I will conclude.

THE CHAIRMAN: I will ask Sir George Croydon Marks, M.P., to speak.

SIR GEORGE CROYDON MARKS, M.P.: *Mr. Chairman, my Lord, and Gentlemen*—I am very glad that our friend has wound up with a suggestion which I think gives the key to a great deal of the criticism which has come from that table. He speaks about being concerned with a company that has £140,000 written as the asset connected with patents, and he touches upon the financial side rather more strongly, I think, than he touches upon what I would call the commercial side. I, unfortunately, have had to deal with inventors and with manufacturers and engineers and others for a great many years, and I have not found that there is a disinclination upon anyone's part to improve their position or to improve their works, given a favorable opportunity. I have found, however, that in this country there is a lack of initiative, and a great deal of caution that one does not find in other countries. That goes a very long way to explain why some people succeed elsewhere, and others fail here. There are businesses in existence in this country which have failed, not because of foreign competition, and not because of foreign patents, but because the sons connected with the business that they found made for them by their fathers have not that initiative, have not that personal touch, and have not that knowledge that their fathers had to make the business. Hence it comes about that we find young men, who succeed to good commercial businesses, doing all that they can to show the people in the district in which they live that they belong to a different class from those poor manufacturers and the others; and if, perchance, they do happen to go to a works they just pass through it and pretend to have but a little acquaintance with the details; and is it any wonder that by and by the old-established firm finds it necessary to convert itself into a limited liability company in order that its declining trade may be bolstered up by capital caught from credulous people knowing nothing about the real decline; and then, when that business has failed, you have some of these prophets of woe coming along and suggesting: "We have lost our business owing to the wretched foreigners sending things here or patenting things here that we are not allowed to make"? I am perfectly certain that I could, within twenty minutes, satisfy any gentleman tomorrow morning that if you have some very good article here and you submit it to a number of old-fashioned firms, making them offers of it, they will turn that down straight away, and say they have no need for it; they have all the skill that they want in connection with their own firm; and if they cannot produce what is wanted then that which we offer them is no good at all.

Our friend spoke just now about the terrible things that are going to happen if, perchance, some patent connected with munitions of war happens to be held by a foreigner when war breaks out. Well, if we have to make up our minds that we have to depend upon that which we can do in these Isles, only upon that which we ourselves can construct and bring about, we have to look to something a little bit broader than patents: we have to look to food; because the same suggestion about starving a nation out could be quite as readily made as killing our industries by working us out. I know from my own personal knowledge a firm in America who have supplied the British Admiralty and the British War Office with things used on the British guns; and I have seen cheques today to the extent of over £1,200 in connection with these things used during the last six months on British guns supplied from America, and there is not a single British firm connected with munitions of war that will take the patent up or be bothered about it when they have been approached. I could show our friends tomorrow letters from large firms whose attention has been called to these particular things; they mark it "secret" when they examine it, and then they send and tell you they do not need it. Why? It would be a reflection upon some member of their staff if they recognized that a person outside of that staff could do anything better than is there being done, and therefore it is refused. No, Gentlemen, you have to get a little nearer if you want to find the reason for some of the decline of our industries. You have to get a pride in industry as much as a pride in position: you have to make people as satisfied to be concerned in a manufacturing industry as they are to be concerned, say, with the profession of law or with the profession of medicine: they have to be as zealous in their work, and as eager to develop there as their fathers were if they are to hold the trade. The trades that exist today that were formed by good men years ago are only continued today very often by new blood having been brought in, owing to the sons having shown a disinclination to carry on the business; they take their money and clear out. I could give one illustration from Birmingham: the firm, who were fathers of the whole industry of the civilized world in connection with mechanical power, was that of Boulton and Watt, and yet their works in Birmingham were subsequently acquired and became works, not for the great engineering industry, but for the manufacture of scales, and so are used today; while the works on the adjoining piece of ground, employing about 3,000 men, was formed within the last forty years into the great world-wide engineering business of Tangye's, Limited, by four men, two of whom are still alive today. Those men formed an industry and developed it, not solely by their patents, but by their zeal and by their personal industry. The other firm, that had the world at its feet, let the thing go, because those who were to succeed them had not that personal pride and initiative in that which they were doing.

Patents cannot be put upon the same footing as ordinary

articles. A patent is a monopoly, and to talk about free trade in patents is to put one opposite against another. The real remedy for the trouble in connection with the abuse of patents is that, if a patentee does not work it in this country after, say, four or five years, it should be automatically open to people in the trade, who desire to work it, to go to the Patent Office and require a license to be given on reasonable terms—in order that they should work that patent; and then by so working it they would develop and bring from abroad that skill which would enable them to improve that which was originally initiated from abroad.

When the Patent Act of 1907 was being discussed in Parliament I fought it every line in connection with the compulsory working proposals. I pointed out then that the people who were clamoring for it did not know what they were clamoring for—and by and by they would be sadly disappointed, as they have been. I pointed out that they were not aware of the difficulties that inventors had to get their inventions adopted—and I was considered to be a man who was only professionally interested in these things; but, unfortunately, since then inventors and others have found out that this wonderful Act, which was going to bring about such a large amount of extra work for them, has disappointed them, and it has not only disappointed them, but it has disappointed the public to some extent. That Act of 1907 had marvelously good points in connection with it quite outside the compulsory working and quite outside those things connected with that part of the subject that we are now discussing, but those points have been largely overlooked. It was a new charter which was given to the same people who clamored a few years ago under the idea that if they stamped every article when it came into this country with the name of the country from which it came then that would make people demand English things, if they happened to see "Germany" marked on it or "Belgium" marked on it. Those people were then known by some of us to be deluded people and working for a "Will o' the wisp." They got the "Will o' the wisp," and, they did not burn their fingers or get any light, but after they had apparently got it they looked for it, and found it was not there; but what was there all the time was a departing trade that the foreigners had captured owing to the immense advertisement that we had given them by requiring that stamp upon the goods "Made in Germany;" thus making people, when they wanted a cheap article, say: We must go to Germany for it; England cannot possibly do it.

No, Gentlemen, we made a big mistake when we introduced into that Act of 1907 the compulsory working—a very big mistake, as the whole industry now recognizes. The "Inventors' Institute," I am glad to find, recognizes it; I am very glad to find that the commercial people recognize it and I would ask them now to direct their attention to getting a reform, not in the matter of compulsory working, but of automatic licenses, so that if a man does not work it, you can go and demand that you may work it. And if you demand that you shall work it he will then be obliged to come forward to prove that he is already properly commercially working it. That will be a very easy way of getting what our friends there desire, the proof that it is being actually worked, and the opportunity to work it, if the other man is not doing it.

Gentlemen, I have run past my time; but I am very glad to have had the opportunity of speaking. As one who was concerned with that 1907 Patent Act, who was on the committee when it was being discussed, who was present when Mr. Lloyd George received the deputation to which our friend referred, I am glad to be able to point out that that which was then originally declared by me as being something which would be bound ultimately to bring disappointment, has brought disappointment; and tonight here we must remedy it by going on a new path altogether.

THE CHAIRMAN: I am now allowed to call upon Mr. Alexander Siemens to speak to you.

MR. ALEXANDER SIEMENS: *Mr. President and Gentlemen*—What I think about the working of patents I said in a lecture before the Society of Arts some time ago, when I had this honor, that Lord Alverstone was in the Chair and Lord Moulton criticized. I will say at once that both those gentlemen sat upon me and flattened me out. They said I was absolutely wrong. Now I want, all the same, to repeat what I said then. First, I wish to back up Mr. Walter Reid in his statement that the Act of Monopolies originally made an exception in favor of those people who introduced a new industry into England; and I want to protest against giving the dog a bad name and calling it compulsory working. It is not compulsory working. Now, to make my reasoning clear, who is an inventor and what is inventing? According to my notion a man who wishes to improve processes which are in use ought to have a perfect knowledge of the natural laws referring to the subject. He ought to know what has been done before, and especially he ought to know the endeavors to improve some methods which have failed, because you learn more through failures than through successes. I will put everything very shortly, but you know perfectly well what I mean. And he ought also to know what is the demand; in what direction ought improvements to be made.

Now, what I contend is that the inventor, so-called, who is represented in the novels and children's books as going to bed one evening—quite sober, of course—having a lucid idea during the night and getting up the next morning a saviour of society, or a benefactor of his fatherland, and all that sort of thing, does not exist. As I have said already, the people who really can propose improvements which are worth having are those who have to do with the things all the time, who know what they are about and—I am coming presently to a point which displeased Lord Moulton very much—I think it is the manufacturers themselves who know best where the improvements ought to come in, and how to make experiments and conduct their researches in order to effect their purpose. The outsiders have no idea. It is, of course, always a story that medical men were the greatest electricians; look at Volta and Helmholtz, and goodness knows how many more; but if you come to look into it, take the medical profession, they devoted themselves entirely to electricity (I am just taking that example), and, of course, they were capable of suggesting the proper improvements. Now, the outsiders come with all sorts of rubbishy inventions, and it is almost impossible to convince some of them. In that respect, I would only retail to you a saying of Sir William Siemens. He used to say: "I have an appointment with an inventor this afternoon; that means I shall waste two hours of my valuable time, and I shall make an enemy for life" because no inventor ever believes that he is wrong. On the other hand, I want to go a little further about this compulsory working, or putting the thing into practical use. I want to protect the inventor in this way, that if he has introduced his invention so that it is used on a commercial scale, then it shall not be possible to upset the patent by anything but proving that the same thing had been commercially done before and that is really the point. I am sure you are all well acquainted with patents which are fishing patents, which put something, for instance, about wireless. Wireless is in the air: somebody puts down a sort of provisional specification with all sorts of notions, and then he looks afterwards into complete specifications which are dated perhaps later than his own provisional, and when he files his final specification he embodies all sorts of things which he has picked up in the meantime. That such a man should be protected is wrong, and it is really only the practical introduction of an idea (an expression which I prefer to use to compulsory working) which should protect it. If you like to suggest any topic to me whatever, I will suggest at once a patentable idea to improve it, but whether it will work

is another matter, and that is the essential matter. If a novel idea really shows by practical introduction that it is worth having, then it deserves protection, but the mere stating of a novel idea is no good whatever. In support of that statement I would ask you: Do you know many inventions which are worked in accordance with their specifications? I think those of you who are practical people will know that there is hardly any invention which is worked as stated in the final specification. There are always practical modifications, modifications of detail as they call it, but it is the details which are the essential things, and which prove whether the thing is practicable or not, and therefore the working of an idea is the essential thing, and not merely stating something which is beautiful to look at.

THE CHAIRMAN: We are now to have the pleasure of hearing Mr. Oliver Imray, ex-President of the Chartered Institute of Patent Agents.

MR. OLIVER IMRAY: *Mr. Chairman, my Lord, and Gentlemen*—A good many of my views have already been expressed by Sir George Croydon Marks. I fully endorse everything that he says.

Gentlemen, what we have to consider is: What is a patent? A patent is a monopoly; and without the grant of a monopoly of some kind you cannot expect any capitalist, any manufacturer, to introduce a new invention into this country. He must have some sort of protection so that if he puts capital into a patent he is going to have the monopoly for a certain period. Now, Gentlemen, the monopoly granted to a patentee is absolutely absurd as compared with that granted to the author of a book. Further, Gentlemen, a patent can be attacked, first of all on disconformity between the provisional specification and complete specification, on novelty, either prior publication or prior user, on the question of subject matter, on the question as to whether the specification properly describes the invention—there are four or five grounds on which a patent can be attacked. Compulsory working introduces a further ground upon which to attack that patent.

Now, Gentlemen, if you come to think of it, there are 100,000 patents in force, in existence, at any time you like to mention. I have taken out the statistics. I know it for a fact. There are 100,000 patents. What has been the result of the 1907 Act? To take an average, there have been five patents a year revoked on the ground of non-working. For the sake of those five patents a year, you introduce an additional clause for revocation of a patent, or for attacking the validity of it. Is it worth while doing that? I say it is distinctly not. Gentlemen, are inventors to be encouraged? They not only produce an income of over £100,000 a year to the Revenue, but they supply employment for the Patent Office and its officials to the amount of £150,000 a year. Surely you ought to consider an inventor, and do the best you can for him! I have had thirty-five or forty years' experience of, not only the working clauses of this country, but the working clauses all over the world, and I say the compulsory working is a great farce, absolutely. You can always get outside of it.

Now, Gentlemen, I agree that compulsory working to the general public is an absolutely ideal measure. It is supposed to introduce inventions into this country, and to encourage the employment of labor. That is true enough, but the result of compulsory working from my experience, and from the first few actions brought for revocation, was not to introduce the industry into this country, but to revoke the patent, and allow Germans and Belgians, and French people, to dump their goods in this country.

Gentlemen, I hope, if any other legislation takes place, it shall not make the compulsory working clause more drastic, but shall amend it in this sense: that before a person can apply for revocation of a patent on the ground of non-working he should in the first instance say that he has applied for a license, and it has been refused—that is a very good ground; and not only that, but that he is prepared to actually manufacture in this country if the patent be revoked.

THE CHAIRMAN: I will now call upon Mr. A. J. Walter, K.C.

MR. A. J. WALTER, K.C.: *Mr. Chairman, my Lord Moulton, and Gentlemen*—The motion which I apprehend we are gathered here tonight to discuss is the proposal made by the Manchester Chamber of Commerce to the effect that the Association urges upon His Majesty's Government to amend the Rules under the Act of 1907 in such terms as will place the burden of proof of working in this country upon the patentee. A more mischievous resolution I have never had the opportunity of seeing.

What is the meaning of a patent? It is that reward which every State has found it necessary to institute in order to encourage invention. Various countries, Belgium and Switzerland among others, decided that they would have no monopolies. They found that invention dropped off at once, because there was no incentive to inventors to employ their inventive faculty. Compulsory working is dictated by nothing else than the desire of others to destroy the monopoly which the State has given to the man who has made the invention and to enjoy the fruits of that invention. Compulsory working has been suggested purely and simply by the desire to appropriate the brains of others, by persons who have not the intelligence to invent themselves. It is the destruction of the very right which the State has given to the man as a reward for his having exercized inventive faculties.

I have had, perhaps, more experience than anyone in this room of the class of persons who present petitions for the revocation of Letters Patent. I have known no case where petitions have been presented by persons who desired to work the invention in this country. Petitions are always presented by persons who have in some instances initiated manufacture abroad in order to come and present a petition to the Courts of this country so that they may say that there is a greater working abroad than there is in this country, in order, as has been graphically and euphemistically described by an earlier speaker, that they may dump their goods in this country; and I know of no *bona fide* petition presented by any person in this realm for the revocation of Letters Patent for the purpose of encouraging manufacture in this country; but, on the other hand, all petitions have been presented for the purpose of encouraging manufacture abroad, and destroying manufacture in this country.

I am, to a certain extent, with the motion in the sense that a patent is essentially a territorial monopoly presented by the Government of a country to an inventor who has benefited the country by making an invention for which they have granted him the patent, and who, if he is a *bona fide* inventor in the realm, will work that invention without any legislation of any kind or description. My experience is that if a man has an invention that is worth working there are very few commercial people who in time will not ascertain its value and assist him in working it without any legislation of any kind. If it is not worked it is for one of two reasons: either that it is valueless, and therefore had better be left alone, or else that the patent has been obtained by a person not domiciled in this country for the purpose of preventing working in this country, and manufacturing abroad, and importing into this country. I should draw a broad distinction myself in the case of inventors of other countries who take out patents in this country, not to benefit this country, but in order to dump their goods here, and prevent anybody manufacturing in this country. That is one class of harmful monopoly at which undoubtedly legislation might properly be aimed. I would apply that equally to English inventors in foreign countries. If any inventor takes out protection in countries other than his own in order to stop people in those countries working in-

ventions, I would devise measures to see, as Sir George Marks said, that he shall be compelled to grant licenses; but in the case of the inventor in this country who is working in this country, and who has not taken out patents in other countries, or, even if he has taken out patents, is not able to work them there, I would not allow him—as the law at present is—to be liable to have set up against his volume of trade in England the volume of trade in the patented article all over the world, over which manufacture he has no control whatever, and probably knows nothing about—to be put in the pillory to answer questions as to whether or not the manufacture in this country is greater than the manufacture abroad. That is the law in this country on the interpretation of the Act of 1907, a position which I venture to think no sane person can ever have contemplated in Parliament, though the words of it undoubtedly do imply so. Lord Parker held, under the terms of the Act of 1907, that a patentee in this country, having only a patent in this country, could have a petition presented against him for revocation of the Letters Patent if the manufacture abroad, which he neither controlled nor had anything to do with, was greater than the manufacture in this country. I say that to put a patentee in such a position is absolutely unjust. (MR. J. E. EVANS-JACKSON: "Monstrous.")

I have no objection, personally, to a system which would compel a person who takes out any territorial monopoly, the territory being that in which he is not domiciled, to grant licenses, as Sir George Marks says. Supposing a German takes out a patent in his own country and in this country, and does not work the patent in this country at all, but uses England as a dumping ground I should compel him to grant licenses. Similarly, I would compel an Englishman who works in this country, and takes out a patent in Germany, and does not work there, but dumps his goods into Germany, to grant licenses in Germany.

What is the present position of compulsory licenses? It has been my privilege, I think, to be in every compulsory license case which has come before the Courts since the Act of 1888, and what has been my experience with regard to those? There has been no *bona fide* petition presented. It has always been the desire of the "Have-nots" to share in the benefits of the "Haves." Take the great monopolies of recent years: the Dunlop and the Welsbach, where there were huge industries introduced by reason of the patent monopoly granted. In every case the petitions presented against those companies were by persons who made fictitious improvements, not of any value whatever, and who then applied for licenses to work the monopolies of the Dunlop Company and the Welsbach Company. Is that the sort of way in which inventors are encouraged by a country to exercise invention? The conditions under which compulsory licenses are granted should be entirely altered from those which exist at present; and all those persons whom I call the "Have-nots," who desire to share in the blessings of the "Haves," should be by rules prevented from troubling patentees with their desire to reap where they have not sown.

Personally, I object to the whole of this grandmotherly legislation. It is grandmotherly. Commerce will look after itself, and if inventions are worth anything they will be worked, and the industrial members of the community will look after them. It is no good quoting as Mr. Alexander Siemens did, a remark of his great ancestor: "that most inventors wasted a couple of hours of his time." It is quite true that there are so-called inventors of that type; but a man of the ability of anyone of the name of Siemens would in five minutes recognize whether he was dealing with a crank or whether he was dealing with a man who had goods to sell, and if he found that he had got goods to sell, and they were goods in which he dealt, he would very readily make a bargain and deal in them. On the whole, therefore, though, as I say, I do not oppose anything which would prevent patents being used by citizens of other countries to stop working in this country and to assist the dumping of their goods in our country, I think that the whole legislation, both with regard to compulsory licenses and with regard to compulsory working, is a hindrance to trade, and a hindrance to invention, and should be abolished *in toto*.

THE CHAIRMAN: I will now call upon Mr. Douglas Leechman.

MR. DOUGLAS LEECHMAN: *Mr. President, my Lord, and Gentlemen*—So much has been already said that I wanted to say that I shall not trouble you very long. I take it that the object of this Club is to promote the industries of the country, and we will all admit industries are very largely founded upon inventions. Inventions, therefore, should be encouraged, and they should be encouraged in the form of granting Letters Patent, and the Letters Patent should be worked in this country as much as possible. I think everybody wants to see inventions carried into practice and not merely left on paper. Further than that, the patent when granted should be maintained if possible. In that connection I should like to say right away that you are not going to encourage trade or invention or patentees by saying, "Either work your patent or lose it." If you are going to get the benefit out of the inventions that are made by the patentees you must preserve the patents and not hold a pistol at a man's head and say, "Work it or die," because nobody wants, or I will not say nobody, but in very few cases do manufacturers care to take up an invention for which they will have no protection. If a man is to take up a new thing he wants to have some privilege in connection with it.

Now, I should like just to echo Mr. Imray's reference to the extracting of £100,000 a year from poor inventors by the Patent Office. I do think that the Government are not quite doing their duty to inventors in that connection. If they want to encourage the poor inventor, as the present Patent Act is supposed to do, they ought not to say, "You shall pay 9d. for 4d."

Mr. A. J. Walter, K.C., has so amply dealt with the result of these petitions for revocation that I need not dwell upon that subject; but these petitions do not go to promote industry in this country; they throw the invention open to everybody if the petition is granted; and, as I have already said, that does not promote our trade.

Now, the working of inventions should be promoted, and to that extent I am in favor of compulsory working, but not in the form of threatening a man with revocation. If you want to insist upon an invention being worked you should make the inventor grant a license, if he will not work it, or cannot work it himself. The patentee is not a dog in the manger. There may be a very few patentees who are dogs in the manger, but theirs is not a typical case. If I may echo what Sir George Croydon Marks has said, the dog in the manger is the manufacturer. He says, "I do not believe that you have anything better than I have got, but even if you have, I am not going to look at it." He feels that his sense of dignity is lowered if he takes up an outside invention.

What I would advocate would be the simplification of the grant of compulsory licenses. At present we have this extraordinary position. The Comptroller-General will forgive me for likening him to a magistrate. At present the position is that the magistrate may pass the death sentence in the form of revocation; but if you want to commit a man for six months, or whatever the period of the license is, you have to go to a Judge of the High Court. I would like to make compulsory licenses as easily obtained as compulsory working is at the present time. One should file an application with the Comptroller, and he should be able to deal with it. The reason why compulsory licenses have not been popular in the past has probably been because of the difficulty of working the machinery. I should like to see Sections 24 and 27, those relating to compulsory licenses

and compulsory working, amalgamated. One should give the control of the matter to the Comptroller-General, and revocation might come in as a possible alternative. That is to say, if a man refused to grant a license on reasonable terms, then he should be told, "Very well, then you shall lose your patent altogether."

Finally, I should like to say how thoroughly I disapprove of the idea of throwing the onus of proving the "main" and "extensive" and "adequate" and "satisfactory" working in this country upon the patentee, upon the mere allegation of the applicant for revocation to the contrary. If an applicant has not got enough information to make out a *prima facie* case to support his application, then it is not worth much.

THE CHAIRMAN: Mr. H. A. Colefax, K.C., will now kindly speak to us.

MR. H. A. COLEFAX, K.C.: *Mr. Chairman, Lord Moulton, and Gentlemen*—I should like at the outset to express my appreciation of the kindness you have done me in inviting me here this evening. When I received the invitation I was acquainted at the same time with the fact that it was proposed that this question of Compulsory Working should be discussed here tonight. I confess I was a little surprised; because it seemed to me rather as if to discuss that question was an unwarranted interference with what I had regarded as the certain but slow death of an unsatisfactory statutory enactment. However, I discover that in that conclusion I was wrong, because I did not know at the time what I know now, that the Manchester Chamber of Commerce is apparently still on the war path. We know that in large measure the Manchester Chamber of Commerce was responsible for this provision in our statute law that we are discussing tonight. See what it is that they are proposing now. They have got their enactment, and surely, from the standpoint of cheapness and ease with which anyone can come forward and claim on this ground that a patent should be revoked, the provisions in force I should have thought left nothing to be desired; but, apparently, they do not satisfy the Manchester Chamber of Commerce, and they are asking now that there should be an alteration in the rules; and that alteration, I think, we can put quite shortly in this way. They are proposing that when the plaintiff has put forward his case, not proved it, but merely alleged it, then the defendant, the patentee, should be called upon to disprove that case. Well, I venture to think that that is really an unheard-of proposition and would be a gross injustice to patentees in this country and more particularly when one thinks for a moment what is the position under these provisions. We have heard a great deal lately of the common informer, and I cannot help thinking that these provisions which are in force today do really put into the hands of a man, who need be nothing more than a common informer, a right to come to the Patent Office and demand the revocation of the patent. Now, I think it was Mr. Reid at the outset of our proceedings tonight who suggested that these provisions had as their object to give more employment in this country. I do not think that is correct. I remember one of the very earliest cases, and I have been engaged in a good many of them, and I dare mention this case, because although the Comptroller is present, it was not his decision, but the decision of his predecessor. It was a case of this character. There was a patent here for a certain invention, and by an oversight no patent had been applied for in Germany. There was no question that the patent could have been obtained, but by an oversight it had not been applied for. The applicant for the revocation of that patent was a foreigner, who did, I believe, a commission business in the City of London; and his object in applying for revocation was not in any way to give employment in this country except to himself. But what he did seek to do by revoking the British patent was that he might be able to import a German-made machine into this country and so sell it freely. That is one of the very first cases that I remember under this Act.

Something has been said also, I think it was by Mr. Reid, about Imperial unity. I confess that that is a subject that I feel strongly about myself and in every way desire to further. But it does not seem to me that these provisions in any way make for that, because, unless I am mistaken, our Colonies have copied our Act in so far as they have altered their legislation since the 1907 Act has been passed, and in several instances have incorporated into their Statute law provisions exactly similar to those which we have in force in this country; and therefore so far as Imperial unity is concerned it seems to me that it rather makes away from than in favor of that valuable objective.

Now, upon this question I, personally, have not a shadow of doubt. I have had a good deal of experience, and I am absolutely convinced that at present there is no countervailing advantage obtained under these provisions. The path of an inventor is beset with very considerable difficulties and every one of us who has to work in connection with patents, and deal with this question, knows the enormous pitfalls there are in the way of a man who has made an invention obtaining with certainty valid protection for that invention and I venture to think that he ought not to be saddled with these provisions unless it is absolutely clear that there are paramount countervailing advantages, and of those at present I know of no evidence.

One aspect of this question has not been alluded to tonight, and I should like just to mention it, because you will remember that under the Act it is not only possible to apply to the Patent Office for revocation, or by petition to apply to the Courts for revocation, but it is also possible for a defendant to raise by way of defense a plea that the invention the subject of the patent has not been worked in this country. I do not know how many times that defense has been raised, but it is within my own knowledge that it has been raised a great many times. One case I remember in which it was raised—I could cite more than one, but one occurs to me just now, namely, the Vidal Dyes Syndicate *vs.* Levinstein. It is germane to what we are discussing tonight. What happened there is what I think has happened in every case. The defendant was raising among other defenses, that the invention would not give any useful result at all. Well, he very soon found himself in this curious position, that in urging that it had not been worked to an adequate extent in this country as compared with abroad, he was relying upon a defense which conflicted with the plea that the invention could not lead to any useful result. There are many other cases; but I believe that in no single case up to now has that defense ever been presented to a Judge for his consideration or his judgment. So far as the application to the Patent Office is concerned, I, personally, join with what has been said by more than one speaker tonight, and that is this, that this procedure is not a wise one, and if in truth what you want to do is to make it so that a man who is enjoying the monopoly of an invention should either himself put in operation in this country his invention, or that otherwise it should be put into operation, then I feel myself most strongly that the proper and fair course is to alter, if not satisfactory at present, the procedure for compulsory licenses and that by a compulsory license you have the right way to attain that end.

Now, there are only one or two other matters I would just mention before I sit down. Something has been said by my learned friend, Mr. Walter here, about the decision of Lord Parker. I am not questioning its soundness from the standpoint of a legal decision, but I confess that if these provisions are to stand, and that decision is to stand, there is something very wrong in the application of the Act, because I cannot believe myself that it was ever intended that you should on the one hand look at the extent of manufacture abroad and contrast that with the extent of manufacture here, when all the time the

poor unfortunate patentee here may have absolutely no control whatever over the manufacture abroad. Surely, if you are going in any way to endeavor to apply such provisions as these, they ought to be provisions applicable only under these conditions, that what is contrasted is the sale of the article, whether imported or otherwise, in this country, with the extent of manufacture abroad, and nothing beyond that. It is quite true that the patentee at the moment has an offset to that position as decided by Lord Parker, in that he may include among the working in this country the infringing working, which also has always seemed to me a somewhat curious decision. At any rate that is the position of affairs.

Well, Gentlemen, so much has been said upon this that I do not believe I can usefully add more; but I would join with those who take up the standpoint that if we are anxious to see that an invention enjoying a monopoly in this country should be worked here the proper course is by compulsory license, and not by these provisions as to compulsory working.

THE CHAIRMAN: Gentlemen, you will have noticed with very great pleasure, I know, the presence among us of the Right Honourable Lord Moulton. We are very grateful to His Lordship for coming here this evening, and I am grateful to him, and so will you be, that he has consented to address us.

THE RIGHT HON. LORD MOULTON OF BANK, P.C., F.R.S.: *Mr. Chairman and Gentlemen*—I have enjoyed these speeches very much, but there has been a tinge of regret. There was a time when I could have made just as fiery a speech as Mr. Walter and, in fact, there was a little in the swing of his sentences which made me think that perhaps I had not been wholly strange to his education in that matter. But you see I am a tennis player turned umpire, and I have grown to look at strokes with a very much cooler head than I used to in those days when I played, and I have been trying, while this very interesting debate has gone on, to keep myself in the attitude of mind that one tries to keep one's self in when one hears a case: you hear the arguments on both sides and then you give your judgment. It does not follow that your judgment will not be strong. It is quite possible that the case may be so good, or so bad, that you not only use verbs and nouns, but you also use adjectives.

Well, Gentlemen, so far as the legislation as it stands, about compulsory working is concerned, I am afraid I am going to use adjectives. I think it is not only mischievous, it is also idiotic. It is one of those cases which are growing to be common, where the layman rushes into legislation with little or no acquaintance with the subject on which he is legislating. Knowledge has gone so far that the layman cannot keep up with the technical knowledge of a subject, even in politics. In my opinion, it would have been impossible for any man who understood this matter to devise the present legislation.

Now, let us take one example, and remember when you are testing whether a thing is right or wrong by an example, you must never take an extreme example; you must take one which fairly represents it. Let me suppose that a man makes an invention and contents himself by taking out an English patent. The invention turns out to be of world-wide utility; it is adopted, we will say, by every civilized nation in the world: but the inventor has no rights abroad: he has rights in England only. Then comes some person and says, "Your patent is worked mainly abroad." Of course it is. Big as England is, the world outside is bigger. Then he appeals to this legislation, and claims that the patent must be revoked because it is worked mainly abroad. In this he is justified and the consequence is that an invention that is universally valuable and universally appreciated stands in the eye of the legislation of England, as it at present exists, as condemned to death, and it will be revoked unless the poor inventor can explain how it is that a useful thing is used more abroad than it is in England.

It is no use arguing about legislation of that kind. It is self-condemned. We should be wasting our time here, if we discussed whether it should or should not be altered. Accordingly, I prefer to utilize the time in considering what is the real mischief that has driven people to such extravagant and ill-judged legislation. I do not hesitate to say that the very able Minister who fathered that Bill and got it through the House of Commons literally saw red when the word inventor was mentioned. He looked upon this poor harmless set of people as wolves ravening on the unhappy British public. And he apparently is not the only person who does so. I have heard here the representative of a great name quoting the authority of one of the greatest members of his family to the effect that whenever he met an inventor it meant two wasted hours and the making of an enemy. He is quite wrong. I could mention an inventor whom I very often saw, and sometimes was lucky enough to have two hours with. But I neither made an enemy nor wasted my time, for that inventor's name was Sir William Siemens.

MR. ALEXANDER SIEMENS: You are not a manufacturer.

LORD MOULTON: I have seen many inventors, and so many of them are people whose lives are almost eaten up by the idea that they are trying to nourish into usefulness and strength, and I think that if I had one of them before me, and he did not know anything about the legislation as to patents, and I told him, "You know that now they have passed a law for the compulsory working of inventions," he would have said, "Oh, thank God, that is all I want" because he would firmly believe that his idea was such that if it was only worked he would prosper. Such compulsory working of inventions would be the greatest possible boon for an inventor, but the present law as to compulsory working is well-nigh fatal to the chances of remuneration which he would otherwise have. It punishes him for want of success which is not due to his fault. I challenge anyone of those here present, whatever view he takes of this subject, to answer me this question. Did you ever know an inventor (who was not also a manufacturer) who was not eager to have his invention worked everywhere? The mischief that has stirred up people to pass this legislation is that manufacturers, not inventors, stop the use of inventions in this country. Just think of the cases. Do you think that a man who invents a new dye would not like it to be made by Mr. Levinstein as well as everybody else. But it is a different question when a great foreign firm gets it. They do not want to protect the inventor's rights. They want to protect the manufacturer's rights. The consequence is that the whole cause of the outcry is the manufacturer who wants to get a monopoly by means of the rights which we have given to the inventor as a reward for his original thought, and you never find any mischief of the kind that it is supposed we must guard against as long as the patent remains in the inventor's hands. I smile when I hear those who take the opposite side in this controversy talk about the advantage of compulsory working because it brings trade into England and gives work to our working class. Mr. Levinstein is an old friend and an old client of mine, but do you think he conducts his campaign in order to bring the Badische Anilin und Soda Fabrik into England? No, no, no. If you strip the cases of the formal language in which they are put, you will always find that the man who wants to revoke a patent is a manufacturer who wants to prevent the inventor proper from getting the return of his invention. I have said that I never knew any inventor, who kept the interest in his invention in his own hands, who was ever unwilling that it should be worked as largely as possible in every country in the world. Occasionally you may find a crank who puts too high a value on his invention, and will let the few years of the patent pass and his invention remain unused, simply because he thinks that the royalties offered are too low, but those cases are so rare that they may be neglected. No, the applications to revoke patents are not for the purpose of in-

creasing the manufacture in England; they are for the purpose of increasing the importation into England. It is this which makes it so important to give to people clear ideas on the subject. As you know, it is quite possible that the specious appearance of a movement in favor of English manufacturers (and it can be clad in those words) may bring some attempt to increase the severity of the law. This can be resisted only by showing to the world, first of all, that the movement is always from the manufacturer—the inventor has no interest in limiting the use of his patent—and, secondly, that the aim of all these attempts is to increase importation into England, and not manufacture in England.

So much for the real substance of the case. What then is the true remedy? The true remedy is that you ought to protect the monopoly of every inventor who behaves reasonably and punish those only who act unreasonably. If an inventor sells his rights to a foreign manufacturer, and that foreign manufacturer uses the English patent to prevent manufacture in England, a manufacturer who is willing to make the article in England ought to be able to get a license to do it. No patent ought to be used for the purpose of checking work in the country itself. But let me point out the dangers that there are in taking a principle like that and using it without knowledge and without caution. There are many things that are best manufactured by one or two firms. The demand is small for them, and one or two firms can well satisfy it. If you threw it open to hundreds of firms you would get no greater benefit to the country. (A voice: "Less.") Therefore we have adopted the rule, and I think it is a wise one, that the inventor should be left to manage his own patent, fix his own royalties, and get as much from it as he can with his own personal knowledge of the matter. But if he acts so unreasonably that the patent is having the effect of seriously checking working in England, then give the power to the Courts to grant a compulsory license. That is remedy enough, and I should counsel you not to do anything else whatever. If you do you will find that all you are doing is to help people to take the ideas of the inventor without giving any fair return, and to help people who manufacture abroad to import their goods into this country without remunerating the inventor. We do not want to see that, because we desire to see English manufactures increase, for we feel that we have a growing working population. We are glad to welcome new industries to develop in our midst; but, if we try to bring that about by unjust laws, you may be perfectly certain you will do more harm than good, and ultimately you will regret it.

MR. ALEXANDER SIEMENS: Mr. Chairman, may I say one word about what Lord Moulton said with reference to my remarks about Sir William Siemens? Sir William Siemens was interviewed by an inventor, who wanted him to pay him money, but when Sir William Siemens interviewed Mr. Fletcher Moulton, as he was at that time, he was consulting a barrister.

THE CHAIRMAN: It is interesting that the next name on my list is that of the Hon. Hugh Fletcher Moulton, and I will ask him to address us.

THE HON. HUGH FLETCHER MOULTON: *Mr. Chairman and Gentlemen*—The Chairman's conduct explains something for which the reason at first was not obvious and that is why it was not he but somebody else who was called on to say grace. Obviously, this was on account of his lack of scriptural knowledge, for there are certain things which you learn in the Scriptures and one is: Do not first place your old wine before your guests and then the new, because truly they will say the old is better. I very strongly object to the order in which the members of my family have been called on.

With regard to the subject of the debate I will say this: the whole of my natural instincts are in favor of compulsory working. On the other hand, the whole of my trade knowledge shows me how useless it is.

Now I have a great deal of sympathy with the principle of introducing working in England, but I do feel that with regard to the means for accomplishing this we shall find again that the old is better. The old idea of introducing a new manufacture was to give it a monopoly, to protect it from competition. I am a believer in Free Trade; I am a believer in the principle that it is a good thing to give a healthy baby a cold bath; but I am not a believer in the principle of exposing a baby, who has been judicially found to be in a weakly state, under Niagara, and it seems to me that, when you find a manufacture is being wholly or mainly practised abroad, to say that the best way of introducing it into England is to destroy the protection of monopoly, is an utter fallacy.

The gentleman who opened this debate has appealed to the Colonies. I also appeal to the Colonies, and I say we might very well follow them. Take the case of Australia. In the case of Australia they did not wholly reject the assistance of men who knew something about the Patent Law. There is a gentleman present here tonight who had a great deal to do with the drafting of the Australian clause. And what did they draft? They drafted a law which provided that in the case where a patent was not sufficiently worked there you could get a compulsory license. That ought to be the principle here. That enables the manufacture to be introduced here under the protection of a monopoly. Even in an extreme case, if you wanted to say to the patentee that he is to forfeit his whole right, I should say that he ought to forfeit it to the Crown and that the Crown should keep the monopoly and grant licenses to British manufacturers rather than to say: This industry is established abroad and we are going to abolish all possibility of introducing it here under the protection of a monopoly.

There is one thing we have been discussing, *viz.*, the proposals of the Manchester Chamber of Commerce, and nobody has ventured, perhaps in courtesy to the opener and to those who support him, to refer to the provisions of the Bill prepared by them. I propose to break through that convention. This new change is supposed to be in the interests of business men. I wonder how many people here have read the Bill which the Manchester Chamber of Commerce wish to introduce. (MR. J. E. EVANS-JACKSON: "Not one.") One of the proposals is, that if anyone has a patent, a common informer can come forward and say, "I believe this is being worked more abroad than it is in this country; I call upon the firm to produce the whole of its books and demonstrate to us that it is not"—a pleasant prospect for a really business firm. Here is another of the proposals: Any contract in reference to any patented article is to be filed with the Attorney-General for publication. I wonder how many business firms would have supported that provision if for one moment they had understood what it meant? I do not want to be severe on our friends here, but I do feel that we have a duty to the business community and one of those duties is to protect it from its so-called friends. Now, Gentlemen, time is nearly up, but there is one thing for which I am going to thank the opener from a purely personal point of view, and that is, for referring to the glass industry in Germany. Why I am glad he referred to it is because it refers to a project which is very near my own heart and because there are at least two members of the London County Council here. Anybody who knows anything about why the German glass industry is so prosperous knows that it is because of the munificent sums which have been spent in Jena in cultivating research in optical glass. For some ten years that same project has been before the County Council in London, and I ask our friend, Mr. Urquhart Fisher, to weigh those remarks and see that they are brought to a practical conclusion and to found that optical institute which has been promised for so many years.

I only ask our friend who opened the debate to consider whether the opinion of so many people who pass their lives in

close touch with inventions ought not to be considered—whether it ought to be brushed aside as interested or whether he ought not to feel that there may be something in it and that perhaps the best interests of the inventors and the best interests of trade generally will not be served by those who "see red," but by those who think how best to introduce an industry to England without unduly penalizing inventors.

THE CHAIRMAN: Mr. J. Hunter Gray will perhaps speak.

MR. J. HUNTER GRAY: *Mr. Chairman, Lord Moulton, and Gentlemen*—The description Mr. Walter Reid gave us of his visit to the President of the Board of Trade reminded me of the gentleman who had a slight headache from time to time and who went to a specialist and asked him what was the best and absolutely safe cure. The specialist said, "If you get your head taken off you may be quite sure you will never have a headache again." I suggest that the section which is now under discussion was drafted on those principles.

For my sins I have had a very close association with the litigious aspect of this section from the time it became law, and I think I may say that without exception the applicant for revocation under this section was, so far as I remember, in every case a foreigner, and in no case had the applicant any intention whatever of manufacturing in this country. It is the greatest satisfaction to me to hear tonight that the master of the last two generations in the theory and practice of patent law agrees with the opinion, so far as I can gather, of the whole of this meeting, that this section can be detrimental only to invention in this country.

I want to tell you one experience, and I assure you it is not the only one (there are some here who can corroborate what I say) that I had not very long ago where an application was made under the following circumstances: A well-known motor firm was asked to give an advertisement to a particular paper, the circulation of which was stated to be 10,000, but which circulation, on inquiry, was found to be a free circulation. Naturally enough, the motor firm did not think it desirable to give an advertisement at the price asked; whereupon this particular paper informed the firm that they would apply to revoke the patents, and the result was that there were some ten or twelve—I forget the number, someone here will correct me—applications, costing 1s. each, applying to revoke the corresponding number of patents. These applications were filed in due course. Under the then practice of the Patent Office it would have been the duty of this particular firm, who are carrying on a very large business in this country, and a very profitable business both for the public and for themselves, to disclose all their books, to say what their sales were and to say to whom they sold; but, fortunately, some of us were determined that we would find out what the particular applicants knew. It cost them, I think, 14s. to make the applications. I may tell you that the capital of the Company that made the applications was 2s. paid up. Upon that it was thought proper by those who advised the patentees to object to putting in any evidence disclosing their sales, where they made them, or where they got their patented articles. The result was that these applicants, on being asked to appear before the Comptroller of Patents, decided that rather than be cross-examined they would drop the applications. But, in the meantime there had appeared all over the country advertisements about the size of one wall of this room: "10,000 motorists involved; 20 patents to be revoked." And that was the sort of thing that was exhibited all over the country.

This Section of this Act of Parliament stands today as it did then; fortunately for the public, fortunately for inventors, the High Court and the Patent Office have thought fit to make it necessary that any person who applies to revoke a patent should put forward a *prima facie* case. But, nevertheless, difficulty remains as regards the High Court because there the procedure is entirely different from that of the Patent Office. I say that the Section is an un-English Section in an English Act of Parliament; because it introduces, for the first time, the principle that a person is guilty until he proves his innocence. In any other proceeding of any kind a person is presumed to be innocent until he is found guilty; but a patentee is a criminal; he is a person who is to be loathed; he is to be attacked and he is put on his trial; he has to prove that he is an innocent man before there has ever been any evidence that he is guilty. I submit to the industry—there are many members of the industry here—that this section only requires to remain long enough to not only seriously affect invention in this country, but to ruin it. There can be no question that, although there may be thousands of perfectly useless inventions which are made by private inventors, there is the one in a thousand which is enormously valuable. One knows that the difficulties of inventors apart from this section are enormous at present, but when you have the added difficulties of compulsory working, an inventor having once been put to the trouble of having to spend £5, £10, £15, £20 or £100 on an application to revoke his patent by a foreign firm who knows nothing whatever about him, will never invent again.

In my view the position is amply covered by the 24th Section of the Act which says that anyone who wants to work a patent is entitled to apply for a compulsory license. I agree that in the past that provision in the previous Acts was a difficult one. It was provided under the jurisdiction of the Privy Council. One knew that was an expensive and a difficult proceeding. Now it is in the hands of the High Court and there is no difficulty. Every single thing that any honest person wants in order to work a patent can be got by a very simple, comparatively inexpensive method by applying for a license. It seems to me that it is perfectly ridiculous to have a section for compulsory working in view of the fact that you can apply for a compulsory license under Section 24.

THE CHAIRMAN: I am certain that you will all agree that this discussion will not be complete without our hearing the views of our Honorary Secretary, Mr. Evans-Jackson, on the subject.

MR. J. E. EVANS-JACKSON: *Mr. President, my Lord, Gentlemen, and Fellow Members*—I am quite certain you will all agree with me that the President has made a great mistake and that he ought to have closed the proceedings without calling upon the Honorary Secretary to say anything. At the same time, in the few minutes remaining, I would just like to make one or two remarks on a subject with which I am closely connected. Last year, at the Congress of the Associated Chambers of Commerce in Antwerp, I was able to carry, by a large majority, a vote of the delegates postponing the discussion on compulsory working until this year. At the last meeting of the Associated Chambers held in March last, and I have here to confirm me in what I say, Mr. Dunwoody, who is the Secretary of the Associated Chambers and Mr. Wright, who is the Secretary of the Birmingham Chamber, *viz.*, that the delegates of the various Chambers went to that Congress pledged as to the way in which their votes were to be recorded. That, to my mind, is rather an extraordinary sort of business. You have what is called the Associated Chambers of Commerce, meeting in the greatest city in the world, listening to the arguments of the greatest experts on various subjects that this and other cities can find. The delegates have put before them every argument for and against, I do not care which side it is; but when the discussion is finished the delegates have to hold up their hands in accordance with a decision which has been given probably a month before in their respective Chambers. Mr. Dunwoody, who is the Secretary of the Associated Chambers of Commerce, is here and he will confirm that what I say is correct. Now I ask whether a decision given in a meeting like that is to carry any weight with the authorities. The decision is given before the arguments are placed before the delegates.

Now, Gentlemen, on this question of compulsory working

I suppose it will probably be admitted that I have possibly some small professional experience (over thirty years); but I am putting myself tonight in the position of a business man and a man representing, to some extent, the commerce of England; and I am going to ask you this question, and it is a serious one: Whether Great Britain will benefit by the fact that John Smith, an inventor of a horseshoe, the most meritorious and extremely beneficial horseshoe, and who applies for a patent in London, also applies for patents in forty foreign countries, Germany, France, Belgium, Austria, etc. Is it to the advantage of British commerce that that inventor should be compelled to erect forty factories, one in each of forty foreign countries, to make those horseshoes, or is it more to the advantage of this country that he should manufacture the whole lot here at a cheaper rate and send them abroad?

Now, what is my point there? Of course, you do not know. I am going to put it to you. We are going to compel John Schmidt, a German, who has invented a horseshoe in Berlin, and who has taken out a patent in forty countries, including Great Britain, to build a factory here to make those horseshoes. The thing is purely illustrative of the argument as to manufacturing certain articles. We compel one foreigner to manufacture in this country the quantity required for use of this country alone, while we lay ourselves open by retaliation on the part of foreign Governments to be compelled to manufacture in forty countries the invention which has been thought out in this country.

Now, the point which appears to me to be essential is whether it is beneficial to secure the wages to the working class in manufacturing one foreign invention here and to lose the wages (which would otherwise be paid here) by being compelled to manufacture goods to meet the requirement of forty countries of a British invention abroad. Now, put it purely as a commercial and a business proposition: Ask Mr. Gordon Selfridge or Mr. Gamage or any thoughtful business men and see what they will say to you. I imagine the reply would be that the proposition was a most foolish one.

Well, I should like to say in conclusion that this question, if it is going to be carried any further with us, means retaliation. I said that at the Chamber of Commerce the other day. It has met with retaliation already. What was the effect of passing that Compulsory Working Act? The United States of America never had any compulsory working: Germany had. The moment we passed that Act in England, Germany approached the United States and completed a treaty whereby working in the United States was equivalent to working in Germany, and working in Germany was equivalent to working in the United States. Since then a similar treaty has been enacted between Germany and Switzerland, Germany and Italy, Germany and Spain, and Germany and Sweden. Now take Switzerland. Up to the time that we passed that Act here, working in any country was working in Switzerland. Now a British inventor must work his invention in Switzerland, otherwise his patent is liable to be revoked. Previous to that Act all he had to do was to work in Great Britain. Now we have under that Act no power whatever to negotiate with the United States, with Germany or with Italy and get equal conditions with those which have already been arranged and signed and sealed between the United States and Germany and other countries. I think it is neither more nor less than monstrous that Great Britain is not in a position to negotiate on reciprocal terms with other countries and say, "If you will let our people off working in your countries we will let your people off working here."

Then the last word I have to say is this, that, if any further change is made in our law at all, it should be this, that a petitioner should be compelled to go to the Comptroller and say, "I am prepared to work this patent in Great Britain, and that is the ground on which I ask that the patent shall be revoked if it is not already worked." And I should insist that in any rules or in any laws which are made in future no foreigner should come here and be allowed to revoke a patent solely for the purpose of dumping foreign goods into Great Britain.

MR. OLIVER IMRAY: Gentlemen, I just want to say this one word. I ought not to speak a second time, but it has come to my knowledge only today that the German people, in view of the Manchester Chamber of Commerce agitation for a more drastic interpretation of the present law as to the working, have approached their Government to retaliate. That is all I want to say.

MR. W. TEMPLE FRANKS, C.B., Comptroller-General of Patents: *Mr. Chairman, Lord Moulton, and Gentlemen*—It is my great pleasure and privilege to ask you to drink a toast which is not upon the list, but which none the less I think you will drink with every kind of enthusiasm and honor, and that is the toast of our Chairman tonight, Sir George Wyatt Truscott. On behalf of the guests I should like to offer him my most grateful thanks for the delightful hospitality which this Club has afforded to us and for the opportunities given us of hearing one of the most interesting debates.

As the unhappy man who has to decide the cases which have been so much discussed tonight, and whose only pleasure in that position is to hear the eloquence of my old friend, Mr. Walter, and of Mr. Colefax, and Mr. Gray, I have not been able to take part in the debate, but none the less it has been a debate fraught with the greatest interest to me and one which may have real educational influence upon those who may have in the future to decide what amendments, if any, should be made to the present Act. Whether it will be possible at any time to bring in an amending Bill to the present Act lies, I think, with my friend, Sir George Croydon Marks and his party. At present it is almost impossible to introduce legislation of that kind.

I can assure you that the substance of what has fallen from the speakers tonight, and especially from Lord Moulton, whose genius has left its mark upon all the legislation and practice in respect of industrial property in this country, will certainly be conveyed by me to the Board of Trade. The only thing I feel it possible to say in this connection is this, that I hope if any amendment is made that it will not throw further and more arduous duties upon me. The problems I have to decide at present are quite complicated enough for me and for my poor intellect; and when I confide to you that the Copyright Act has been entrusted to my care, you will understand that my time is sufficiently taken up with difficult legal problems.

If I intervene at all in the discussion, it is only to say that there may be, perhaps, between the contending parties a happy line of peace, and that is this: I understand the supporters of the present Section lament the fact that the applications for revocation of patents have enormously fallen off, and maintain in consequence that the Section is a dead letter. In that case the opponents of the Section ought really to be satisfied. On the other hand, I think it is quite possible that the mere presence of the Section, even in its present form, does assist to bring about a result which many most earnestly desire, and that is a greater willingness on the part of patentees to grant licenses with regard to patents. I only throw that out as a possibility. In any case, the debate, if I may venture to say so, has been to me of the most interesting and delightful kind, and I can only convey again my thanks to the President for allowing me the privilege of being here. I am sure I am speaking on behalf of all the other visitors here, and I ask you to drink with the greatest enthusiasm and cordiality the health of our Chairman.

THE CHAIRMAN: *My Lord and Gentlemen*—When Mr. Temple Franks first rose and addressed us I came to the conclusion that he was introducing entirely foreign matter and that I should have to call him to order; but he went on to redeem the situation and to make a very pretty contribution to our discussion here tonight. I should like to thank him on behalf of the Club for the compliment of appreciation which he has paid to us and which I very gratefully acknowledge.

# ORIGINAL PAPERS

## PURIFICATION OF SEWAGE BY AERATION IN THE PRESENCE OF ACTIVATED SLUDGE

By Edward Bartow and F. W. Mohlman

Received March 12, 1915

In a paper[1] read before the Illinois Section of the American Water Works Association, November 11, 1914. it was stated that experiments in the purification of sewage by aeration in the presence of activated sludge were to be carried on in the laboratory of the Illinois State Water Survey at the University of Illinois. With the advice of Professor G. J. Fowler of the University of Manchester, the experiments are following the lines described by Ardern and Lockett.[2] While we have tried to avoid a repetition of the work of Ardern and Lockett, we have found it necessary to repeat some of the experiments described by them in order to familiarize ourselves with the process, to obtain the necessary activated sludge and to study the reactions involved.

We are studying the necessary mechanical devices, the physical, chemical and biological conditions of the process and the properties of the sludge.

Since Ardern and Lockett have abandoned, for the present, experiments with continuous flow devices, we also are confining our experiments to an intermittent system. Our first experiments were made using bottles of three gallons capacity. Later, we constructed a tank 9 inches square and 5 feet deep. This tank has plate glass front and back to permit easy observance of the condition of the sewage and sludge. A porous plate was placed 4 inches above

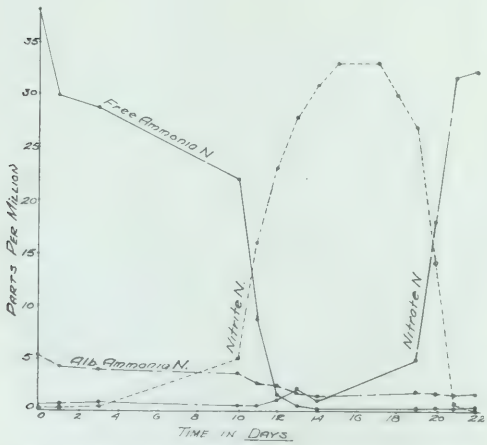


Fig. I—Nitrification of Sewage. No Activated Sludge Present

the bottom. An inlet for air and an outlet for any water which might pass through the plate were provided in the space below the plate. Compressed air furnished by the University power plant is used. All air is measured through an ordinary gas meter. The purified sewage is removed by means of a siphon. Experiments have been carried out in the laboratory at room temperature, thus far, with no special precautions to regulate the temperature.

For our experiments, sewage from the city of Champaign is used. It is collected from a point in the main

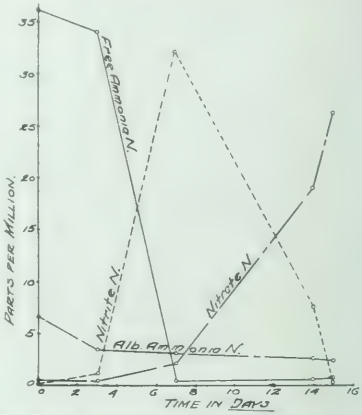


Fig. II—Nitrification of Sewage. No Activated Sludge Present Uniform Distribution of Air through Porous Plate

sewer at the edge of the city, at least two miles from the outfall. When taken it is fresh. Average analyses indicate that it is a fairly strong, domestic sewage. It contains no trade wastes.

### Aeration of Raw Sewage Without the Addition of Sludge

Air has been blown into five separate portions of sewage until complete nitrification was accomplished. To show the progress of the reaction, tests for free ammonia, nitrites and nitrates were made at intervals during each treatment. The time required for complete nitrification has varied from 15 to 33 days. The best result was obtained in the tank, where the air was distributed through the porous plate. For all analyses, samples of the supernatant liquid were taken after one hour settling without filtration. In each case, the *free ammonia* nitrogen was almost quantitatively changed to *nitrite* nitrogen, then the *nitrite* nitrogen in turn was changed almost quantitatively to *nitrate* nitrogen. This change is illustrated in Table I, A and B and Figs. I and II.

The formation of nitrate in the tank was accomplished in 15 days with the use of 4830 cu. ft. of air.

### Aeration of Raw Sewage with Sludge

The supernatant liquid was siphoned off and a fresh portion of sewage added to the sludge. In this, the second treatment, the effect of a small amount of sludge is very nicely illustrated by the reduction of the time required for complete nitrification from 15 to 4 days, and the reduction in the amount of air used from 4830

[1] "Observations of Some European Water Purification Plants and Sewage Disposal Works," *Jour. A. W. W. A.*, March, 1915.

[2] *J. Soc. Chem. Ind.*, **33**, 523–39, 1122–4.

to 1270 cu. ft.: 34 parts per million of free ammonia nitrogen in the raw sewage produced 23.8 parts per million of nitrate nitrogen in the supernatant liquid.

TABLE I—NITRIFICATION OF SEWAGE: WITH AND WITHOUT SLUDGE

| Date | Time Days | Parts per Million Nitrogen as Free $NH_3$ | Alb. $NH_3$ | Nitrites | Nitrates |
|---|---|---|---|---|---|
| A—No Activated Sludge Present | | | | | |
| Dec. 18, 1914 | 0 | 38.00 | 5.20 | 0.07 | 0.37 |
| 19 | 1 | 30.00 | 4.20 | 0.02 | 0.38 |
| 21 | 3 | 28.80 | 4.00 | 0.11 | 0.45 |
| 28 | 10 | 22.00 | 3.60 | 5.00 | 0.20 |
| 29 | 11 | 8.80 | 2.60 | 16.00 | 0.40 |
| 30 | 12 | 1.60 | 2.40 | 23.00 | 1.00 |
| 31 | 13 | 0.36 | 1.88 | 28.00 | 2.00 |
| Jan. 1, 1915 | 14 | 0.16 | 1.48 | 31.00 | 1.00 |
| 2 | 15 | —— | —— | 33.00 | —— |
| 4 | 17 | —— | —— | 33.00 | —— |
| 5 | 18 | —— | —— | 30.00 | —— |
| 6 | 19 | 0.28 | 1.92 | 27.00 | 5.00 |
| 7 | 20 | 0.44 | 1.84 | 14.00 | 18.00 |
| 8 | 21 | 0.28 | 1.68 | .30 | 31.70 |
| 9 | 22 | 0.24 | 1.60 | .05 | 31.95 |
| B—No Activated Sludge Present: Uniform Distribution of Air through Porous Plate | | | | | |
| Jan. 4 | 0 | 36.00 | 6.60 | 0.01 | 0.71 |
| 7 | 3 | 34.00 | 3.40 | 1.20 | 0.60 |
| 11 | 7 | 0.40 | 3.00 | 32.00 | 2.00 |
| 18 | 14 | 0.60 | 2.60 | 7.50 | 18.50 |
| 19 | 15 | 0.80 | 2.20 | 0.10 | 25.90 |
| C—Activated Sludge Present (1 Sludge: 5 Sewage): Uniform Air Distribution | | | | | |
| | Hours | Free $NH_3$ | | | |
| Feb. 24, 1915 | 0 | 27.00 | | 0.05 | 0.59 |
| | 1 | 13.00 | | 2.40 | 6.00 |
| | 2 | 8.20 | | 2.80 | 10.80 |
| | 3 | 3.70 | | 3.40 | 15.00 |
| | 4 | 0.20 | | 2.60 | 18.60 |
| | 5 | 0.20 | | 0.30 | 22.10 |

The supernatant liquid was again siphoned off, fresh sewage added and aeration continued. In this, the third treatment, nitrification was complete in two days and but 720 cu. ft. of air were used: 33 parts per million of free ammonia nitrogen produced 22.3 of nitrate nitrogen. In the twelfth treatment the purification was completed in less than 8 hours with the use of less than 128 cu. ft. of air and 36 parts per million as free ammonia nitrogen produced 29.5 parts per million of nitrate nitrogen. In the thirty-first treatment with sludge and sewage in the proportion of 1:5, purification was complete in less than 5 hours: 35 cu. ft. of air were used, equal to 0.20 cu. ft. per sq. ft. of surface area per minute, or about 3 cu. ft. per gallon of sewage. We have not yet attempted to determine the minimum amount of air required.

Samples taken at the end of each hour of aeration during some of the treatments have been tested for stability. A sample taken at the end of one hour aeration in the thirty-first treatment had not decolorized methylene blue at the end of twelve days. Since in one hour nitrification was not complete, it is, therefore, evidently unnecessary to obtain complete nitrification in order to obtain a stable effluent. Since it is impossible to separate the oxidized liquid entirely from the sludge it is probable that the stability is promoted by the oxidizing action of the nitrate in the residual liquid.

The progress of nitrification in the presence of activated sludge is apparent. The results are shown in Table IIIC and Fig. III. From this and from other series of analyses it is indicated that there is no quantitative conversion of free ammonia to nitrite, followed by oxidation to nitrate, but that nitrates are formed simultaneously with nitrites.

The number of bacteria were determined during one treatment. Samples were taken after one hour settling. The raw sewage showed a bacteriological content of 750,000 per cc. The supernatant liquid after aeration and settling one hour showed but 20,000. Further tests are planned. These we expect will include the determination of species.

Through the courtesy of Professor Frank Smith, Professor of Systematic Zoölogy of the University of Illinois, biological examinations have been made of the sludge. Among the microscopic animals found are many Vorticella and Rotifera, but the predominant organism is an annelid worm, known as *Aeolosoma hemprichi*. This organism is about 2 to 5 mm. long and quite slender. It abounds in various kinds of freshwater bodies where there is an abundance of decaying organic material, and thrives especially well where there is much fermentation and in waters contaminated with sewage, provided there is an abundance of oxygen. It belongs to a group of worms in which reproduction occurs very rapidly by asexual methods. A fission zone is formed near the middle of the body of the parent worm and develops the head of one daughter worm and the tail of the other, and thus two

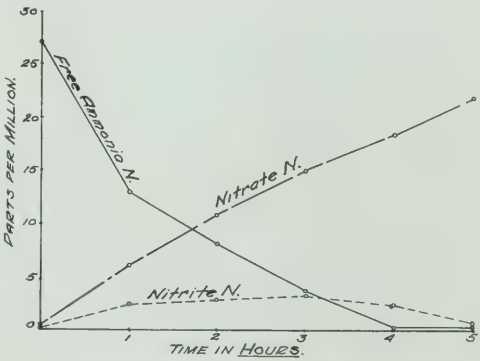


FIG. III—NITRIFICATION OF SEWAGE. ACTIVATED SLUDGE PRESENT. 1 SLUDGE: 5 SEWAGE.

new worms are formed from one. This requires not over two or three days and is repeated for an indefinite number of generations. It feeds greedily and almost continuously on any small organic particles that it can obtain and presumably destroys at least its own weight of organic matter every day and probably more. Because of the mode of reproduction, it takes but a short time to produce extensive colonies with great capacity for the destruction of organic material.

SLUDGE—The activated sludge has evidently been developed by the multiplication of these worms originally present in the sewage, and the species found at varying points might differ. The sludge does not have an unpleasant odor, due to the fact that it consists largely of living organisms. If kept for a long time in a moist condition without air, it will putrefy.

COMPOSITION OF SLUDGE—Analyses of the sludge made by Hatfield have shown the following results: After drying first on the water bath and then for three hours in an oven at 100° the loss, or moisture, was 95.54 per cent. The dried material contained 6.3

per cent nitrogen, 4.0 per cent fat, 1.44 per cent phosphorus (equivalent to 3.31 per cent $P_2O_5$) and 75 per cent volatile matter by loss on ignition.

From this chemical data the dried sludge would evidently have value as a fertilizer. If we calculate the value as 20 cents per lb. of nitrogen and 12 cents per lb. of phosphorus, it would have a market value of $29.00 per ton. In order to determine whether the theoretical value would correspond to the actual value, pot cultures have been started. Portions of dried sludge were added to two pots, an equivalent amount of nitrogen from dried blood to a third, and nothing to a fourth. At the end of 18 days the cultures containing the dried sludge show better growths than the culture containing an equivalent amount of nitrogen from dried blood and far better growth than the culture to which no additional nitrogen was added.

A plant to operate on a larger scale is under construction and the authors propose to continue the experiments.

STATE WATER SURVEY, UNIVERSITY OF ILLINOIS
URBANA

## A COMPARISON OF THE RELATIVE DRYING POWERS OF SULFURIC ACID, CALCIUM CHLORIDE AND ALUMINUM TRIOXIDE WHEN USED IN ORDINARY SCHEIBLER DESICCATING JARS[1]

By J. W. MARDEN AND VANNA ELLIOTT

Received January 28, 1915

In spite of the many objections put forward to $CaCl_2$ and $H_2SO_4$ for ordinary desiccating purposes, these substances are still quite generally used. Nearly every analyst knows from experience that if a perfectly dry sample of coal, for example, is placed in a desiccator containing $CaCl_2$, which has been used for some time, or concentrated $H_2SO_4$, the coal will increase in weight. When the desiccator is opened some moisture enters from the atmosphere, to be sure, but not enough to account for the increase in weight of the coal.

As compared to the wide use to which $H_2SO_4$ and $CaCl_2$ are put as drying agents for organic substances which cannot be heated, the literature on the subject is meager. The desiccating efficiency of several substances like $CaCl_2$, Na, fused NaOH, $P_2O_5$, etc., has been tried. Baxter and Warren[2] tried $CaBr_2$, $ZnBr_2$ and $ZnCl_2$ by passing moist air over them. They found that $H_2SO_4$ was more efficient than any of these. Johnson[3] has published a note on the use of $Al_2O_3$ as a desiccating agent in which it is claimed that $Al_2O_3$ is more effective than $H_2SO_4$ for removing moisture from air saturated with water vapor.

In the hope of suggesting a good substitute for the time-worn $CaCl_2$, if not for $H_2SO_4$, in ordinary desiccation, the present work was undertaken. Also, a series of experiments with $H_2SO_4$ has been run to show the effect of the concentration of the acid on drying certain substances, and it is hoped that the results will throw some light on the vagaries of $H_2SO_4$ as a desiccant. Many analysts seem in doubt regarding the total amount of moisture that is obtained by $H_2SO_4$ drying; some have the opinion that they get all but two- or three-hundredths of one per cent in most cases, while others think that they obtain very much less than that percentage of moisture. At best, any drying method with $H_2SO_4$ can be only an arbitrary one. Since this is an old subject, most of the experimental work for this paper is given in abstract.

Many experiments have shown that from certain substances all of the moisture cannot be obtained by the ordinary $H_2SO_4$ drying method at 25° C. A sample of pure sugar syrup, for example, containing 49.89 per cent moisture, mixed with ten times its weight of sand, yields an average of about 48.17 per cent moisture. With maple syrup, even with vacuum, the same condition is observed. The percentage of moisture obtained by $H_2SO_4$ drying is less than that obtained by the refractive index or by heating at 100° C. This behavior of sugar, although somewhat exaggerated, is typical of the behavior of other substances. The water-vapor pressure of some materials still containing residual moisture is as low as that of the $H_2SO_4$ over which they have been dried. It has been shown that considerable amounts of $H_2SO_4$ distil off in vacuum, and for this reason Gore[4] suggests the use of CaO for high vacuums. By graphic interpolation, concentrated (95%) $H_2SO_4$ has a vapor pressure of about 0.03 mm. at 25° C.

According to Thorpe[2] the speed of drying is hastened but no more moisture is obtained by the use of vacuum. In a series of trials with cheese, syrup, coffee, etc., using both $H_2SO_4$ and $CaCl_2$, slightly more moisture was obtained with vacuum than without.

In one instance it was as much as 0.7 per cent and in other cases quite small.

The effect of a fairly large variation in the concentration of $H_2SO_4$ changes the total amount of moisture removed from some substances very slightly; in other cases, however, the change is marked. Table I shows the results obtained with flour, cane-sugar syrup and cheese dried to constant weight over various concentrations of $H_2SO_4$. Each sample for each concentration was dried in an individual desiccator.

TABLE I—EFFECT OF CONCENTRATION ON DRYING POWER OF $H_2SO_4$
Atmospheric pressure and laboratory temperature
Total time of drying: about three weeks

| Per cent $H_2SO_4$ | Vapor pressure mm. of Hg (approximate) | PER CENT WATER IN White flour | Cane syrup | Cheese |
|---|---|---|---|---|
| 95 | ( 0.03)? | 12.48 | 48.28 | 26.51 |
| 84.8 | 0.18 | 12.28 | 48.25 | 26.10 |
| 78.3 | 0.8 | 10.04 | 48.27 | 25.58 |
| 65.6 | 2.7 | 7.22 | 48.10 | 24.88 |
| 62.6 | 3.5 | 2.89 | 47.97 | 23.47 |
| 37.0 | 15.0 | 0.10 | 47.30 | 21.18 |
| 29.6 | 17.5 | ... | 34.70 | ... |
| 21.9 | 20.0 | ... | 22.01 | ... |
| 15.2 | 21.0 | ... | 0.29 | ... |
| 7.0 | 22.5 | ... | 49.4 (increase in weight) | |
| Per cent moisture found by drying at 100° C. to constant weight.. | | 11.85 | 49.78 | 26.65 |
| Polariscope..... | | ... | 49.89 | ... |
| 100 per cent(*a*) $H_2SO_4$..... | | 12.55 | 48.28 | 26.65 |

(*a*) Values obtained by plotting percentage moisture against percentage $H_2SO_4$.

It will be seen from Table I that cane syrup could be dried about as well, although, as laboratory ex-

[1] This work was started in the laboratory of the South Dakota State Food and Drug Department.

[2] *J. Am. Chem. Soc.*, **33** (1911), 340

[3] *Ibid.*, **34** (1912), 912.

[4] *J. Biol. Chem.*, **15**, 259–61.

[5] "Dictionary of Applied Chemistry," Vol. II, p. 210 (1912). Longmans, Green & Co.

perience showed, not as quickly, over 75 per cent as over 100 per cent $H_2SO_4$. With cheese the percentage of moisture obtained over 100 per cent $H_2SO_4$ is about the same as that by drying to constant weight at 100° C. Flour shows another example of the increase in weight of some materials on heating, due to a certain amount of oxidation. Skertchly[1] has pointed out inconsistencies of this kind which he found while drying biscuits.

As has been suggested by several authors, exposing a substance over varying concentrations of $H_2SO_4$ and finding the concentration at which it neither gains nor loses weight indicates the concentration of $H_2SO_4$ which has the same vapor pressure as the material. In this way flour had a vapor pressure of about 15.0 mm. and cane-sugar syrup of about 21.0 mm.

Hempel[2] has shown that the rate at which substances dry depends upon the rate at which water vapor is transferred. Since air saturated with water vapor is less dense than unsaturated air, Hempel puts the $H_2SO_4$ in the upper part of the desiccating jar. Similarly, if air currents can be formed in the jar, the drying will go much faster. To show this point, samples of maple syrup were dried over 95 per cent $H_2SO_4$ at room temperature in two desiccators; in one a small motor was introduced and the air stirred vigorously during the experiment. In one and one-half hours as much moisture was removed with stirring as was removed without stirring in six hours.

Several portions of $Al_2O_3$ were prepared for comparison with the other desiccants. The $Al_2O_3$ used in the preliminary trials was prepared from "technical" $Al_2(SO_4)_3$ by dissolving the salt in water and precipitating the $Al(OH)_3$ with $NH_4OH$. The aluminum hydroxide was filtered off and dehydrated in the glass tube of a combustion furnace with the smoky flame. The $Al_2O_3$ employed in the later experiments was made in the same way, except that "C. P." $Al_2(SO_4)_3$ was used in the preparation and the $Al(OH)_3$ was washed many times to remove any impurity which might lead to erroneous results.

Preliminary experiments comparing $Al_2O_3$ with $CaCl_2$ showed that in nine days at laboratory temperature and pressure, a sample of coffee yielded 0.2 per cent more moisture over $Al_2O_3$ than over $CaCl_2$. In the same length of time a sample of sugar yielded the same weight of moisture over either. The percentage of moisture in this case, however, was very low. Trials were made, also, by placing weighed dishes of $Al_2O_3$ over $H_2SO_4$ and $H_2SO_4$ over $Al_2O_3$ to see which would increase in weight more rapidly. The moisture introduced by opening the desiccator was enough to vitiate the results somewhat, but the $Al_2O_3$ increased in weight faster than the $H_2SO_4$. The following table shows the percentage of moisture obtained with three common materials dried over the three desiccants and kept in a thermostat at 25° C. Each percentage shown is the average result of duplicate experiments in individual desiccators over the same weight of desiccant.

[1] *J. Soc. Chem. Ind.*, Jan., 1913.

[2] *Ber.*, **23** (1890), 3566.

TABLE II—PERCENTAGES OF MOISTURE BY DIFFERENT DESICCANTS

| Substance | Flour | | | $CuSO_4.5H_2O$ | | | Coffee | |
|---|---|---|---|---|---|---|---|---|
| | $H_2SO_4$ 95 per cent | | | $H_2SO_4$ 95 per cent | | | | |
| Time Days | $Al_2O_3$ | $H_2SO_4$ | $CaCl_2$ | $Al_2O_3$ | $H_2SO_4$ | $CaCl_2$ | $Al_2O_3$ | $CaCl_2$ |
| 1 | 8.42 | 8.42 | 8.47 | 14.12 | 15.08 | 15.22 | 1.31 | 1.17 |
| 2 | 9.51 | 9.56 | 9.21 | 18.76 | 19.47 | 16.84 | 1.98 | 1.82 |
| 3 | 10.30 | 10.33 | 10.06 | 23.73 | 25.51 | 21.31 | 2.66 | 2.38 |
| 4 | 10.67 | 10.61 | 10.35 | 28.11 | 28.74 | 25.40 | 3.11 | 2.92 |
| 5 | 11.08 | 10.96 | 10.62 | 29.36 | 29.46 | 28.77 | 3.30 | 3.11 |
| 6 | 11.21 | 11.13 | 10.75 | 29.43 | 29.45 | 29.32 | 3.44 | 3.22 |
| 7 | 11.46 | 11.33 | 10.96 | 29.53 | 29.54 | 29.42 | 3.54 | 3.32 |
| 8 | ... | ... | ... | ... | ... | ... | 3.66 | 3.46 |
| 10 | ... | ... | ... | 29.53 | 29.54 | 29.42 | .. | .. |
| 11 | 11.75 | 11.64 | 11.15 | ... | ... | ... | .. | 3.46 |
| 13 | 11.75 | 11.64 | 11.15 | 29.53 | 29.54 | 29.42 | .. | .. |

The time values in Table II are given roughly in days, which intervals are close enough to show the points in question. Some of the moisture in the blue vitriol was lost in grinding the sample.

The work in Table II was repeated in vacuum desiccators at a pressure of about one-tenth atmosphere and at laboratory temperatures. As before, three substances, flour, blue vitriol and tea, were dried over the three desiccants. Although there was some difficulty in obtaining desiccating jars with the same power for "holding" the vacuum, the average results were in the same order as in the above table. For small amounts of moisture $Al_2O_3$ appears to be somewhat superior to either $H_2SO_4$ or $CaCl_2$, when used in this way, while with $CuSO_4.5H_2O$, which has a larger percentage of moisture, there seems to be but little choice between $Al_2O_3$ and 95 per cent $H_2SO_4$. $CaCl_2$ seems to be inferior to either of the others. It is possible that $H_2SO_4$ methods of drying may give better results when the acid has frequent agitation, and when two or three charges of fresh acid are added during a determination. $Al_2O_3$ has the further advantages that one need not guard against slopping, burns, etc., as when using $H_2SO_4$ and that this oxide can be reheated when it becomes saturated with water and used again and again.

UNIVERSITY OF MISSOURI, COLUMBIA

## THE OLEORESIN OF SAND PINE

By A. W. SCHORGER

Received December 28, 1914

The sand pine (*Pinus clausa*, Sarg.) is practically confined in its range to the State of Florida. It is a small tree whose branches extend to the ground, the height being usually 15 to 20 feet, while a diameter of 1 foot is rarely exceeded. The material examined was obtained on the Florida National Forest from near Ocala, Florida.

OLEORESIN—The oleoresin contained considerable water and small trash of such a nature that an unusually low-grade rosin for virgin "gum" was obtained. Analysis gave the following results:

| | Per cent |
|---|---|
| Volatile oil | 18.93 |
| Rosin (Grade G) | 72.30 |
| Trash | 2.67 |
| Water | 6.10 |

VOLATILE OILS—The volatile oils obtained from two samples of oleoresin were practically identical. Their properties were as follows:

| | $d_{15}^{15°}$ | $n_{D15°}$ | $a_{D20°}$ |
|---|---|---|---|
| (1) | 0.8725 | 1.4768 | —22.49 |
| (2) | 0.8723 | 1.4767 | —22.80 |

On fractional distillation with a 12-inch Hempel

column, 60 per cent of the oil distilled between 161° and 165°, and 35 per cent between 165° and 167°. The above data show that the volatile oil is entirely different from ordinary gum turpentine.

IDENTIFICATION OF CONSTITUENTS

α-PINENE—Repeated fractionation yielded 48 g. (9.6 per cent) boiling between 157° and 160° and having the constants $d_{15°}$ 0.8656, $a_{D20°}$ —30.17°. The oil gave a low yield of pinene nitrosochloride, which was transformed to the nitrolpiperidine compound melting at 119°.

CAMPHENE—Between 160° and 162°, 50.5 g. (10.1 per cent) of oil were obtained having the following properties: $d_{15°}$ 0.8671, $a_{D29°}$ —29.31°. The oil was treated with a mixture of glacial acetic acid and sulfuric acid in the usual way. The oil recovered by steam distillation after saponification would not crystallize on cooling in a freezing mixture. On distilling the oil and rejecting the portions boiling below 190°, the residue readily crystallized on cooling. After removing the crystals with the aid of a force filter and recrystallizing four times from petroleum ether the isoborneol melted at 207–209°, resolidifying on slow cooling at 208°. A fifth crystallization did not raise the melting point.

β-PINENE—The β-pinene fractions constituted about 75 per cent of the oil, so that this terpene is the major constituent. A portion of the β-pinene was oxidized with alkaline potassium permanganate. Ten grams of the sodium nopinate obtained yielded on further oxidation 2 grams of nopinone whose semicarbazone melted at 189°.

Since the oil consisted so largely of β-pinene it was thought possible to isolate this terpene in a fairly pure state. After 10 fractionations over metallic sodium, two fractions were obtained that showed fairly constant boiling points. Below will be found the properties of the two fractions and of one of the synthetic β-pinenes prepared by Wallach:

| | B. p. | $n_{D20°}$ | $d_{20°}^{20°}$ | $[\alpha]_D$ | M found | Calculated for $C_{10}H_{16}$ |
|---|---|---|---|---|---|---|
| (1)..... | 164–165° | 1.4772 | 0.8700 | —26.00° | 44.19 | 43.54 |
| (2)..... | 165–166° | 1.4784 | 0.8709 | —23.73° | 44.23 | 43.54 |

Wallach's[1] synthetic β-pinene:

| B. p. | $n_{D22°}$ | $d_{22°}$ | $a_D$ | M found | Calculated for $C_{10}H_{16}$ |
|---|---|---|---|---|---|
| 163–164° | 1.4724 | 0.8660 | —22° 20′ | 44.13 | 43.54 |

Fraction 2 was about four times as large in quantity as Fraction 1. The values obtained for all the constants are higher than those recorded by Wallach, and this had been the author's general experience in the examination of various essential oils in which β-pinene was the chief constituent. To determine whether this condition was due to the presence of camphene, 50 g. of Fraction 2 were treated with the mixture of glacial acetic acid and sulfuric acid. No isoborneol, however, could be detected.

ROSIN—The rosin, grade G, had an acid No. of 172.5 and a saponification number of 178.7. It yielded 4.01 per cent of resene soluble in petroleum ether.

The rosin crystallized very readily from acetone or alcohol. After ten crystallizations from acetone, the crystals obtained began to soften at 147°, melted at 150–151°, and were completely liquid at 157°. Another portion of the rosin was first crystallized twice from alcohol containing 10 per cent concentrated hydrochloric acid and then recrystallized repeatedly from 95 per cent alcohol. When allowed to crystallize slowly the abietic acid was obtained as large triangular crystals. The crystals finally obtained began to melt at 157–158° and were completely liquid at 167°. Using an alcoholic solution the abietic acid had the specific rotation $[\alpha]_D$ —85.46° calculated from the following values:

| | | |
|---|---|---|
| $a$..... | 6.74° | $p$ 9.433 |
| $l$..... | 1 | $d$ 0.8357 |

The silver salt was obtained by neutralizing an alcoholic solution of the acid with sodium hydroxide and adding the calculated quantity of $AgNO_3$ in a large volume of alcohol. The silver salt was filtered off, washed repeatedly with alcohol, then with ether and dried at 70°. Analysis of the silver salt follows:

0.4685 g. silver salt gave 0.1234 g. Ag = 26.34 per cent Ag
Calculated for silver abietate, $Ag(C_{20}H_{29}O_2)$, 26.37 per cent Ag

CONCLUSIONS

The volatile oil of the sand pine (*Pinus clausa*, Sarg.) has approximately the following composition: *l*-α-pinene, 10 per cent; *l*-camphene 10 per cent; *l*-β-pinene 75 per cent; losses by polymerization, etc., 5 per cent.

The "rosin" contains 4.0 per cent resene while the remainder consists mainly of abietic acid.

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[1] *Ann.*, **363** (1908), 1.

## THE CONDITIONS OF NATURAL GAS IN THE EARTH'S STRATA[1]

By GEORGE A. BURRELL

Received November 28, 1914

In this paper are recorded some observations and experiments regarding the liquid or gaseous occurrence of natural gas in the earth's strata. This question has been a subject for conjecture in the past, but to date, in the case of most natural gases, no exact data have been available from which to draw definite conclusions, because the exact composition of natural gases has not been known. Knowing (1) the composition of a natural gas, (2) rock pressures that prevail in natural-gas strata, (3) temperatures that prevail in natural-gas strata, and (4) the temperature and pressures that are necessary for the liquefaction of the gaseous paraffin hydrocarbons, one can obtain evidence regarding the liquid or gaseous occurrence of natural gas in the earth. The vapor pressures of some of the paraffin hydrocarbons are shown in the following tables. The data were taken from Landolt and Börnstein's "Physikalische Chemische Tabellen."

The results of a complete analysis including the quantity of each paraffin hydrocarbon as found by liquefaction and fractionation follows. For compari-

[1] Paper presented at the Spring Meeting of the American Chemical Society, Cincinnati, Ohio, April 6–10, 1914, by permission of the Director of the Bureau of Mines.

TABLE I—VAPOR PRESSURES OF SEVEN PARAFFIN HYDROCARBONS

| NAME | Formula | Boiling point ° C. | Critical temperature ° C. | Critical pressure Lbs. | Critical pressure Atmos. |
|---|---|---|---|---|---|
| Methane | $CH_4$ | —160 | —99.5 | 735 | 50 |
| Ethane | $C_2H_6$ | — 93 | 35 | 662 | 45 |
| Propane | $C_3H_8$ | — 45 | 97 | 647 | 44 |
| *N*-Butane | $C_4H_{10}$ | 1 | .. | ... | .. |
| *N*-Pentane | $C_5H_{12}$ | 36.4 | ... | . | .. |
| *N*-Hexane | $C_6H_{14}$ | 68.4 | ... | ... | .. |
| *N*-Heptane | $C_7H_{16}$ | 98.4 | ... | ... | .. |

TABLE II—VAPOR PRESSURES OF METHANE, ETHANE AND PROPANE

| METHANE(*a*) Atm. Pr. at ° C. | | ETHANE(*a*) Atm. Pr. at ° C. | | PROPANE(*a*) Atm. Pr. at ° C. | |
|---|---|---|---|---|---|
| 50 | — 95.5(*a*) | 45.3 | 35(*a*) | 44 | 97(*a*) |
| 26.3 | —105.8 | 32.3 | 15 | 9 | 22 |
| 21.4 | —110.6 | 23.3 | 0 | 7.1 | 12.5 |
| 11 | —126.8 | 18.3 | —11 | 4.8 | — 2 |
| 6.2 | —138.5 | 14.5 | —21 | 2.7 | —19 |
| 2.24 | —153.8 | 11 | —31 | 1.8 | —33 |
| 1 | —165(*b*) | 1 | —93(*b*) | 1 | —45(*b*) |

(*a*) Critical constants. (*b*) Boiling point.

son, the results of a eudiometric analysis of the natural gas are also included:

TABLE III—ANALYTICAL RESULTS OBTAINED BY TWO METHODS

| PERCENTAGES | Liquefaction and fractionation | Eudiometric analysis |
|---|---|---|
| Methane | 84.7 | 79.2 |
| Ethane | 9.4 | 19.6 |
| Propane | 3.0 | .. |
| Butane (chiefly) | 1.3 | .. |
| Nitrogen | 1.6 | 1.2 |
| Totals | 100.00 | 100.00 |

Included in the above analysis is 0.03 per cent carbon dioxide. It is scarcely necessary to state that the eudiometric determination shows only approximately the quantity of hydrocarbons in a natural-gas mixture.

From the fractionation analysis and other data one can calculate the pressures that would be required to liquefy the different constituents at particular temperatures. To start the liquefaction of the methane there would be required a pressure of at least $\left(\frac{100}{84.7}\right)735 =$ 868 lbs. per sq. in. at —95.5° C. That is, in order to put 735 lbs. pressure on the methane there would be required a pressure of 868 lbs. on the mixture; as liquefaction proceeded and the partial pressure of the methane decreased proportionally greater pressure would be required to continue the liquefaction.

To liquefy the ethane there would be required a pressure of at least $\left(\frac{100}{9.4}\right)662 = 7064$ lbs., at 35° C. To liquefy the propane at 97° C., there would be required a pressure of $\left(\frac{100}{3.0}\right)647 = 21{,}567$ lbs. These calculations were made at the critical temperatures and pressures of the paraffin hydrocarbons. The critical constants for butane have not been determined.

Earth temperatures increase about 1° C. for each 60 or 70 ft. of depth. This is a thermal gradient that has been determined by measuring temperatures in many bore holes, although increases in temperatures different from the foregoing have been determined by some investigators. If the initial temperature is 20° C., and an increase of 1° C. for each 70 ft. takes place, strata at a depth of 2000 ft. (not an uncommon depth for a gas well) should have a temperature of 48° C.

Methane may be dismissed as ever occurring in the liquid condition because even at —95.5° C. there is required a pressure of at least 735 lbs. per sq. in. to liquefy it when it occurs in the pure state. Mixed with other gases, so that its partial pressure is less than one atmosphere, there are required proportionally greater pressures at any particular temperature.

The critical temperature of ethane is 35° C., which is not far from gas-strata temperatures. However, the pressures required to liquefy the ethane in Pittsburgh natural gas at the critical temperature is 7064 lbs. and is far above gas-strata pressures. It is questionable whether pressures as high as 1500 lbs. have ever been measured in a gas well. 1000 lbs. per sq. in. is high.

The vapor pressure of liquid propane at 22° C. is 132 lbs. (9 atmospheres). Vapor pressures at temperatures closer to gas-strata temperatures than this have not been determined. To liquefy the propane in Pittsburgh natural gas at 22° C. there would be required a pressure of $\left(\frac{132}{3.0}\right)100 = 4400$ lbs. This is also a pressure much greater than is found in natural-gas strata.

Vapor pressures of butane at different temperatures other than the boiling point have not been determined. At 1° C. (boiling point) there would be required a pressure of about 1153 lbs. to liquefy the butane in Pittsburgh natural gas. At higher temperatures there would be required greater pressures. Hence, the butane in Pittsburgh natural gas can also be dismissed as occurring in the liquid condition in the earth.

In view of the above considerations, it can be stated that the essential constituents of Pittsburgh natural gas never occur in the strata in the liquid form, because rock pressures are not high enough, rock temperatures are not low enough, and the quantities of the more easily condensable constituents in the gas mixture are not great enough for this condition. The natural gas used in Pittsburgh is typical in composition of gas that is supplied to many cities to the extent of billions of cubic feet per year.

The condition of natural gas in the earth is of importance, for, if present therein as a liquid, it would be possible for a single subterranean reservoir to furnish a much larger supply of gas than if present in the gaseous condition. The foregoing vapor pressures and percentage composition of the gas are also instructive as showing the pressure that would have to be applied to liquefy the various constituents in a compressor plant.

As somewhat different from the natural gas mentioned above, which is contained in rock strata under heavy pressure, there may be mentioned those natural gases that issue from the casing heads of oil wells under slight pressure, or are withdrawn from the casing heads at pressures less than atmospheric. These gases frequently contain, besides some of the gases already mentioned, enough of the vapors of the liquid paraffin hydrocarbons to warrant the installation of a plant for the condensation of gasoline.

The question arises as to the liquid or gaseous condition of these casing-head gases in the earth. The quantities of the more easily liquefied gases are much higher than in the so-called dry gases, but, on the other hand, the pressures in the rock strata from which they issue or are drawn are almost invariably much lower,

so that the chances of them occurring in the liquid condition are small. No account is taken herein of gases that are closely associated under heavy pressure with oil in the sands. Under such condition there is a solution of gases in the oil to a great extent. The natural gas used in Pittsburgh is not associated with oil in the earth's strata.

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## THE ANALYSIS OF CHROME YELLOWS AND GREENS

By A. Given

Received January 22, 1915

From inquiries received at this laboratory, it appears that the determination of the composition of chrome yellows and chrome greens is not well understood in many color and paint works; and the excellent publications of the Bureau of Standards on the analysis of inks help only in a degree. The method here given is the result of a great deal of work and experience with these colors, and has given excellent satisfaction.

### METHOD

MOISTURE AND LEAD CARBONATE—Weigh out accurately about 1 gram of the yellow or green into a small beaker, and dry for 4 hours at 105–110° C. Calculate the loss in weight as water. Add 50 cc. of 50 per cent acetic acid to the dry substance in the beaker, mix thoroughly, and let stand over night. Filter through a tared Gooch, wash with hot water, dry, cool and weigh. Calculate the loss from dry weight as lead carbonate.

LEAD SULFATE AND CHROMATE—Weigh out accurately about 1 g., wash into a 250 cc. beaker, add 50 cc. water and 50 cc. of 25 per cent caustic soda and boil for 5 or 10 minutes. Filter through a tared Gooch, wash thoroughly with hot water, cool the filtrate and make up to 250 cc. Save the residue. To 50 cc. of the solution add an excess of hydrochloric acid and 5 cc. alcohol and boil until the chromate is reduced to chromic chloride. Add an excess of barium chloride, boil, let settle, filter on an ashless paper, wash, burn and weigh as barium sulfate. Calculate to per cent lead sulfate.

To 50 cc. of the above solution add an excess of nitric acid, heat to boiling and add 25 cc. boiling saturated solution of potassium bichromate. Boil 1 minute, let settle, filter through a tared Gooch, wash, dry and weigh. Calculate as per cent lead chromate. From this amount subtract the lead sulfate and lead carbonate, both calculated to lead chromate, and call the difference actual lead chromate present.

RESIDUE—Fill the Gooch containing the residue from the solution for lead sulfate and chromate with hot 1 : 1 hydrochloric acid, let stand 10 minutes, filter and wash with hot water. Repeat twice, wash thoroughly, dry and weigh. Calculate remaining residue as per cent barytes or china clay according to base.

PURE BLUE—The sum of all the previous determinations is subtracted from 100, and the difference called pure blue.

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## THE UTILITY OF SULFUROUS ACID AND PURE YEAST IN CIDER VINEGAR MANUFACTURE

By W. V. Cruess, J. R. Zion and A. V. Sifredi

Received January 4, 1915

A study of methods of alcoholic fermentation of apple juice destined to be made into vinegar in various California factories showed that in almost every case no attempt was made to control the microörganisms of fermentation. A brief description of the various ways of handling the cider stock will no doubt be of interest.

In one of the largest factories the cull apples and peels and cores from apple driers are ground or "grated" in an Ohio apple grater as soon as received. The juice is pressed out with heavy screw presses driven by a motor and cog gearing with a capacity of 60 tons per day. The juice goes to 20,000 gallon tanks. The first tank of the season is started with a large starter of compressed yeast. When this tank is in fermentation, about one-third of its contents is used to start the next tank. The third tank is started from the second, and so on through the whole series of tanks. Over 500,000 gallons are made in this way during a season. Examination of the fermented juice showed it to be "dry;" that is, practically free from unfermented sugar, but it was shown by microscopical examination to contain large numbers of lactic acid bacteria and the large tanks soon developed a heavy growth of *mycoderma* (wine flowers) after alcoholic fermentation. The lactic bacteria develop a "mousey" flavor and the mycoderma rapidly oxidizes alcohol to $CO_2$ and $H_2O$ without forming any corresponding amount of acetic acid.[1] Laboratory tests demonstrated that mycoderma isolated from cider was capable of destroying all of the alcohol of a fermented orange juice containing 4.5 per cent alcohol in three weeks. The gravity of heavy mycoderma growth may be seen from these figures.

Another large factory stores its cull apples, peels and cores in a large wooden bin. Often this material undergoes a fermentation, resembling silage fermentation, before it can be crushed. The juice after crushing and pressing is allowed to undergo spontaneous fermentation in 30,000-gallon tanks. Wild yeasts, lactic bacteria and mycoderma develop profusely, giving a very cloudy cider. Occasionally a tank "sticks" with some unfermented sugar, but in general the fermentations are complete.

A third factory (until 1914) crushed its apples and allowed the crushed apples to undergo spontaneous fermentation 3 or 4 days before pressing. This method gave a high yield of juice, due to the softening effect of the fermentation. Beginning with this season, this factory used pure "Burgundy" wine yeast on the crushed apples with good results. The yeast was propagated according to *Bulletin* **230** of the University of California Experiment Station. No sulfurous acid is used on the crushed apples, consequently the fermented cider shows a strong tendency to develop mycoderma.

The above factories all use the generator process

[1] A. V. Sifredi, Thesis for M. S., Univ. Calif., Dec., **1914**.

for converting the alcohol to acetic acid. A fourth factory making 50,000 to 75,000 gallons per year uses the slow process throughout. Fermentation is allowed to take place spontaneously with the result that lactic acid bacteria, as well as mycoderma, grow vigorously in the fermented cider. There are also a few fermentations that "stick," *i. e.*, stop before the sugar is completely transformed to alcohol.

On account of these obvious defects in present methods, the experiments described below were carried out to see if the beneficial effects of pure yeast was added. It took three days to fill the 30,000-gallon tank. By the time the tank was full in each case, fermentation had progressed so far that no attempt at a fermentation record was made. Table II shows the effects due to the sulfurous acid and pure yeast: gain due to pure yeast and $SO_2$ was found by subtracting 15.20 from 16.27 to give difference in sugar = 1.07 per cent. This was divided by 1.7 to get its alcohol volume per cent equivalent as it is considered that 1.7 per cent sugar gives 1 per cent alcohol in practice. This figure, 0.73 per cent, subtracted from 2.05 gives

TABLE I—RESULTS OF EXPERIMENTS WITH SULFUROUS ACID AND PURE YEAST IN BARREL TESTS

| FERMENTATION RECORD BARREL A (NATURAL FERMENTATION) | | | FERMENTATION RECORD BARREL B (PURE YEAST AND $SO_2$) | | | ANALYSES OF BARRELS A AND B | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Date | Balling | Observations | Date | Balling | Observations | Sample | Balling (Brix) | Total acid as acetic | Total reducing matter as sugar | Alcohol per cent by vol. |
| Sept. 5 | 16.0 | Filled barrel A | Sept. 5 | 16 | Filled barrel B and added $SO_2$ | Original juice | 16.0 | 0.60 | 15.00 | 0.00 |
| Sept. 8 | 13.5 | Fermenting vigorously | Sept. 6 | 16 | Racked into another barrel and added 2 per cent by volume of pure Burgundy yeast | | | | | |
| Sept. 13 | 5.0 | Fermenting slowly | Sept. 8 | 14 | Fermenting vigorously; taste clean; aroma much cleaner than "A" | Barrel A Jan. 9 | 0.0 | 0.84 | 0.55 | 6.20 |
| Sept. 19 | 3.0 | Fermenting very slowly | Sept. 30 | 1 | Fermenting slowly; microscope shows absence of wild yeasts or bacteria of any kind | Barrel B Jan. 9 | 0.0 | 0.61 | 0.037 | 8.00 |
| Sept. 30 | 3.0 | Strong "mousey" flavor: many lactic bacteria | | | | Barrel A Apr. 5 | ... | 1.18 | 0.60 | 5.60 |
| Oct. 13 | 3.0 | | | | | | | | | |
| Jan. 9 | 0.0 | Still tastes sweet | Jan. 9 | 0 | Taste clean and dry. Much clearer than "A" | Barrel B Apr. 5 | ... | 5.90 | ... | 2.56 |

and sulfurous acid obtained with wine fermentation in 1911[1] could be duplicated with apple juice fermentation.

## SMALL SCALE FERMENTATIONS

Two barrels of the same juice were taken. Barrel "A" was allowed to ferment naturally; barrel "B" was treated with potassium metabisulfite ($K_2S_2O_5$) at the rate of 12 oz. per 200 gallons or approximately 175 mg. $SO_2$ per liter. It was allowed to stand 24 hours; was then drawn off into another barrel and pure "Burgundy" wine yeast was added. A summary of the two fermentations appears in Table I and may be stated as follows:

1—Increase of 1.8 per cent alcohol.

2—More complete fermentation of sugar.

3—Elimination of wild yeasts and lactic bacteria; probably due to action of $SO_2$ during first 24 hours.

4—More rapid clearing of the cider and the vinegar.

5—Improved and cleaner flavor.

6—More rapid acetification after alcoholic fermentation.

## 30,000-GALLON FERMENTATIONS

A 30,000-gallon tank (No. 10—Table II) of apple juice was filled with juice from culls, peels and cores during a pressing period of three days. Samples were taken during filling and analyzed for Balling degree, alcohol and total acid. The juice was allowed to ferment spontaneously and was handled by methods ordinarily used in this factory.

A similar 30,000-gallon tank (No. 16) was filled with similar juice. Before going to the large tank, each 1,000 gallons as it came from the press was held temporarily in a 1,000-gallon vat and treated with 8 oz. metabisulfite per 200 gallons. This was added from a solution of 8 oz. metabisulfite per gallon in water. The first 2,000 gallons to go into the large tank were started with 100 gallons pure "Burgundy" yeast and left till next morning before any more juice

[1] F. T. Bioletti and W. V. Cruess, University of California Expt. Sta., *Bull.* 230.

1.32, the "net increase" in alcohol due to pure yeast.

The results of the large scale fermentation were satisfactory, showing a very material increase in al-

TABLE II—RESULTS OF 30,000-GALLON TANK TESTS

Results in Percentages

| | Tank No. 10. Natural fermentation | Tank No. 16. Pure yeast and $SO_2$ |
|---|---|---|
| BEFORE FERMENTATION: | | |
| Total solids + (alcohol × 1.7). Average of samples | 15.20 | 16.27 |
| AFTER FERMENTATION: | | |
| Total acid as acetic | 0.568 | 0.652 |
| Volatile acid as acetic | 0.160 | 0.108 |
| Extract | 3.70 | 3.60 |
| Alcohol: Volume per cent | 6.35 | 8.40 |
| CALCULATIONS: | CALCULATIONS | |
| Difference in total solids + (alcohol × 1.7) in tanks 10 and 16 | 1.07 | |
| Alcohol equivalent to difference in total solids | 0.73 | |
| Difference in alcohol in fermented liquids | 2.05 | |
| Net gain in alcohol due to pure yeast and $SO_2$ | 1.32 | |

cohol due to pure yeast and sulfurous acid. Microscopical examination showed that the pure yeast and sulfurous acid gave a much cleaner fermentation than the natural fermentation.

## SUMMARY

The use of pure yeast and sulfurous acid in barrel fermentations gave increased yield of alcohol, more complete fermentation of the sugar, a better flavor, more rapid clearing, a fermented liquid practically free from lactic bacteria and *mycoderma vini*, and a more rapid change of alcohol to acetic acid after alcoholic fermentation. This indicates disappearance of practically all of the active sulfur dioxide because acetic bacteria have been shown to be very sensitive to it. Large scale fermentations with pure yeast and sulfurous acid gave an increased yield of alcohol and a cleaner fermentation. Examination of several factories shows the extreme need of some method of control of alcoholic fermentation, and to supply this need the use of small amounts of sulfurous acid to eliminate wild yeast and the addition of pure selected yeast to give a rapid and complete fermentation seems the most practical means of producing the desired results.

ENOLOGY LABORATORY, EXPERIMENT STATION
UNIVERSITY OF CALIFORNIA, BERKELEY

# THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH AND SCHOOL OF SPECIFIC INDUSTRIES OF THE UNIVERSITY OF PITTSBURGH

## THE DEDICATION OF THE NEW BUILDING OF THE MELLON INSTITUTE

By W. A. Hamor[1]

The new $350,000 building which now forms the permanent home of the Mellon Institute of Industrial Research and School of Specific Industries of the University of Pittsburgh, was formally dedicated on February 26, 1915. This building, the gift of Messrs. Andrew William Mellon and Richard Beatty Mellon, of Pittsburgh, who consented to allow their family name—an illustrious one in the annals of Pittsburgh—to be placed upon it, possesses the strength and force characteristic of the Grecian Doric order and is distinctly modern in construction and equipment, having been especially designed by the architect, Mr. J. H. Giesey, for the needs of the Institute.[2]

Fig. 1—The New Building of the Mellon Institute of Industrial Research and School of Specific Industries

The Chancellor of the University, Dr. Samuel Black McCormick, presided at the dedication ceremonies, which took place at 11.00 A.M. in Soldiers' Memorial Hall, in conjunction with the annual Charter Day exercises of the University. Following the address of the day by Dr. Rossiter Worthington Raymond, the dean of American mining engineers, on "Knowledge and Research," which is reprinted in full below, Dr. W. J. Holland, Director of Carnegie Museum and formerly Chancellor of the University, made the presentation speech in connection with the dedication of the Mellon Institute, on behalf of Andrew W. Mellon and Richard B. Mellon, the donors. After a brilliant eulogy of the Messrs. Mellon and a splendid tribute to their generosity, Dr. Holland said in part:

"In a certain sense, Mr. Chancellor, this building is a memorial to Robert Kennedy Duncan. On one side of the entrance is a bronze slab inscribed with the name of Thomas Mellon; on the other side of the entrance is a bronze slab inscribed with the name of Robert Kennedy Duncan. But, Mr. Chancellor, this splendid edifice erected upon the campus of our University is more than a cenotaph. It not merely commemorates the names and careers of those of whom I have spoken, but it is intended to serve as the seat of advanced inquiries along scientific lines, which will tend to the promotion not merely of intellectual culture, but of industrial success, and that not merely in this great 'workshop of the world,' where it is located, but throughout the land. In creating this institution our dear friends have been actuated by a high and intelligent purpose. Large experience in great industrial enterprises has taught them the importance of chemistry and physics in their applications to the industrial arts, and they feel that, wonderful as has been the progress made within the last century, there are untold mysteries in nature, which have not yet been revealed but which, if uncovered, are capable of being used for the welfare of mankind. And so

[1] Assistant to the Director of the Mellon Institute.

[2] See the description which follows.

they have created and are today placing in the custody of you, gentlemen of the Board of Trustees, this institution, which is capable of becoming, when wisely and intelligently administered, a mighty implement for the advancement of human welfare."

Dr. George Hubbard Clapp, President of the Board of Trustees of the University, delivered the speech of acceptance. He expressed appreciation of the gift and understanding of the importance of the work for which the building has been erected.

The final ceremony of the exercises was the conferring of fifteen honorary degrees, as follows:

DOCTOR OF LAWS

EDWARD WILLIAMS MORLEY, Honorary President of the Eighth International Congress of Applied Chemistry.

JOHN ULRIC NEF, Head of the Department of Chemistry of the University of Chicago.

ARTHUR AMOS NOYES, Professor of Theoretical Chemistry and Director of the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

ROSSITER WORTHINGTON RAYMOND, Secretary Emeritus of the American Institute of Mining Engineers

IRA REMSEN, Former President and Emeritus Professor of Chemistry, Johns Hopkins University.

THEODORE WILLIAM RICHARDS, Professor of Chemistry and Director of the Gibbs Memorial Laboratory, Harvard University.

DOCTOR OF SCIENCE

JOHN JACOB ABEL, Professor of Pharmacology, Johns Hopkins University.

GEORGE HUBBARD CLAPP, President of the Pittsburgh Testing Laboratory and of the Board of Trustees of the University of Pittsburgh.

ELBERT HENRY GARY, Chairman and Chief Executive Officer of the United States Steel Corporation.

JOHN HAYS HAMMOND, Consulting Mining Engineer.

HENRY MARION HOWE, Emeritus Professor of Metallurgy, Columbia University.

DOCTOR OF CHEMICAL ENGINEERING

WILLIAM HULTZ WALKER, Professor of Chemical Engineering, Massachusetts Institute of Technology.

MILTON C. WHITAKER, Professor of Industrial and Engineering Chemistry, Columbia University.

DOCTOR OF CHEMISTRY

CHARLES LATHROP PARSONS, Chief Mineral Chemist, United States Bureau of Mines.

EDGAR FAHS SMITH, Provost University of Pennsylvania.

Immediately after the close of the dedicatory exercises, the trustees, faculty and guests of the University met at a luncheon in the University Club. The remainder of the afternoon was devoted to an inspection of the new building of the Mellon Institute.

The recipients of honorary degrees were the guests of the University at the annual alumni banquet held at the Schenley Hotel from 6.00 to 8.30 P.M. The speakers at this dinner were Dr. Raymond F. Bacon, Director of the Mellon Institute, who responded to "The Mellon Institute;" Dr. Walther Riddle, who gave an historical sketch of the department of chemistry of the University; Hon. Elbert H. Gary, Chairman of the United States Steel Corporation; Dr. Theodore William Richards, who spoke on "The Practical Use of Research in Pure Science" and extended Harvard's congratulations to Pittsburgh upon the acquisition of the Mellon Institute; and Chancellor Samuel Black McCormick, who completed the toast list with an eloquent response to "The University," in which he stated that the gift of the Mellon Institute had placed a great responsibility upon the University of Pittsburgh as well as having been a priceless acquisition; that the University was ready to meet the responsibility and, he felt sure, would show the donors and the country at large that it would make the most of the great benefaction.

Judge Gary's address was, in part, as follows:

"In humankind there is an element which is interested in, if, indeed, it does not actually enjoy reading or listening to, adverse references to the character or conduct of an individual or association of individuals, and, by reason of this fact, agencies for the collection

FIG. 2—THE LATE DR. ROBERT KENNEDY DUNCAN

and distribution of unfavorable comments have become more or less popular. A questionable kind of success is often realized by the individual or the publication whose energies are devoted to frequent and furious personal attack against the standing or the action of others. These efforts sometimes take the form of individual work, investigations by committees or commissions created by the Legislatures or Congresses, or, in exceptional cases, even by judicial branches of Government, such as grand juries, with their inquisitorial power. Oftentimes the investigators are not only utterly incompetent, but they are prejudiced and wilfully repress many of the pertinent and material facts. They seek to produce for circulation and criti-

cism only information calculated to bring reproach upon the persons involved in the inquiry. No one is exempt from these criticisms.

"Circumstances seem to show that we are approaching the time when the investigator will be investigated; when the criticizer will be criticized; when committees and commissions will be brought before other similar bodies for judgment. It would be interesting to the public if it could be informed of the real motives which have prompted some of the official inquiries, and if it could learn of the unfair methods which have been sometimes pursued, and if it should know the amount of governmental funds which have been appropriated for the use of committees and how they have been disbursed; in fact, if some of those participating could be subjected to the same scrutiny which they have exercised.

"The general attitude of the great newspapers of today is fair and just. They influence and are influenced by the general public. They reflect the general sentiment. This is most important in considering the future welfare of this country.

"If the picture which I have drawn is a true one, then the course before us, which leads to prosperity, success and happiness, is plain, and we will pursue it.

FIG. 3 RAYMOND FOSS BACON, PH D., DIRECTOR OF THE MELLON INSTITUTE

We must conduct affairs in our charge with the expectation that we shall be criticized."

After the banquet, the new building of the Mellon Institute was thrown open for a reception of friends of the Institute. The rooms of the main floor were used for the reception, although the entire building was open for inspection. On the evening of February 27th, the first Mellon Lecture was delivered by Professor John Jacob Abel, of Johns Hopkins University, in the assembly hall of the Institute; Dr. Abel's subject was "Experimental and Chemical Studies of the Blood and Their Bearing on Medicine."

## KNOWLEDGE AND RESEARCH[1]

By Rossiter Worthington Raymond

This notable chapter in the history of one of the most ancient American institutions of learning irresistibly recalls the situation of 1787, the year in which the first charter of what is now the University of Pittsburgh was granted. That was the year of the Convention which framed the Federal Constitution. It was notable also as practically the beginning of two other agencies which, though derided at the time, proved afterwards to represent the most potent elements in the cementation of that solid union founded by the Constitution. For it was in 1787 that John Fitch ran his steamboat up and down the Delaware; and it was in 1787 that the fierce discussion of the improvements proposed by Noah Webster may be said to have reached its climax. That controversy resulted in Webster's Dictionary and Webster's Spelling Book, which gave us one language throughout our wide and ever wider domain. Thus the bond of political union established by the Constitution was reinforced by the beginnings of internal transportation and of a common speech, without which the growth of our continental empire would scarcely have been possible.

The wonderful changes effected in personal, social and national life during the century which ensued, would make an easy theme for any orator who might choose to tell the thrilling history of this particular region alone, beginning with the little group of cabins under the guns of Fort Pitt which constituted Pittsburgh, and tracing the conquest and rapid settlement of the Ohio valley (which was never equaled for revolutionary transformation except by the settlement of California under the special world-excitement caused by the discovery of gold), the development of commerce and industry, the accumulation of wealth, and the concomitant advance in education, culture and fullness of individual and social life. I shall not rehearse to you this familiar story, but I would point out the significance in such a sweeping torrent of change, of the things which abide.

One of these is Pittsburgh itself. Instinctively recognized, even in our colonial period, as a strategic point, to be defended at all costs, it has remained, through the astounding revolutions of its history, always the center of power and progress, demonstrating in these later days that the wealth accumulated in the service of man through smoky industries is available for man's service also in the fair fields of science and art.

And another thing that abides is the conviction of the value of knowledge which inspired our grandfathers and possesses us. They founded colleges while they

[1] Principal address delivered at the Dedication of the New Building of the Mellon Institute of Industrial Research and School of Specific Industries of the University of Pittsburgh, February 26, 1915.

FIG. 4—THE RECIPIENTS OF HONORARY DEGREES AT THE DEDICATION OF THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH
Front Row, left to right: Ira Remsen, Theodore William Richards, Samuel Black McCormick, Edward Williams Morley and Arthur Amos Noyes
Middle Row, left to right: Elbert Henry Gary, Henry Marion Howe, John Jacob Abel and Milton C. Whitaker
Back Row, left to right: Charles Lathrop Parsons, Edgar Fahs Smith, John Hays Hammond and William Hultz Walker
Absent: George Hubbard Clapp, John Ulric Nef, Rossiter Worthington Raymond

were fighting Indians and leveling forests and devising governments. The progress of the world and the eminence of Pittsburgh in that progress are alike, due to science. And we Americans recall with just pride that our fathers always provided for education as a part of their social scheme. It would be absurdly superfluous, in this presence, to explain that the wonderful natural advantages of Pittsburgh would have amounted to nothing without the science which has utilized her fuel and her means of transportation. It is not manual labor alone, but, in a much greater degree, the labor of the educated brain, that creates wealth and constitutes power. And it is a peculiar characteristic of this source of power that no one can foretell the scope and value of its results. We know how many foot-pounds of energy a man or an animal can furnish in a given time; but we cannot prophesy what may be done with that energy if applied, under intelligent guidance, to the utilization of the inexhaustible forces of nature. The assertion that "knowledge is power" is an "act of faith;" but this faith has proved itself a thousand times to be well-founded. No one doubts today that the knowledge we now have is power, and must, therefore, be preserved by transmitting it to each succeeding generation—even were there nothing more to know. But we have learned also that the enlargement of the circle of things known increases the boundary beyond which lie the things yet to be known, and hence we attach a practical value to research. We need not claim for our own time alone this recognition of the importance of research. Let us modestly remember that the things we now know are the results of the research which our fathers encouraged and conducted—nay, more: that their faith in knowledge and inquiry was supported by much less evidence of valuable results than encourages us. In fact, we may be said to walk in this path, no longer by faith, but by actual sight.

Nevertheless, it is unquestionably true that the conception of university education has undergone, during the last century, an important change. Even so recently as fifty years ago, when I was a student at German universities, the traditional organization of the four faculties of Theology, Law, Medicine and Philosophy was still maintained, but "Philosophy" (originally intended to cover metaphysical subjects) had been gradually made the receptacle of everything that was not theology, law or medicine—including such trifles as mathematics, languages, literatures and sciences. And the old satire was still current: "Theology yields a man honor but not bread; law, bread but not honor; medicine, both bread and honor; and philosophy, neither bread nor honor." Yet already it was becoming evident that in the disparaged department of "Philosophy" lay the studies which were certain to yield both the bread and the honor of the future.

Today, we care little for the old classification. Our notion of a full university is that of the motto of Ezra Cornell, who founded the one which bears his name, as a place where anyone could receive instruction in anything. Towards this all-comprehensive ideal, which no institution, perhaps, has completely reached, we are all striving. And the strength, the inspiration, the fruitfulness of our development is in the increased emphasis which we lay upon research and the function which we assign to it in the modern scheme of education.

I need not make a distinction here between theoretical and practical research. There used to be a vague

and uncertain attempt to divide pure science from applied science. But, in fact, they are inextricably blended. It was Sir William Thomson, afterwards Lord Kelvin, the profound student of the nature of matter, the weight and movements of worlds, whose acute genius devised the perfect mariner's compass and constructed the apparatus by which the Atlantic cable was able to transmit intelligible messages—turning industrial failure into triumph. When Thomas Edison was perfecting his great electrical inventions, he went to Ira Remsen, the distinguished teacher of pure science, for the mathematical formulas which determined the dimensions, proportions and relations of his machines. The researches of Hertz and others into what seemed at first to be a sphere of electrical disturbances beyond the reach of human analysis, have led already to the miracles of wireless communication and control—messages signaled, or even simply spoken, across oceans and continents, and boats steered by inaudible commands from the shore.

The difference between knowledge and research is the difference between the expert and the discoverer. An expert is one who knows what has been done or is provisionally established in a given science or art. He can say, with regard to a new discovery or improvement, only whether or not it contradicts or transcends what is generally accepted as the result of previous experience. But the discoverer is a prophet, and, if he has not "spoken presumptuously," his message becomes a new revelation, and a part of the science of his day—or the day after.

It seems but yesterday that I read in the newspaper how Charles Sumner, of Massachusetts, had proposed in the United States Senate an amendment to a pending appropriation bill, granting a considerable sum for the conduct of experiments in sending telegraphic messages without the employment of conducting wires. I was an expert then, and, as an expert, I knew (or thought I knew) that the thing had never been done and, therefore, was impossible. I remember reflecting how easily non-scientific people were carried away by the eloquence of fanatics or charlatans, especially when the schemes proposed were such as all the experts declared to be absurd. The common sense of the United States Senate, taking the same view, rejected the amendment; and it is my impression that the distinguished proposer of it (having, perhaps, introduced it at the request of some sanguine constituent) did not fight very hard for its adoption. It is possible that I recorded my opinion of it at the time with sarcastic humor in the columns of the technical journal of which I was editor. I have made no investigation as to that question; and, indeed, I would rather not know the answer!

At a later period, Le Conte, one of the most eminent scientific authorities in America, and one who, in his own department, and in the general exposition of the philosophy of evolution, was a leader and commander, published an essay demonstrating the theoretical, that is to say, the mathematical and irrevocable, impossibility of the navigation of the air by vehicles heavier than air. Now mathematics, as defined long ago by Benjamin Peirce, is the one science which draws necessary conclusions; but the necessity of its conclusions is simply their relation to its premises. Prof. Le Conte's judgment was based on the evidence before him. It was the utterance of Science without the testimony of Research. And already another eminent scientific authority, my dear friend and yours, Prof. Langley, long of your University, reinforcing science with research, had devised a flying-machine, heavier than air, which is now, I believe, admitted to have furnished the first solution of this problem. True, an accident not due to any unsoundness in Langley's theory and design wrecked his experimental machine, and, perhaps, broke his heart too. But time has vindicated his fame and has given us another instance of the value of scientific research to industrial progress.

But it must be real research, not merely the cloudy anticipation of things to come. Many years ago, I was visited by a "seedy" young stranger, who desired my assistance in the form of a loan which would pay his fare to Colorado, where he wished to introduce the use of electricity in metallurgy. Under cross-examination, he explained that he expected to get his electricity, Franklin-fashion, from the clouds, and, having heard that there was a good deal of it up in the Rocky Mountains, he thought Colorado was a good place for his process! If that young man has survived (which I doubt, since he did not look like a future survivor), he is doubtless saying today that he was the real inventor of the whole art of electro-metallurgy! He was a feeble specimen of the host of professional inventors who try to pre-empt territory in realms not yet explored, substituting prophetic intuition for patient and skilful research. These are the prophets who "speak presumptuously." The Book of Deuteronomy, after describing such a prophet, adds, "Thou shalt not be afraid of him." Yet, in spite of that encouraging exhortation, we are afraid of him; he hangs as an incubus upon every real inventor whose work has been based upon real research; for research is not fruitful unless it is, or until it is, scientific.

The essential quality of Science is that it is quantitative, while mere invention may be in the beginning only qualitative. After the great blizzard, more than a quarter of a century ago, a storekeeper in Brooklyn undertook to apply quantitatively the qualitative proposition that heat would melt snow. Having a 16 ft. heap of snow in front of his store and a lot of old boxes in his cellar, he dug in the snow a chamber with a chimney, crammed this stove with pine wood from the cellar, lit the fire, and looked for the mountain to dissolve in fervent heat. Being a qualitative man, he did not know the difference between temperature and heat-units, or dream of the work he was expecting his little fire to do. When he had burned all his wood, he abandoned his faith in science! Yet there is never a heavy fall of snow in New York but somebody berates the authorities for their stupidity in not thawing it away!

And this brings us to the proposition that real research must itself be based upon scientific knowledge.

There is nothing more pitiable than the spectacle of an enthusiast, fancying himself a pioneer, laboriously digging in ground already explored, exhausted and abandoned by others. My friend Clarence King told me once how he set his heart upon the ascent of a certain high peak in the Sierra. With infinite exertion, and no little peril, he scaled the precipitous mountainside, and reached at last the summit, only to find there an empty tomato can and a copy of a newspaper, relics left by a picnic party, which had ascended by an easy trail on the other side of the mountain! A little preliminary research would have saved him from this scientific fiasco.

Moreover, the careful and thorough study of science—that is, of what has been done, and has come to be believed already—will often mightily aid research with significant and invaluable suggestions; for the records of scientific experiment contain many observations which were simply noted *en passant* and left for future explanation. A distinguished electrician once said to me that, notwithstanding the amazing advance of his art, he still found in the old, simple, homely notes of Benjamin Franklin valuable hints and suggestions.

It is narrated in the biography of Sir John Lawrence, that, in 1849, after the annexation of the Punjab to the British possessions in India, the famous jewel known as the Kohinoor or "Mountain of Light,"—for many centuries the booty of successive conquerors, Turks, Moguls, Afghans, and what not—fell, with other public treasure, into the hands of the new government, represented by the Board of Administration of the Punjab, of which Lawrence was a member. At one of the early meetings of that Board, the Kohinoor was formally delivered to it, and temporarily consigned to the care of John Lawrence, perhaps because he was supposed to be the most practical and business-like of the three members. So he was, in many respects; but he had no use for jewelry, never wore it until it was forced upon him in the form of well-earned decorations—which, we are told, he used to pin on in the wrong places, to the despair of court officials—and never thought about it. So he took the Kohinoor, wrapped in numerous strips of cotton cloth, thrust it into his waistcoat pocket, and thought no more of it, while he devoted himself to the multifarious and much more important business which lay before the Board. The session over, he changed his clothes for dinner, throwing his waistcoat aside, without recalling the precious contents of its pocket. But the authorities in London were less forgetful; six weeks later came the order to forward the Kohinoor to the Queen. When this was presented to the Board, Lawrence said, "Let us send for it at once and forward it." "But you've got it," was the reply—at which a remembrance of the whole matter flashed upon him, together with the sickening certainty that the Kohinoor was not in his waistcoat pocket then! As he used to tell the story afterwards, he said to himself, "Well, this is the worst trouble I have ever yet got into!" But, with wonderful self-control, he suppressed all signs of anxiety, remarking, "Oh, yes, of course; I forgot about it," and went on with the business of the session as if nothing had happened. But at the earliest opportunity, he slipped away to his private room, and questioned his native body-servant. "Have you got a small package that I left in my waistcoat pocket some time ago?" The servant had saved it with other pocket rubbish, produced it from a battered old tin box, and, unrolling its bandages, handed the great diamond to his master, remarking, "You see, Sahib, it was nothing but a bit of glass." And thus ended a new chapter of adventure in the marvelous history of the Kohinoor.

I have told this story because of its romantic interest, and because I think it will be new to many of you, as it was to me when I came upon it in the life of the hero of the Indian mutiny, in the splendor of whose achievements even the luster of a diamond fades. But I think you will agree with me when I make of it, in harmony with its far Eastern scene, an Oriental apologue, deducing from it the moral that research, even amid the rubbish of the past, may bring to light forgotten treasure, and that a common bit of glass may prove to be a "Mountain of Light."

If knowledge and research are thus intimately related, each reinforcing the other, the manner in which they are combined in this institution must be recognized as largely novel and wholly admirable; for effective research requires suitable apparatus, and under apparatus we include books. Moreover, research is promoted by definiteness of object. The man who knows what he is looking for is more likely to make discoveries than he who merely launches into space, hoping to make discoveries through accidental collisions. And again, not only motive and apparatus and previous knowledge, but also the capacity of clear and accurate thinking, must belong to the equipment for useful research; and no man thinks accurately who cannot put his thought into words which will convey it to another man qualified by knowledge to comprehend it. We may feel, but we cannot think, unutterable things. What our patent law requires of an inventor, that his invention shall be so stated as to enable any one skilled in the existing art to practice it, is equally required of every discoverer, whether he seeks the reward of a patent or the recognition of his fellow men in other ways. He must be able to describe and to define as well as to discover.

Now, there is no discipline like that of teaching to perfect the art of precise and intelligible statement. Indeed, the teacher enjoys a continuous practice in that art which cannot be had in any other way. Our best text-books of science are the work of teachers who have learned in the classroom how to communicate knowledge. These industrial fellowships, therefore, which give to their incumbents, in addition to all the other advantages mentioned, the opportunity of practice as instructors, are likely to develop both fresh and effective teaching and fruitful research.

Moreover, such an arrangement must be welcome to the overburdened members of regular faculties of instruction, to whom the mechanical routine of teach-

ing leaves too often neither time nor strength for that original study and progressive intellectual activity which alone can keep them sources of inspiration.

In short, the genius and wisdom of your beloved and lamented Dr. Duncan seem to me to have found a wonderful solution for a difficult problem in this scheme of industrial fellowships. May genius and wisdom still preside over its development, as they foresaw and welcomed its birth!

But this occasion emphasizes to my thought another principle, perhaps the most fundamental and far-reaching of all. In this dedication of a building erected through the intelligent munificence of private citizens, we have another instance of the method and means by which American institutions of learning, as well as of philanthropy and religion, have rapidly grown in a single century to proportions rivaling those which ancient origin, cherished traditions, and age-long growth have given to such institutions abroad. The generosity of private citizens, since the beginning of the nineteenth century, has surpassed among us all the endowments bestowed upon science and learning by the Governments of Europe in modern times, and its results may challenge a corresponding comparison. Our democratic individualism makes mistakes, no doubt; but so does paternal government. The difference is that the mistakes we make we also correct; while the mistakes of paternalism are likely to lie like a permanent, heavy blight upon progress. It is fashionable in some quarters to decry "foundations" established by private wealth; but we may challenge the critics to adduce a single instance in which, under our American system, an institution of learning or research thus supported has ever been productive of harm. Knowledge and the opportunity to pursue knowledge are the only gifts that do not pauperize the recipient. Nay, more: under free institutions and in the atmosphere of liberty, the recipient of such bounty inevitably returns it in benefaction to society. Long may it be, ere this gracious, wise and fruitful American habit of great private endowments yields to the assaults of either the demagogue or the doctrinaire!

Perhaps the chief advantage of numerous private institutions of science and research is to be found in the consequent multiplication of independent students and investigators. The victorious advance of civilization and culture is not an organized conquest, like that of a drilled and equipped army under a single head. It is rather like the free, yet invincible, advance of the forest over denuded areas—each tree sending forth its seeds, wind-blown, each seed fighting its own battle with heat and cold or vigorous competitors, and the victorious survivors constituting the forest of the future. Apart from all considerations of government or statesmanship, I thank God for the numerous separate States of our Union, and for the numerous independent institutions in each State which permit the testing of new propositions in science, industry, politics, sociology or statesmanship on a working scale not fatally extensive.

Finally, let me congratulate the University of Pittsburgh upon its retention of the old College course as the center of its wide modern activities. As a member of a technical profession, I place the highest value upon that liberal preparation which, in my judgment, is still the best foundation for usefulness and success in any specialty of modern training.

The Cooper Union of Science and Art, organized in New York more than half a century ago, was primarily intended by Peter Cooper to give to working men and women whatever they most needed for the immediate satisfaction of their conscious desires and the immediate increase of their wage-earning power, or, in other words, their value to the community. Having been connected with that pioneer institution in one way or another for twenty years, I can testify that this original purpose was at all times respected by its Trustees. They rated the importance of each special department by the pressure of applicants. In this respect, they were like the old "paradoxer" of whom De Morgan tells, who, after many failures in obtaining a comfortable chair, at last procured a large lump of shoemaker's wax, sat on it for several hours, and then gave it to the cabinet-maker with the terse injunction, "Make me a chair with a bottom like that!" In other words, they let the pressure of public demand determine their supply of special facilities; and sometimes, while they were still (as I trust they are no longer) obliged by insufficiency of means to curtail one department if they enlarged another, this policy compelled them to sacrifice courses of instruction good in themselves and needed to complete the symmetry of their plan, but not patronized by students in proportion to their cost in money and room. Yet through all these years of compromise between curriculum and immediate popular demand, the Trustees of the Cooper Union maintained, for those who chose, and could afford to take it, the regular, old-fashioned, four years' liberal college course. For they felt that while they ought to furnish to those who had not enjoyed the opportunity of a thorough education such partial substitutes as circumstances would permit, it was equally their duty to hold up as the ideal a completer culture, embracing the wisdom of the past, as well as the special accomplishments demanded by the present.

Alas! While we thus launch in hope another stately ship of peace, bearing blessings to our children and our children's children, the nations are building and sailing and sinking battleships, the cost of one of which would establish a great university. War is squandering recklessly the inheritance of centuries, and burdening with intolerable loss and labor a generation of orphaned paupers. Is this the triumph of science and research, to devise new kinds of murder? Have we conquered the domain of the sky, only to drop from it the thunderbolts of reckless hate? Do we navigate the depths of the sea, only that we may suddenly wreck, without warning, the unsuspecting sailors on its surface? Is this the highest achievement of our chemistry—to make explosives which will poison while they mutilate? And have centuries of mechanical and metallurgical progress enabled us only to construct guns which will carry our horrible missiles further than we

can see our targets, so that we kill according to trigonometrical calculations made for us by surveyors in the air above us?

The spectacle of such an unparalleled world-catastrophe reminds us indeed of the grim old truth that, while "knowledge is power," power itself has no moral quality, and may be equally useful, for the time being, though not for ultimate results, to the workers of evil and the workers of good. Yet this we knew before, and with it the world has had to deal at every step in the slow advance of the sense of human brotherhood. History has recorded many world-catastrophes. Over and over again, power has wrought ruin, which seemed to be final and irreparable. Yet over and over again the darkened earth has emerged from the shadow which seemed to be death, but was only eclipse. Let us have faith, born of experience, in the solar system!

Many years ago, at a banquet of the American Institute of Mining Engineers in Pittsburgh, Prof. Langley made an exquisitely graceful speech, in which he described a vision he had seen. That was in the early days of natural gas in Pittsburgh. The great iron and steel works had not yet universally adopted its use, and the black smoke from innumerable chimneys still enveloped the city. But everybody was prophesying and hoping great things from this gaseous fuel; and Prof. Langley's vision was that of a regenerated, clean, sootless Pittsburgh—radiant angel of a happy industry.

Well, the vision became a fact. For a period all too brief, Pittsburgh, burning natural gas, was clean—that is to say, reasonably so, to her great pride and delight, and to the great comfort of her visiting guests. But natural gas grew scarcer and dearer, and the furnaces went back to coal, and the black pall descended again upon the great city. Was there no cure, no hope of a higher, purer life for the thousands who toiled in grime and darkness? Behold the answer in this higher Pittsburgh, in the midst of which we stand!

May we not make of this homely history a parable and a prophecy? Did we not dream of a purer atmosphere for all mankind? Had we not seen already upon the mountains the beautiful feet of the dawn of that happy day? And now that the war-cloud, blacker than ever, has descended upon us, let us still look forward, with unfaltering faith, to the ultimate fulfilment of our hopes, our labors and our prayers in a New White World!

## DESCRIPTION OF THE NEW BUILDING OF THE MELLON INSTITUTE[1]

By W. A. Hamor[2]

It may first be noted that the plan of the new building which now forms the permanent home of the Mellon Institute of Industrial Research and School of Specific Industries, was laid down in accordance with the destiny of the Institution, as judged by its past, its immediate demands and the probable development within the next half-century. Over the doorway of the new edifice, in bronze, is this inscription: "This Building is dedicated to the service of American Industry and to young men who destine their lifework to the Industries, the goal being Ideal Industry, which will give to all broader opportunities for purposeful lives." This inscription gives an excellent idea of the purpose for which the building has been erected.

Secondly, in the design, erection and equipment of the building, three basic considerations, all very closely related and having to do with efficiency and economy, have been borne in mind. These are, in the order of their importance: research, engineering and administration.

Since the building was designed primarily as an industrial problem workshop, some of the factors which were involved in its construction from this viewpoint are presented rather fully below, in the first section of this paper, owing to the growing appreciation of the value of industrial research. A detailed account of the construction is given in the section entitled Engineering Details; it may be mentioned here, however, that the building is in harmony with the architectural features of the others on the University of Pittsburgh campus.

### RESEARCH CONSIDERATIONS

The ground plan of this five story and attic laboratory building was laid out to secure the greatest amount of light, air and compactness. The basement contains seven rooms: the main storeroom, the boiler room, the electric furnace room, a heavy apparatus room, a room equipped for low-temperature work, the machine shop, and a kitchen. On the first, the main, floor, are located the general office, the Director's suite, the office of the editorial department, the library, the office and laboratory of the Assistant Directors, the Assembly Hall, a special apparatus room, and a dark-room laboratory. The second and third floors each contain ten large research laboratories and nine small ones; the fourth floor, which is not finished, will contain an identical number of laboratories as soon as the growth of the Institute warrants its completion.

The facilities which the Mellon Institute now offers for research are primarily instanced in its

### RESEARCH LABORATORIES

In general, there are two sizes of research laboratories for the use of the Fellows of the Institute; twenty laboratories 20 ft. 6 in. x 20 ft. 6 in. and eighteen laboratories 10 ft. 6 in. x 20 ft. 6 in., on the second and third floors, have been finished and assigned. This number will later be increased by ten large laboratories and nine small ones on the fourth floor. All laboratories are connected with the general office by an electric call-bell.[1]

The laboratories are not too deep for good light throughout from without. To ensure the latter, the ceiling on the second floor was made 10 ft. 8 in. in the clear from the floor; on the third and fourth floors, the ceilings are 10 ft. 2 in. above the floors.

[1] Published with the approval of Dr. Raymond F. Bacon, Director of the Mellon Institute.

[2] Assistant to the Director of the Mellon Institute.

[1] See ELECTRIC WIRING SYSTEM in the section on ENGINEERING DETAILS, *infra*. A telephone is conveniently located in each of the corridors.

LABORATORY TABLES—The laboratory table tops, which are supported on pipe standards, and are 3 ft. 1 in. clear from the floors and 2 ft. wide, are constructed throughout the building of alberene stone, 2 in. in thickness. All table tops have a $^1/_4$-in. slope to the back, with a 3-in. gutter, cut in the top, having a fall to the sinks; and there is a drip cut in the underside of each, on the outer edge, to prevent dripping. Each table is equipped with four sets of gas, water, vacuum, and compressed air supplies; the water outlets are $^1/_2$ in., all others are $^3/_8$ in. On each table there is an alberene stone back, 14 in. high and $1^1/_4$ in. thick; this is equipped with A. C. and D. C. plugs.

Above the tables are two alberene shelves, $1^1/_4$ in. thick x 7 in. wide, and a top shelf, 12 in. wide; the shelves are spaced 14, 10, and 12 in., respectively, and are supported on alberene stone slab-brackets, with a curved front at the top to meet the 12-in. shelf.

In each large laboratory there are nine sections of one large and two small drawers each, with a compartment underneath, provided with double doors, fitted with friction catches and wooden knobs. In the small laboratories there are eight sections of drawers.

The cupboards or cases on the first floor are made of quarter-sawed white oak; on all other floors the construction is of plain-sawed red oak.

HOODS—All laboratories, large and small, are provided with one double hood, 6 ft. long over all, constructed of alberene stone; the inside measurements are: 1 ft. 6 in. deep x 5 ft. 8 in. long x 4 ft. 3 in. high. Each hood is equipped with two sliding sashes, glazed with polished plate wire-glass; the sashes are suspended on bronze sash chains and are balanced with lead weights. At the end of each hood is a light of polished plate wire-glass, 12 x 26 in.

In each hood there are an A. C. plug, gas, water,

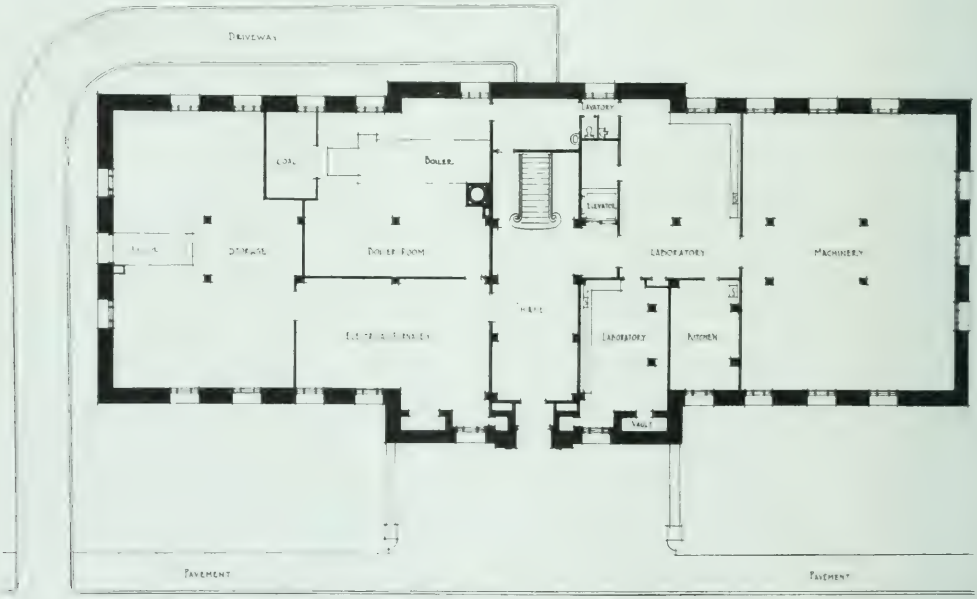



FIG. 5—BASEMENT FLOOR PLAN, MELLON INSTITUTE OF INDUSTRIAL RESEARCH

In each laboratory there are three 14 x 20 in. porcelain-enameled sinks. These sinks are set on $^3/_4$-in. galvanized pipe frames, having flanges on the floors, with braces half-way up and binders on top, and so put up that the tops of the sinks set 3 ft. above the floors; the frames received two coats of asphaltum paint after being installed. Each sink has a $1^1/_4$-in. extra strong lead waste pipe, fastened to the board under the table, with open ends emptying into the receptors.

There are alberene stone drain boards, 20 x 39 in., back of each sink; these boards are equipped with rubber-tipped wooden pegs. There is also one set of gas, water, vacuum, and compressed air lines over each sink.[1]

[1] For a detailed description of the cold water lines, hot water system, and vacuum and compressed systems, see the account of the PLUMBING under ENGINEERING DETAILS, *infra*.

steam, vacuum, and compressed air outlets. In one end of every hood a 3-in. opening connects with the hood-ventilating system.[1]

### LABORATORIES FOR SPECIAL WORK

SPECIAL APPARATUS ROOM—On the first floor, a room 38 ft. x 20 ft. 6 in. contains the instruments of precision.

This room is provided with two alberene stone tables and shelving. There is also, in the center of the room, a raised platform, 12 x 18 ft., of reinforced concrete supported on reinforced concrete columns extending down through the basement, with separate footings underneath the columns; this platform and its supporting columns are so arranged that they do

[1] See PLUMBING in the section on ENGINEERING DETAILS, *infra*.

not come in contact with any portion of the building construction, there being a $^1/_2$-in. space around the columns at both floors. A fire-proof vault, 2 ft. 6 in. x 9 ft., is provided for the storage of platinum ware, radium preparations, and other valuable equipment for research.

HEAVY APPARATUS ROOM—The 23 x 33 ft. room adjoining the kitchen in the basement, just off the hall, is equipped with two laboratory tables and with systems of grinding and pulverizing machinery and filter presses.

DARK-ROOM LABORATORY—A special dark-room, 16 ft. 4 in. x 18 ft., has been provided on the first floor for work in photography and for photochemical research. It is equipped with two alberene stone work-benches and a hood.

ELECTRIC FURNACE ROOM—A basement room, 20 ft. 6 in. x 37 ft., is fitted up for electric furnace work. There are four power outlets in the floor, and two induction regulators and the important types of electric furnaces are installed.

REFRIGERATING PLANT—A No. 3 Audiffren Singrun refrigerating machine, having a cooling effect of 40 lbs. per hr., an ice-making capacity of 27 lbs. per hr., requiring 95 lbs. of condensing water at 70° F. per hr. and 1 to $1^1/_4$ H.P., and possessing a speed of 280 R.P.M., is located in the basement in a room 14 ft. 6 in. x 20 ft. 6 in. Adjoining this machine is a cork-lined cold-storage room, 6 x 8 x 7 ft., provided with storage shelves and a bench. The machine is guaranteed to keep this room at 37° F. and to make 50 lbs. of ice per day in summer.

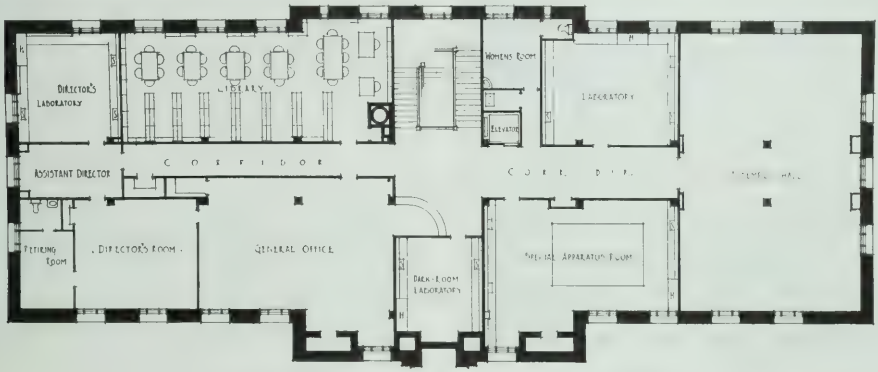



FIG. 6—FIRST FLOOR PLAN, MELLON INSTITUTE OF INDUSTRIAL RESEARCH

SUPPLIES

THE MAIN STOREROOM, 34 ft. 8 in. x 51 ft. 4 in., is located in the basement. It is furnished with an installation of steel shelving having a total shelf surface of 3,200 sq. ft.; the greater portion of this equipment is shelving, the remainder consisting of 96 bins carrying a volume of 1,070 cu. ft. and six double cupboards having a volume of 114 cu. ft. Special provision is made at the ends of the cases for metal racks to care for all glass tubing and rodding. All shelving is finished in acid-proof baked enamel.

The storeroom is in charge of a curator of supplies whose sole duty is to tend the stock and order materials required by the thirty-eight Fellows now engaged in research. It is in telephonic communication with each floor of the building, and a dumb-waiter, capable of lifting 50 lbs., has been installed for distributing small supplies.

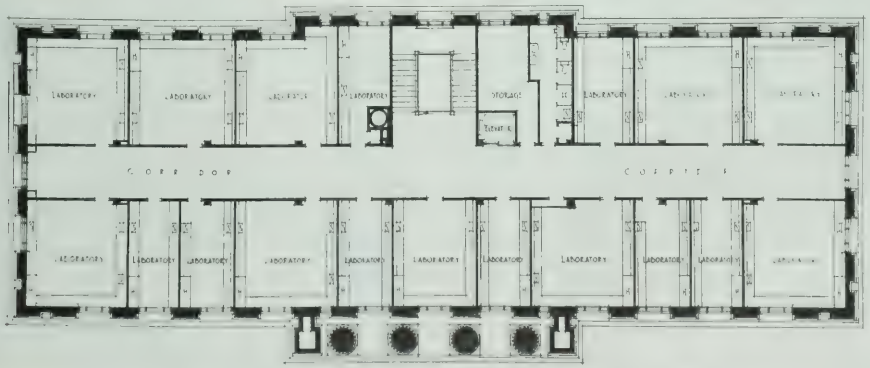



FIG. 7—SECOND AND THIRD FLOOR PLAN, MELLON INSTITUTE OF INDUSTRIAL RESEARCH

DISTILLED WATER—A Barnstead automatic water still, having a capacity of 5 gals. per hr., is installed in the attic of the building. The distilled water storage tank has a capacity of 125 gals.; it is constructed of No. 16 gauge galvanized iron, lined throughout with pure block-tin, and is furnished with a tin-lined cover.

FIG 8—INTERIOR VIEW OF TYPICAL SMALL RESEARCH LABORATORY
Eighteen Laboratories of This General Type Are Finished and Assigned

There are six distilled-water fountains throughout the building; five of these are in the corridors and one in the general office. The fountains are supplied by gravity from the storage tank in the attic, through a $^3/_4$-in. main of block-tin pipes, with $^1/_2$-in. block-tin branches to each fountain.

### MACHINE SHOP

The machine shop occupies one-half of a room 51 ft. 4 in. x 40 ft. 4 in. in the basement. At the present time it is in charge of two skilled mechanicians and is equipped to produce the various special mechanical appliances likely to be required in industrial research. In addition to all necessary small tools and to carpentry and pipe-fitting equipment, there are installed a Lodge-Shipley selective-head motor-driven[1] lathe, 22 in. x 14 ft. bed; a 12-in. Star motor-driven lathe; a 20-in. Cincinnati motor-driven shaper; a Cincinnati-Bickford plain 30-in. motor-driven radial drill; a 14-in. Washburn motor-driven sensitive drill; a Springfield Manufacturing Company's double-end motor-driven grinder; a 36-in. motor-driven band saw; complete oxy-acetylene welding apparatus; a Schoop metals coating pistol; and a hydraulic press.

### LIBRARY

The library occupies a room 58 x 21 ft. It contains a unit book-stack, 6 ft. 10 in. high, running around the room, which forms adjustable shelves, 10 in. deep; and seven book-stacks running out 6 ft. from the wall. The latter stacks are double, each side having a depth of 8 in., and the total shelf capacity is about 12,000 volumes. Opposite the stacks and along the windowed side of the room are four reading tables, 3 x 5 ft., with four arm-chairs at each. There is also a larger table, 3 ft. 6 in. x 8 ft., for periodical reading, at which table eight people may be seated comfortably at one time. This table faces shelves containing 72 technical periodicals which are received currently by the library. All the woodwork and furniture in the room are solid antique oak.

At present the library possesses 2,000 carefully selected volumes, not including government publications and pamphlets, of which there are several thousand.

Among the features of this library are a file of reprints of the contributions of all the Fellows, a file of all patents of the Fellows, and a trade catalogue file. This last is a very important department of the library; at present over a thousand catalogues of 415 different firms are on file, and this number is added to, daily. There is a complete subject and name index, making all the material accessible.

The library is in charge of a librarian who is also an expert translator.

### ASSEMBLY HALL

The assembly hall, located on the first floor, occupies a space 34 ft. 3 in. x 51 ft. 4 in. It is provided with a movable lecture table, and a lantern with cinematograph attachment is installed in the mezzanine floor in the first floor corridor adjacent to the hall.

This hall is used for seminar work and staff meetings, and as the lecture room of the School of Specific Industries. Its walls are decorated with photographs of eminent chemists and with pennants of the various universities represented on the staff, presented by the Fellows in pledge of their fidelity to the ideals of the Institute.

### CORRIDORS

The corridors on the second and third, the research laboratory floors, are 10 ft. wide and 161 ft. 6 in. long.

FIG 9 INTERIOR VIEW OF TYPICAL LARGE RESEARCH LABORATORY
Twenty Laboratories of This General Type Are Finished and Assigned

A dumb-waiter shaft from the basement to the attic has an opening at the end of the corridor on each floor. There are also two drinking fountains, supplied with distilled water, and a telephone in each corridor.

[1] A floor box for power and light outlets is installed at each machine.

Medicine chests, provided with the ordinary emergency equipment, and fire-extinguishing apparatus are conveniently located in each corridor.

ENGINEERING DETAILS[1]

There are a number of technical features in this, the most modern research laboratory in this country, if

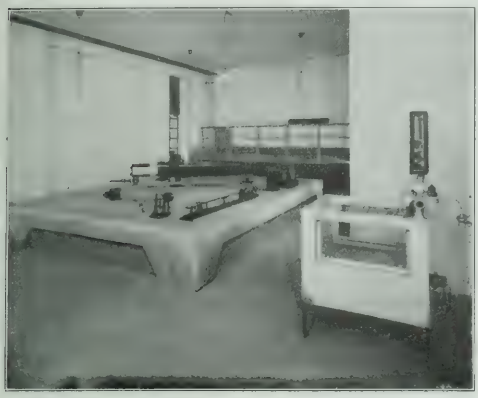


FIG. 10—SPECIAL APPARATUS ROOM, SHOWING RAISED CONCRETE PLATFORM

not the world. Reference will be made to certain of these during the course of the following account of the construction of the building, which is made rather detailed for the special use of ones contemplating or engaged in the erection of similar buildings.

EXTERIOR CONSTRUCTION

The basement and first story facing, entrance, stylobate, mould, columns and pilaster bases and caps, and lintels were worked from white granite. All exposed granite has 8-cut surface; the granite facings have a 4-in. bed and are anchored to the backing with $^1/_4$ in. $\times$ $1^1/_2$ in. galvanized iron anchors, one to each piece smaller than 3 ft. and two to each piece larger than 3 ft.; the joints have a uniform width of $^3/_8$ in. At the time of setting, the joints were left open to a depth of $^3/_4$ in.; after setting had been completed, they were pointed with white non-staining cement mortar composed of one part cement and two parts Ligonier limestone dust. All granite was set in mortar composed of one part cement and three parts sand.

The interior walls, backing-up of granite, exterior walls and flues were laid up with common brick with $^3/_8$-in. joints. The exterior walls above the granite were faced with wire-cut vitrified brick of a uniform ivory-white color. The insides of all exterior walls were lined with hollow brick.

The smoke flue was lined, from the flue holes in the basement to a point 25 ft. above, with fire-brick laid in fire-clay mortar; from this point to the top it was lined with a special flue lining. "Tee" joint outlets were placed in salt-glazed sewer pipe vent flues, to connect with hoods in the various laboratories; these vent flue pipes are extended to the attic and are there connected to a large ventilating fan which effectively removes all fumes from the hoods and rooms. All joints were made with a mixture of kaolin and asphalt.

It may be mentioned in this connection that the partitions were laid, as usual in buildings of such construction, with hollow fire-proof blocks, to which the wood door bucks were anchored with six $^3/_8$-in. round steel anchors to each opening.

[1] Mr. J. H. Gresey, the architect of the building, has courteously supplied much of the information which is given in this section.

ROOFING

The roofing is of 16-oz. soft copper, laid on one layer of tomb brand felt $^1/_8$ in. thick, weighing about 2 lbs. per sq. yd.; the felt is so laid that all joints are under the wood ribs. The latter are $1^3/_4$ $\times$ 3 in., with sides beveled to allow for the expansion of the copper; they are set $22^3/_4$ in. on centers to suit copper 24 in. wide. Copper cleats are placed 15 in. on centers, nailed to wood strips and double-seamed in with the roofing proper and copper strips covering the wood ribs. The cross seams are $^1/_2$ in. single-locked and are well soldered on both sides. At the bottom or gutter line the ribs extend over the gutter $^5/_8$ in. or even with the outstanding edge to which the roofing is attached; the gutter is lined with 16-oz. copper. The outlets are 8 $\times$ 8 in. with No. 12 copper wire baskets standing up at least 4 in. above the bottom of the gutter. The eave pipes from the gutter extending 18 in. into the galvanized iron conductor pipe, are exposed in the attic space to prevent freezing.

The projecting courses at the base of the columns and pilasters around the building are covered with 16-oz. C. R. copper, laid on felt, the lower one formed to make a decided drip at the bottom, outer edge, and to run under the next course. The capitals of the columns and pilasters are covered with 24-oz. C. R. copper, formed so as to lie down closely from the weight of the course of granite above; the outer edge is doubled and bent out to form a drip at an angle of 45°. The top of the main entrance door head is also covered with 24-oz. C. R. copper; it has a small drip gutter at each side, so arranged as to form a drip at each outer corner. All sills are covered with C. R. copper $^1/_8$ in. thick, formed with drip at the outer edge and with the back edge turned up into a groove in the wood sub-sill of the frame. 4 $\times$ 8 in. vent registers are placed in the attic walls and No. 14 $^1/_2$-in. mesh copper gratings are placed in the soffit of the cornice over perforated rosettes.

PLUMBING

MAIN SEWER—A 10-in. terra-cotta sewer, connected to the main sewer on the sidewalk, is run to each receptor, leaving a connection for the house sewer on the sewer side of the re-

FIG. 11—A VIEW IN THE MACHINE SHOP

ceptor. Two receptors, made of 30-in. terra-cotta pipe set on a 6-in. concrete base and having a 6-in. wall of concrete around same, were erected outside of the building; each receptor was provided with a heavy cast-iron perforated lid set flush with the finished grade. The bottom of each receptor is covered by a circular glass disk 1 in. thick. The 10-in. sewer and the 6-in. conductor sewer have terra-cotta well traps in the

receptor set so as to form a seal. The 6-in. acid drains are connected with open ends to the receptors.

CONDUCTOR DRAINS—From each conductor well trap in the receptors a 6-in. terra-cotta sewer was run to 3 ft. from the building, and then a 6-in. extra heavy cast-iron sewer to connect only to the four conductors and French drains; these conductors have no traps at the bottom of the upright lines. The upright lines are constructed of 5-in. galvanized pipe with galvanized drainage fittings, and have copper sleeves at roof gutters, extended at least 18 in. into the galvanized pipe. The upright lines are concealed in recesses in the walls of the finished rooms.

SOIL DRAINS—A terra-cotta sewer, with house trap and fresh air vent, connected to the 10-in. sewer outside of the receptor, was run to 5 ft. from the wall, from which an extra heavy cast-iron sewer with branches was run, to connect with the bell traps, sinks, slop sinks, washstands, shower baths, etc. All

FIG. 12—THE LIBRARY

joints were caulked with oakum and molten lead, and were tested with water.

ACID DRAINS—Six-in. terra-cotta sewers with 4-in. branches were connected to the receptors and run to connect to the acid drains. The upright lines are 3-in. terra-cotta, with 3-in. branches and with a 3-in. terra-cotta P-trap placed at each riser with a concrete receptor 1 ft. square formed at the inlet of the trap. The 3-in. upright lines were extended to a point 1 ft. above the attic floor, leaving 3-in. openings on the fourth and attic floors for future use. From this point the 3-in. upright lines were gathered into four 8-in. extra heavy cast-iron lines and extended through the roof 6 in. on the high side, for the acid drain vent. These 8-in. lines were placed so as to have one-fourth of the vent lines connected to each one, and the lines connecting same were 4 in. for two 3-in. lines, 5 in. for three 3-in. lines, 6 in. for four 3-in. lines, and 8 in. for six 3-in. lines. These lines were suspended from the ceilings by approved pipe hangers every 5 ft. Where the 8-in. vents pass through the roof, heavy copper flashing the same height as the pipe was used. After the flashing had been put on, a piece of 8-in. pipe 6 in. long, with bowl down and securely cemented joints, was placed on top of both. All pipe for the acid drains from the receptor to 1 ft. above the attic floor level was laid in concrete. All concrete casings around the pipes above ground were reinforced with four $^1/_2$-in. twisted rods; these rods were wired against the bowl of the pipe with $^1/_8$-in. wire. All horizontal lines have not less than $^1/_4$-in. fall to 1 ft. All upright lines had a $^1/_4$-in. thick asbestos washer laid in the bowl for the end of the adjoining pipe to rest on, and all joints were made with a mixture of asphalt and kaolin.

COLD WATER LINES—A 4-in. cast-iron pressure line was connected to the city main in the sidewalk and run to the inside of the building; this line has a 4-in. gate valve and an 8-in. gate box in the sidewalk. On the inside of the building a 3-in. iron body gate valve was installed on each side of the 3-in. disc meter.

All cold water lines in the basement are wrought-iron galvanized pipe with galvanized fittings. The branches are as follows: From the meter a 3-in. line runs to the boiler room, and from this line 2-in. lines run to where the risers go up for the laboratory lines. A $1^1/_4$-in. line is run to the storage heater, a 1-in. line to each heating boiler, a $1^1/_4$-in. line for the basement toilet, and, for risers to supply the upper toilet room, this line is run to the attic, a $^3/_4$-in. connection being made for the expansion tank. A $1^1/_2$-in. line is run to the heavy apparatus room, and from this line a $^1/_2$-in. connection is taken to each of the laboratory sinks in the basement and to the sinks which receive the waste from the drinking fountains.

Three-fourths in. galvanized lines, connected to cellar lines in the basement, are run to the inside of the wall where the hose connections are located; at this point, a $^3/_4$-in. compression stop and waste cock is placed, and a $^3/_4$-in. extra strong lead line is run 3 ft. 6 in. under ground to each of the four street washers at the outside of the building.

HOT WATER—There is installed a 300-gal. per hr. storage heater, having 140 ft. of $^3/_4$-in. copper coil, connected to a 250-gal. extra heavy tank; the heater is connected with brass circulators and is provided with a thermometer, pop safety-valve, gate valve near the boiler, indicating thermostat, $^3/_4$-in. drain cock, and gate valve on both hot and cold water lines near the boiler. The boiler is set on a brick foundation 3 ft. 3 in. square $\times$ 9 in. high and is covered with a $1^1/_2$-in. coat of 85 per cent magnesia covering and a canvas jacket.

A $1^1/_4$-in. line, connected to the storage boiler, is run to the branch for the washstand and slop sink on the first floor, and a 1-in. branch to the risers for the toilet room, with a $^3/_4$-in. line to the washstand in the basement and to the Director's toilet on the first floor. All hot water pipes in the basement are galvanized iron suspended on hangers. A 1-in. brass riser runs up through the toilet room, exposed to the fourth floor, and a $^3/_4$-in. brass return line to the basement, with a 1-in. line of galvanized iron pipe from the bottom of the brass return line to the boiler, with gate valve and check valve. From the 1-in. brass riser branches were taken as follows: $^1/_2$ in. to washstands, $^1/_2$ in. to slop sinks, $^3/_4$ in. to shower baths. All the pipe in the toilet rooms is brass, exposed, and each fixture has a separate compression stop. All cold water lines for the toilet rooms above the basement ceiling are brass pipe and are of the same size as the hot water lines.

GAS FITTING—Starting at a point near the water-meter a 3-in. natural gas line is run to the boiler room, a 2-in. line being taken off to the heavy apparatus room, a 1-in. branch to the storage boiler, a 1-in. branch to the live-steam boiler, and a 2-in. branch to where the risers go up to the laboratory lines connecting the 1-in. and the $1^1/_4$-in. risers. All gas pipes in the basement are black pipe with galvanized fittings.

VACUUM AND COMPRESSED AIR—A National air compressor with a 14-in. air cylinder and 12-in. stroke, rated at 321 cu. ft. of air per min. at 150 R. P. M., is installed in the boiler room. This compressor is run by a 40 H. P. rating motor run at a speed not exceeding 900 R. P. M. The motor is connected with a noiseless metal belt and is set on an extension of the metal base for the compressor; both are set on a concrete base. The motor is for 110 volts A. C. 60 cycles, 3-phase current, and is equipped with knife-switch and starting box mounted near by. Near the compressor are installed two 275-gal. black iron tanks, set upright, with $^1/_4$-in. shell and $^3/_8$-in. heads. These tanks have hand-holes at the bottom and are provided with openings to connect to the air compressor, since one tank is used for a vacuum tank and the other as an air storage tank. The air tank has a safety valve set at 30 lbs. pressure, and the line from the vacuum tank has a 3-in. brass check valve and a 3-in. regulating valve set to allow air to feed through the pump when the pressure drops below 25 lbs. on the air tank; the air tank is equipped with an air gauge and the vacuum tank has a gauge to show the vacuum on the tank. From the air and vacuum tanks, lines of galvanized pipe are run to connect the risers to the laboratories; 1-in. lines with $^1/_2$-in. connection also run to all rooms used as laboratories in the basement and first floor.

GAS, VACUUM, AIR AND WATER RISERS—Three sets of risers for gas, vacuum, air and water, exposed and of galvanized iron, are run to 1 ft. above the fourth floor. All exposed pipe running through the walls and floors in the building are run through No. 14 gauge galvanized sleeves with slip flanges on each end; the floor sleeves extend 1 in. above the finished floor. These sleeves were fastened to the concrete forms before the floor was put in. The sizes of the front risers supplying the rooms in the front part of the building are as follows: To connections for second floor gas, vacuum and air $1^1/_4$ in., and water $1^1/_2$ in.; to supply third floor gas, vacuum and air 1 in., and water $1^1/_4$ in.; the ends which run up 1 ft. above the fourth floor being gas, vacuum and air $^3/_4$ in., and water 1 in. The risers to supply the rear rooms to the right and left of the stair hall are of the same kind of pipe and are put in the same as the front risers, except that they are one size smaller, being $1^1/_4$-in. pipe. At a point near the ceiling of the first, second and third floors, $^3/_4$-in. lines for gas, vacuum and air, and 1-in. for water, are connected to risers; these lines are continued about 4 in. apart along near the hall partition to each end of the building, and are supported by $^3/_4$-in. pipe hangers, made square and fastened to the ceiling. There is one hanger in each 10-ft. room. Three-eighths in. lines for gas, vacuum and air, and $^1/_2$-in. for water, are connected to these lines and dropped straight down to each partition. These lines are continued down to the laboratory tables and along above them, leaving $^3/_8$-in. openings for gas, vacuum and air, and four $^1/_2$-in. openings on the water line, in each room. These openings are one above the other, 4 ft. from the hall partition and 4 ft. apart; where there is a sink on each side of the partition, connections are run through the wall by the use of crosses and pieces. The lines from risers at the rear of the building are put in the same as the front line, except that horizontal feed lines are one size smaller. The vacuum and compressed air lines were tested with 30 lbs. air pressure for 1 hr. after all connections had been put in and fastened.

LABORATORY SINKS—One hundred and one 14 × 20 in. sinks with patent overflow were set on $^3/_4$-in. galvanized pipe frames, having flanges on the floors, with braces half way up and binders on top, and made so that the tops of the sink set 3 ft. above the floor. As mentioned, each sink has a $1^1/_4$-in. extra strong lead waste pipe, fastened to the board under the laboratory table, with open ends to empty into receptors.

WASTE SINKS AND FOUNTAINS—Three 18 × 30 in. cast-iron enameled sinks, set on brackets, supplied with hot and cold water, are installed in the basement, two for drinking fountain waste and one for laboratory use: $1^1/_4$-in. galvanized waste lines, connected to 2-in. risers which empty into the sinks in the basement, were run from the fountains. These fountains are

FIG. 13—A VIEW IN THE ASSEMBLY HALL

supplied through block-tin pipe having all joints soldered with pure tin. The water flows by gravity from the still near the center of the building in the attic which has been described. The main lines down are $^3/_4$-in. I. D. 12-oz. block-tin pipe with $^1/_2$-in. I. D. 8-oz. block-tin pipe branches to each fountain. This pipe was furnished and placed by the plumbing contractor, while the still was furnished and installed by the Institute. The drinking fountains, six in number, have self-closing compression bibbs.

VENTILATING SYSTEM AND FAN—A No. 5 full housing multivane exhauster, provided with sub-base for motor, is installed on a concrete slab in the attic. The base for both the motor and fan is set on heavy $^1/_8$-in. sheet lead and 1-in. felt, bolted to the concrete slab. After mounting the wheel on the motor shaft, inside of the housing, it was coated with "Bitumastic" enamel. The exhauster is directly connected and is driven by a 3 H. P. motor, 690 R. P. M. The motor is for 110 volts A. C. 60 cycles, 3-phase.

The sewer pipe risers in the brick walls to the attic floor were built in by the brick contractor, while the plumbing contractor connected all risers with terra-cotta pipe run along the walls on the floor and covered these with concrete. The four risers connecting these lines to the fan are of extra heavy cast-iron, coated inside with "Bitumastic" enamel and supported from the ceiling on pipe hangers spaced 5 ft. apart. The exhaust line from the fan to the stack is connected with a No. 14 gauge galvanized iron pipe coated with "Bitumastic" enamel inside and out. All joints are made with a mixture of asphalt and kaolin.

VACUUM CLEANER RISER—Risers are provided for a vacuum cleaner; these are installed from the basement to 1 ft. above the fourth floor. This pipe is black iron with drainage fittings, and the risers are $2^1/_2$ in. with 2-in. openings on each floor, 1 ft. above the floor and 1 in. back from the finished wall in the hall. There is a total of 8 openings.

FIXTURES—The plumbing fixtures are connected with screw-pipe run exposed under the ceilings; all waste 2 in. and under are brass, and over 2 in., galvanized iron pipe with galvanized drainage fitting. The fourth floor has been roughed the same

as were the second and third floors, the openings being left ready to connect the fixtures, which will not be put in at present.

It may be mentioned in passing that the slop sinks, 18 × 22 in., are provided with Mueller self-closing compression bibbs; that the washstands, 20 × 24 in., are equipped with Mueller self-closing china index compression basin cocks; and that there are three slop sinks, two showers, seven closets, three urinals and seven washstands throughout the building, and three sinks in the basement. A heavy lead pan is placed under all showers; there are two iron ladders for the receptors; and all valves have numbered brass tags.

### ELECTRIC WIRING SYSTEM

CONDUITS—All wiring in the building is run in conduits of wrought iron pipe, enameled, galvanized or sherardized inside and outside, not smaller than $^5/_8$ in. inside diameter; and only one circuit is placed in each conduit. The conduits are fastened at least every 8 ft.; the joints are water-tight with standard couplings of the same material as the pipe, and the corners are turned with elbows on long radius bent on the pipe. No conduits are laid in contact with or near steam piping, and all are concealed. The conduits installed under the basement floor are of pipe known as extra heavy conduit; they have joints made with white lead and are gas- and water-tight. After installation, these conduits were tested with a gas pump and maintained a pressure of 2 in. of mercury with pumping.

OUTLET BOXES—At each outlet a galvanized pressed steel outlet box of not less than No. 12 gauge is placed and securely fastened; each box is provided with threaded insulated studs for supporting fixtures. All outlet boxes for the ceiling or bracket outlets are round and are small enough to be covered by a 4-in. fixture canopy. All switches other than the switches in the cut-outs are provided with square boxes.

The conduits are fastened to these boxes with lock-nuts and bushings, and there is sufficient room for the insulation of the joints, wires and bushings. It may be noted that all boxes are so set that all fixtures stand at right angles to the wall or hang plumb; they are designed so that the concrete, brick, etc., fit the same, in order to have the finished plate cover the joints between the box and the finished surfaces.

WIRES—No wire smaller than No. 12 B. & S. gauge is used and all wires larger than No. 10 B. & S. are stranded. The copper for the conductors is thoroughly tinned and possesses a conductivity of at least 98 per cent of that of pure copper. The wires for the A. C. flush plugs above the first floor and including the laboratories on the first floor, are No. 10 Duplex. The rubber insulation is protected by a braided covering which meets with all the requirements of the "National Electric Code" for high-grade wire.

Tests for insulation were made on a complete length without braiding, of not less than 500 ft., and after 48 hrs. immersion in water at 60° F. The tests were made with a well-insulated battery and galvanometer of not less than 150 volts, the readings being taken after electrification for one minute. It was required that each conductor stand a test of 2,000 volts for a period of five seconds after the insulation test, using the current from a generator and transformer.

All wires are of such sizes that with all the lights called for burning, and with the maximum output of power, there is no undue heating of the wires and cables, and the loss of potential between the service and any outlet is not greater than 4 volts. The drop in potential on any one circuit from the cut-out to the farthest lamp, with all lights on the circuit burning, is not greater than 1 volt. The main feeders are so proportioned that the drop in potential does not exceed 2 volts and the drop in the sub-feeders 1 volt.

The loss of potential is based on 16 candle-power 110 volts, 55 watt lamps. The building is wired for 16 candle-power incandescent lights, and not more than 660 watts or 12 lights have been allowed on any branch circuit.

MAIN FEED CONDUITS—Two 3-in. conduits for light and power, and one 3-in. conduit for telephone are provided from a manhole in front of the building to the transformer room in the basement. Two 3-in. conduits are also installed for light and power from a pole at the rear of the building. These conduits are carried to the main switchboard, with the exception of the telephone conduits, which terminate at the telephone junction boxes.

MAIN FEEDS FOR PANEL BOARDS—Conduits of proper size are installed from the main switchboard to each panel board on every floor. There are two separate lines of conduits to each panel board; one for A. C., the other for D. C. current.

SWITCH LIGHTING—Ten-ampere flush push switches of the "Hart-Diamond H" make are installed in suitable boxes on the face-plate to match the surrounding hardware. The backs of all plates come flush with the finished plaster line.

Where there are more than one switch at any one location, they are grouped under one gang plate.

FLUSH PLUG AND RECEPTACLE OUTLETS—Flush plug receptacles of the "Diamond H" make are installed in suitable boxes with face-plate to match the surrounding hardware, the plates being flush with the wall line. The plugs are 4 ft. above the finished floor line and are arranged for two different currents; the switch plates are accordingly engraved.

SYSTEM—The system for lighting and power is 110 to 220 three-wire A. C. current. For special service 110 two-wire D. C. current is provided.

POWER—There are installed an elevator motor, a ventilating motor, and a vacuum cleaner motor. The motor for ventilating[1] is, of course, installed in the attic.

CALL BELLS—Two 1-in. conduits are installed from a point near the Central Telephone Exchange on the first floor in the General Office to a wire shaft terminating in the telephone junction box on the first floor; it is continued up through the building and a 25-point terminal is furnished. From the telephone junction box a $^1/_2$-in. conduit is carried for the bell located in each room. The 3-in. bells are of the wood box type and "Fartay" manufacture.

SPECIAL OUTLETS—The outlets in the basement, on the floors of the electric furnace room and machine shop, consist of 8-in. square cast-iron boxes, drilled to receive the 2-in. conduit, and have brass water-tight covers set flush with the finished floors. The special outlet for the Assembly Hall is of the "Kleigle" make, of 60 amperes capacity.

HALL LIGHTING—The outlets at the stair landing are controlled by a special circuit from the first floor panel board; the other hall lights are controlled from panel boards located on each floor.

PANEL BOARDS—The panel boards for lighting are of the Pittsburgh Electric Machine Company's manufacture, with 3-wire bus-bars and 2-wire branches, and with 30-in. ampere circuit switches and main switch button. Each panel board is divided into two separate sections, one for lighting, namely, the 3-wire bus-bars, and one for the D. C. current, which has 2-wire bus-bars.

Each additional panel board is included in the flush, tight steel box provided with a door with a Yale lock. The boxes are 6 in. deep inside and have a 4-in. gutter around same. All panels have cartridge fuses and are constructed of 1-in. marble, with the necessary marble lining slotted for wires.

The main panel board consists of two separate panels, one for A. C. current and the other for D. C. current, and is mounted on an angle-iron frame; all necessary switches for the sub-feeders are mounted thereon.

The main switchboard is mounted on this panel board and

[1] See VENTILATING SYSTEM AND FAN, page

allowance is made for leaders; all connections are on the rear of the board, which is built of 2-in. white marble.

The mountings on the panel and main boards are completed with bus-bars mounted on the faces of the boards, with the exception of the main board, and the conducting parts are of highly polished and lacquered copper of ample size and design to prevent heating. Each branch circuit is plainly numbered and suitably lettered, and directory plates are placed, in convenient locations, to indicate the location of lines and power controlled by each switch or fuse.

The main bus-bars and brass and copper bars are in no case less than $1/8 \times 1/2$ in. Only rolled or drawn copper was used in the construction of the mounting, copper castings not being permitted.

Switches or additional panel boards have a carrying capacity of at least 30 amperes, and the jaws of all switches are sweated into the bars.

The fuse connections throughout the building are the N. E. C. enclosed type, of which a full equipment has been furnished.

### ORNAMENTAL IRON

The stairs are constructed with channel outside and plate wall strings, steel beams and angles, cast-iron treads, risers, platforms and base on sections. The hand railings are made from brass pipe and channels. The newels are made from cast iron and the balusters from steel; both received one coat of black paint before and one coat after erection.

The elevator shaft is enclosed with a simple design iron frame and iron doors with wire-glass panels. Both doors are arranged to swing out to permit the loading of large pieces of machinery, and the door openings in the basement hall are provided with channel iron frames.

### MAIN ENTRANCE AND STAIRWAY

A special feature of the main entrance is the bronze doors, each 3 ft. 6 in. × 11 ft. 6 in., leading into a marble vestibule, 4 ft. × 7 ft. 6 in. × 12 ft. 8 in., with enriched cornice and ceiling. The vestibule, main hall (15 ft. 10 in. wide × 43 ft. long × 12 ft. 8 in. high) and stairways have pink Tennessee marble floor and base.

### PLASTERING

All ceilings, walls and partitions in the basement, second and third floors, including the elevator shaft, were plastered with mortar composed of one part cement and two and one-half parts sand, which was skimmed with one part cement and two parts Ligonier sifted dust; this has made a hard surface.

The entire first floor, basement hall ceiling, stair halls and corridors were plastered with a patent plaster, which was skimmed with lime and plaster of Paris. The basement hall walls and the ceiling of the front pavilion were finished in cement in imitation of stone blocks. The ornament in the basement hall is of stucco.

### FLOORING

CEMENT FLOORS—Cement floors were constructed in the basement and at the front and rear entrances as follows: All places where the original grade had been disturbed were soaked and rammed; the surface was leveled off, rammed, and then a 4-in. bed of clean cinders was placed thereon. After soaking and ramming, a 4-in. bed of 1:2½:5 concrete was placed on the cinders. The floors were finished with a 1-in. top coat composed of one part cement and two parts crushed Ligonier limestone, screened through ¼-in. mesh screen. After troweling the top coat, it was kept covered with a 1-in. layer of sand kept wet for six days; the top coat and base were placed on the same day. The concrete floor was cut into blocks 4 ft. square, the cuts extending entirely through the base and top coat. The floors have a uniform fall to the bell traps.

FIREPROOF FLOORS—The first, second, third, fourth, and attic floors are constructed of hollow fireproof blocks, with reinforced concrete ribs and 2 in. of concrete on the top. The floor slabs were composed of 1:2:4 concrete. The tops of the floors were leveled for the reception of the ½-in. top coat of composition floor material.

COMPOSITION FLOORS—The first, second, and third floors, except the Assembly Hall floor, are covered with a top coat of composition floor with 4-in. sanitary cove base of the same material, put down in continuous sections in each room and hall. This material, which was laid by the Marbleloid Company, of New York, under the direction of Dr. R. R. Shively, a Fellow of the Institute, who has worked two years on such compositions, is gratifyingly satisfactory; it is straight, free from all imperfections, possesses resiliency, and is sanitary.

The floors were laid in two layers. The under or fibrous layer, which took care of the inequalities in the cement, is about 5/16 in. thick. The upper layer is ½ in. thick; it is of such composition that the absorption of water did not exceed 9 per cent when test-pieces were immersed for 24 hrs.

The composition floors are practically acid-proof, and are guaranteed not to crack, bulge, change color, nor to show a coating of white material on the surface after standing. When the floors were laid close to steam or hot water pipes, the latter were covered with asbestos ¼ in. thick. After troweling to a smooth surface, the floors received two coats of linseed oil.

LECTURE ROOM FLOOR—In the Assembly Hall, or Lecture Room, 2 × 4 in. beveled chestnut sleepers, 16 in. on centers, were bedded in cinder concrete, covered with one layer of asphalt-coated paper, and then 7/8 × 2 in. tongued and grooved maple flooring was put down.

### INTERIOR FINISH

All interior finish was worked from clear oak. The entire first floor finish is quarter-sawed white oak; all other parts of the building are finished in plain-sawed red oak.

### PAINTING

All exterior woodwork, except the outside doors and frames, received one coat of linseed oil stain and three coats of linseed oil paint. The first floor rooms received one coat of acid stain and two coats of wax; the tops and bottoms of doors and sash were primed and painted with two coats of linseed oil paint. The stair balustrade, newels and other exposed iron work had two coats of linseed oil paint, and the elevator doors and frames were finished with three coats of black paint and left with a dull finish.

The interior finish in all halls and corridors received one coat of acid stain and two coats of interior varnish. The remainder of the building received one coat of linseed oil stain and two coats of linseed oil paint.

All metal ware likely to be exposed to acid fumes in the laboratories has been treated with an acid-proof paint.

### GLAZING

All exterior windows are glazed with selected polished plate-glass; toilet room windows are glazed with double-chipped polished plate-glass, and polished plate wire-glass is used in all hoods and in the elevator doors and frames.

### ILLUMINATING GLASS

The illuminating glass used throughout the building is that manufactured by the Phoenix Glass Company, of Pittsburgh, Pa. This glass has been developed along scientific lines and represents the last word in efficiency; it has very low absorption. The semi-direct system is installed.

"Magnolia" glass bowls are installed in the executive suite, library, Assembly Hall, and corridors; these bowls are of artistic design, the particular feature thereof being the distinctive line etchings characteristic of the Phoenix products. In the general office, the "Phenixlite" is used; this is a simple light of very high efficiency.

### HEATING SYSTEM

The heating system consists of a gravity-return hot water

heating apparatus, erected and so arranged as to insure a free and easy circulation of water throughout the entire system, and so constructed that any of the radiators may be shut off without interfering with the circulation of the rest of the system.

STOKER—There is installed one "Detroit" stoker for a 54 in. x 14 ft. horizontal tubular boiler, including stoker fronts, coal magazines, grates, clinker crushers, firing tools, special fire-brick for stoker arch and fire door opening, engines, and operating mechanism. The stoker is of the reciprocating type, with extension setting, and is furnished with one variable speed A. C. motor with starting boxes attached to the side.

STEEL TUBULAR BOILER—The boiler is 54 in. in diameter, 14 ft. long out to heads; it is of the flush end type, constructed of open-hearth steel of standard quality, $^{13}/_{32}$ in. in thickness, having heads $^{1}/_{2}$ in. thick. It contains fifty lap-welded charcoal tubes, 4 in. in diameter, 14 ft. long, set in vertical and horizontal rows, not less than 1 in. apart each way, except in the middle two rows, which are 2 in. apart vertically. No tube is nearer than 3 in. from the shell. All riveting, lapping, and spacing were done in accordance with the most approved practice of recognized steam boiler inspection. The boiler was designed for a working pressure of 150 lbs. per sq. in.; it was tested under hydrostatic pressure.

A cast-iron top half-front was built in; this was supplied with double flue doors.

CAST-IRON BOILERS—Two horizontal hot water boilers of the "Presto" type, having a rated capacity not less than 6,425 sq. ft. each, are installed. The boilers are covered with 85 per cent magnesia blocks, $1^{1}/_{2}$ in. thick, a 1-in. air space being left between the boiler and the covering; this is covered with a $^{1}/_{2}$-in. coat of cement, skimmed with a $^{1}/_{4}$-in. coat of cement, and finally covered with canvas sewed on and painted. For the relief of the boilers of any excess pressure, a "Crosby" water relief valve is placed on each. Each boiler is furnished with one brass case water-works gauge, $8^{1}/_{2}$-in. dial. A brass case hot water thermometer, of the Hohman & Mauer Company's make, is placed on the flow pipes where they leave the boiler.

An approved gas burner with controlling device is installed complete under each cast-iron boiler.

FIXTURES—The above equipment includes all the necessary boiler castings and iron work, a complete set of hot water fixtures, including automatic fire regulator, thermometers, altitude gauge, etc., for each boiler. There is also installed one complete return tubular "Bayer" steam soot blower, connected with a $^{1}/_{2}$-in. air line near the boiler.

SMOKE CONNECTIONS—The smoke outlets on the boilers are connected to the openings in the smoke flues with black iron smoke connections, No. 16 gauge for the cast-iron boilers and No. 10 gauge for the tubular boiler, these connections being equipped with a full-sized balance damper with locking devices.

EXPANSION TANK—A steel open-expansion tank with cover is erected in the attic. This tank is made of $^{1}/_{4}$-in. plate with angle-iron frame around the top; it has a capacity of 250 gals., is provided with all necessary gauges, fixtures, and a float valve, and is connected to the system by means of expansion and circulating pipes. It is equipped with a 2-in. overflow which spills out on the basement floor. The tank is placed on supports 2 ft. above a 26-in. radiator.

PIPE—The main supply and return lines are supported from the first floor on heavy wrought-iron pipe hangers, spaced every 10 ft. All piping 7 in. and larger has standard flanges and fittings; all other pipe work was made direct into fittings with screwed threads. All flange joints were made with "Rainbow" packing. All pipe is standard merchant black pipe.

VERTICAL RISERS—The riser pipes leading to the first, second, third and fourth floor radiators are concealed in the outside walls; they are extended 1 ft. above the fourth floor and looped. All risers are valved with "Nelson" gate valves and have $^{3}/_{4}$-in. gate valves at the back for drains. All branch connections between the risers and the radiators are run on the ceiling below. Pipes passing through the walls and floors are provided with surrounding escutcheons.

RADIATION—One hundred and one radiators, of the Beaver and Invincible models, manufactured by the Pressed Metal Radiator Company, are installed throughout the basement, first, second and third floors. These radiators contain a total of $5{,}681^{1}/_{2}$ sq. ft. of heating surface.

All radiators in the basement are of the Beaver type, 32 in. high, and hung from the ceiling, except in one room, where the radiator is hung on the wall. All radiators above this floor are of the Invincible type, 26 in. in height, with 6-in. legs.

Generally speaking, the small research laboratories on the second and third floors contain one radiator; the large laboratories are provided with two. These were installed in accordance with a carefully prepared schedule of radiation.

NON-CONDUCTING COVERING—All flow and return mains and their branches, also all rising lines and horizontal radiator connections throughout the building, are covered with the best quality moulded sectional covering of 85 per cent magnesia, 1 in. thick, and then covered with 8-oz. white canvas duck, secured in place with lacquered bands. All fittings throughout the building are covered in the same manner. All covering which is exposed received an additional covering of 8-oz. canvas, sewed on.

PAINTING—The radiators throughout the building are painted with aluminum paint.[1] All exposed piping in the basement and the iron work around the boiler are painted with one coat of the best black japan.

VALVES—A Lavinge packless lock-shield union-angle valve is installed on the return end of each radiator. A return valve is also installed on each riser loop on the fourth floor.

Each radiator, the top of each riser loop, and all points where a reduction of two pipe sizes occurs, are equipped with a nickel-plated lock compression air valve and key.

THERMOSTATIC CONTROL—All radiators are controlled by the American Radiator Company's thermostatic control system. All rooms in which the radiation is placed may be heated to a temperature of 70° F. when the outside temperature is at zero, with the water in the boiler at 180° F.

LIVE STEAM FOR LABORATORIES—A live steam system is installed in the basement with $^{3}/_{8}$-in. opening under each vent hood. This system is constructed of black pipe with cast-iron fittings and has a 10-lb. pressure. All upright and horizontal feed lines are covered with 1-in. thick asbestos covering and sewed canvas jacket. The canvas covering and all exposed pipes received two coats of asphalt paint. All $^{3}/_{8}$-in. branches are galvanized pipe. The horizontal feed lines have a 1-in. fall to 20 ft. towards the return lines.

The boiler for this system is placed in the boiler room. All connections from the feed lines are taken from the top and returned down to the vent hood; the horizontal lines have two pipe hangers in each 20-ft. room and one in each 10-ft. room.

### ADMINISTRATION

The suite of the Director, Dr. Raymond F. Bacon, is on the first, the main, floor, with the general office and that of the editorial department adjacent. The executive suite contains the Director's private office, a room 20 x 24 ft.; Director's retiring room, 11 x 15 ft.; and Director's private laboratory, a room 20 ft. x 20 ft. 6 in., equipped the same as the large size research laboratories on the second and third floors.

The general office occupies a room, 24 ft. 6 in. x 38 ft. 6 in., in conjunction with a telephone central and in-

[1] This paint was kindly donated by Mr. Maximilian Toch

formation bureau counter off the main hall; it is provided with a fireproof vault, 2 ft. 6 in. x 9 ft., a book closet, 4 x 8 ft., and a cloak closet. The secretarial force, which at present numbers five, is in charge of the Secretary to the Director. The walls of the general office are decorated with pennants of the various institutions of learning represented on the staff; it is customary for each Fellow to present a pennant of his alma mater as a pledge of his honor and fidelity to the Institute.

Two of the Assistant Directors, Drs. E. Ward Tillotson, Jr., and Samuel R. Scholes, whose office adjoins the Assembly Hall on the first floor, are in direct charge of the individual researches in progress, with the exception of certain of the multiple fellowships, which are under Director Bacon's immediate supervision; they also exercise superintendence over the maintenance of supplies and equipment.

FIG. 14—THE PRIVATE OFFICE OF THE DIRECTOR, DR. RAYMOND F. BACON

In addition to this administration of the internal affairs of the Institute, another Assistant Director, John J. O'Connor, Jr., attends to the presentation of the work of the Institute to prospective donors of industrial fellowships.

## THE OBJECT AND WORK OF THE MELLON INSTITUTE[1]

By Raymond F. Bacon

The dedication of a permanent home for the Mellon Institute of Industrial Research and School of Specific Industries of the University of Pittsburgh marks an important point in the history of American industry and education. Wherever raw materials are secured or wherever they are made into goods to supply the many wants of man, there is a variety of problems awaiting solution. These may have to do with difficulties in manufacture, with the utilization of wastes, with the improving and cheapening of manufactured products, with finding new uses for products, or with the discovery of new and useful products. To aid industrialists in solving these problems, by bringing the wealth of contemporary science to bear upon them, the Mellon Institute was founded.[1] This Institute represents an alliance between industry and learning, the possibilities of which may be said to be without limit.

The alliance takes the form of what is known as "The Industrial Fellowship System." According to this system, an individual or a company having a problem requiring solution may become the donor of a fellowship by contributing to the Institute a definite sum of money, for a period of not less than one year. This money is used to pay the salary of the man or men selected to carry out the investigation desired, and the Institute furnishes such facilities as are necessary for the conduct of the work. The results obtained belong exclusively to the donor of the fellowship.

### HISTORY OF THE INDUSTRIAL FELLOWSHIP SYSTEM

The idea of this system of practical coöperation between science and industry was formulated by Robert Kennedy Duncan, the late Director of the Mellon Institute, in 1906, while attending the Sixth International Congress of Applied Chemistry in Rome.

For some years previous to this Congress, Dr. Duncan had been in Europe gathering material for two of his books, "The New Knowledge" and "The Chemistry of Commerce." Through visits of inspection to the factories, laboratories and universities of some of the countries of Europe, and through conversations with industrialists and scientists, he had become impressed with the spirit of coöperation which existed between industry and learning which made for the advancement of both. At the same time, he became aware, more than ever before, of the fact that much of American industry, from the standpoint of manufacturing efficiency, was in a lamentable condition. The absence of the application of modern science was one reason for this condition.[2]

To remedy this, it occurred to Dr. Duncan to propose an Industrial Fellowship System. Upon his return from Europe to accept the chair of industrial chemistry in the University of Kansas, he established there the first Industrial Fellowship in January, 1907. The scheme was presented to the public by Dr. Duncan in an article entitled "Temporary Industrial Fellowships" in the *North American Review* for May, 1909, and a little later in the last chapter of his book on "The Chemistry of Commerce."

In 1911, Dr. Duncan was called to the University of Pittsburgh to inaugurate the system in the Department of Industrial Research, and the working of the fellowships began in a temporary building erected at a cost of about $10,000. In March, 1913,[3] Messrs. Andrew William Mellon and Richard Beatty Mellon, citizens of Pittsburgh and sons of the late Judge Thomas Mellon of the class of 1837 at the University of Pittsburgh, impressed by the practical value of the system, both to industry and to learning, es-

[1] Address delivered in abstract at the annual Alumni Banquet of the University of Pittsburgh, Hotel Schenley, February 26, 1915.

[1] "On the Value of Research to Industry," see Bacon, *Science, N. S.* **40** (1914), 871–81.

[2] See especially Duncan, THIS JOURNAL, **3** (1911), 177, wherein the relation between chemistry and manufacture is discussed fully; and Duncan, *Harper's Mag.*, **126** (1913), 385–90.

[3] "On the Status of the Industrial Fellowship System Prior to 1913," see Duncan, *J. Frank. Inst.*, January, **1913**, 43–57.

tablished it on a permanent basis through the gift of over half a million dollars. While the Institute is an integral part of the University of Pittsburgh and works in close sympathetic accord with it, it possesses an endowment of its own and is under its own management. The present annual expenditure for salaries and maintenance is over $150,000.

On February 18, 1914, the Institute lost by death its founder and Director, Dr. Robert Kennedy Duncan. Dr. Duncan was succeeded by the writer, who had been Associate Director.

### THE FELLOWSHIP AGREEMENT

The fellowships of the Institute consist of two kinds, individual and multiple. An individual fellowship utilizes the services of one man, directly responsible to the administration; a multiple fellowship, the intensive services of several men under the direction of a Senior Fellow who, in turn, is directly responsible to and under the administration.

Each fellowship that comes to the Institute is the subject of a definite agreement between the individual or company concerned and the Institute. While the agreement is modified from time to time, depending upon exceptional circumstances, the following is the form of single fellowship agreement now being used by the Institute:

### .....COMPANY'S FELLOWSHIP AGREEMENT

THIS AGREEMENT, made and entered into this....day of ....., 19.., between the Mellon Institute of the University of Pittsburgh, of the City of Pittsburgh, Pennsylvania, hereinafter called the "Institute," and the....., of....., hereinafter called the "Company,"

WITNESSETH: That for the purpose of promoting the increase of useful knowledge, the parties hereto agree as follows:

1—The Company shall pay to the Institute annually in advance for a period of.....years, beginning....., 191.., the sum of.....dollars ($....) for the foundation of an Industrial Fellowship to be known as..... FELLOWSHIP, the exclusive purpose of which is.....

2—The Institute shall accept the sums so to be furnished by the Company and shall devote them to the furtherance of the problem of this Fellowship; and to this end all money received from the Company under this Agreement shall be paid over by the Institute in monthly installments to the holder of this Fellowship, in such amount as may be agreed upon by the Institute and the Fellow concerned, and expended for such apparatus and supplies related to this research as the Director of the Institute may deem it advisable to purchase and for travelling expenses related to the elucidation of the problem concerned. The Fellow shall be provided, at the expense of the Institute, with a separate laboratory and with such apparatus, supplies and reagents as in the opinion of the Director constitute a reasonable provision. The Company, on its part, shall coöperate with the Institute in this research by providing the Director thereof and the Fellow of this Fellowship with its sympathy and whatever knowledge of the subjects of research it may possess, and, on approval of the Company, with its factory facilities for large-scale experimentation.

3—The holder of the Fellowship provided hereunder shall be appointed by the Committee of Management of the Institute upon the nomination of the Director in accordance with the terms of his formal letter of application to and as approved by the Director, and he shall give his whole time and attention to the object of the Fellowship, with the exception, if the Director so elect, of three hours a week which he shall give to instructional work in the University of Pittsburgh. The Fellow shall work under the advice and direction of the Director and shall from time to time through the Director forward to the Company reports of the progress of his work. During the existence of the Fellowship provided hereunder the Company shall have the right, through and with the acquiescence of the Director, to employ and take into its regular service the Fellow of this Fellowship, upon terms to be agreed upon between the Fellow and the Company.

4—The Institute, at the expiration of the Fellowship, shall return to the Company any money paid to it by the Company, in case any thereof shall remain unexpended for the purpose of this Fellowship.

5—Any and all discoveries made by the Fellow during the term of this Fellowship, as well as all information obtained by him germane to the subjects of his investigation, shall become the property of the Company, subject to the terms and provisions of this Agreement, and the Fellow making such discovery or obtaining such information shall promptly and without demand make revelations of all such information and discoveries. Such revelations shall be made to the duly designated representatives of the Company directly, or through the Director, as the Director may determine.

6—The Fellow of this Fellowship making a discovery or invention germane to the subjects of his investigation shall, at any time, at the option and expense of the Company, apply for letters patent, and shall upon demand assign such letters patent and any and all rights to such invention to the Company under the conditions of this Agreement. In case the Company desires to keep secret such discovery or invention, or for any reason desires that letters patent shall not be applied for, the Fellow shall not at any time apply for patent or patents in his own name, and shall not disclose such discovery or invention to others except as herein provided.

7—The Company shall, in addition to the sum paid to the Institute as foundation for the Fellowship, pay to the Fellow a maximum cash bonus of.....dollars ($.....) or any part thereof which in the opinion of the Board of Arbitration (hereinafter provided for) is deserved by the Fellow of this Fellowship, and the amount of this payment and the time or times of payment shall be decided by the Board of Arbitration upon application of either of the parties hereto.

8—In the event of any difference of opinion between the parties hereto as to the interpretation of this Agreement, or the rights of the respective parties to this Agreement, the matters in issue shall be referred to a Board of Arbitration, which Board shall consist of a representative of the Institute and a representative of the Company, and a third person whom these two shall select. The decision of this Board shall be obtained without recourse to the courts and, when rendered, shall be binding upon the parties hereto.

9—During the term of this Fellowship, the holder thereof may publish such results of his investigation as do not, in the opinion of the Company, injure its interests. On or before ....., 19...., the holder shall have completed a comprehensive monograph on the subjects of his research. The subject matter of such monograph shall not contain specific information of the process or methods of the Company, but it shall be confined to a statement of new discoveries of scientific fact obtained by this Fellowship, and such statement shall not contain data or information in regard to the cost of manufacture by any process revealed in such statement. A copy of this monograph shall be forwarded to the Company and a

copy shall be signed and placed in the archives of the Institute until the expiration of three years from the time hereinafter provided for the termination of this Fellowship, when the Institute shall be at liberty to publish it for the use and benefit of the public.

In the event that in the opinion of the Company such publication at such time will unduly injure its interests, it shall have the privilege of appealing at any time for an extension of time of such publication to the Board of Arbitration provided for herein, which after considering the appeal shall, if in its opinion such publication will unduly injure the Company's interests, extend the time of publication to a time when in the Board's opinion publication will not unduly injure the interests of the Company.

10—The Fellowship provided under this Agreement shall terminate.....day of....., 19.....

IN WITNESS WHEREOF, the parties hereto have caused their names to be subscribed the day and year above mentioned by their duly authorized officers.

Witness:
.....
.....

MELLON INSTITUTE OF UNIVERSITY OF PITTSBURGH,
By.....
.....
By.....

It is evident from this agreement that four different parties are affected: the Company; the Fellows; the University; the Public.

1—THE COMPANY

The Company obtains from the Institute such research laboratory facilities as but few industrial concerns possess. Even more important, it obtains complete library facilities, which are so valuable in research work.

There is a scarcity of men gifted with the genius for research, and it requires much experience in selecting suitable men and in training them to the desirable degree of efficiency, after having determined the special qualities required. Important qualifications in industrial researchers are keenness, creative power, and confidence; these are often unconsidered by manufacturers, who, in endeavoring to select a research chemist, are likely to regard every chemist as a qualified scientific scout. The men who are best trained for a particular problem are carefully chosen by the Institute and these work under the supervision of a staff experienced in handling industrial research problems. The Company thus secures at a comparatively small cost ideal conditions for working out industrial problems which would cost any single company probably from $60,000 to $70,000 each year to duplicate in a laboratory which it might establish in connection with its own factory.

The Institute, through its affiliation with the University, is able to offer the Company large and important consultative facilities—psychological, physical, engineering, biological, etc.

The Company has an opportunity to obtain for its own organization young men who have had not only thorough scientific training but very special training in the Company's own lines as acquired through its Fellowship.

There is about university work, as differentiated from the factory, freedom from interference, correct judgments concerning progress, and an atmosphere sympathetic to research.

All these advantages, laboratory, library, consultative and inspirational, together with the supervision and administration of these Fellowships, the Institute offers gratuitously to any company having important problems offering a reasonable chance of solution, and it undertakes, as well, to surround these researches with the necessary secrecy.

Experience has proved that through this system of Industrial Fellowships a company can generally do its research work more efficiently and cheaply in the Institute than in its own laboratory. Finally, it has been found that where there exists a close and sympathetic coöperation on the part of the Company, many remarkable results have been achieved.

2—THE FELLOWS

The agreement gives to ambitious young men an opportunity to work out, in a scientific manner, great industrial problems, and not only to work them out in the laboratory but, if the laboratory solution appears to have commercial possibilities, to go further and to try out the methods evolved on a factory scale and, ultimately, to put new processes into industrial operation.

It gives young men a chance to obtain much experience in practical research while they are receiving a satisfactory remuneration. Each Fellow has the benefit of the Institute's very excellent apparatus, chemical and library equipment—facilities which are so essential in modern research; and because of these opportunities and that of being able to pursue post-graduate work for a higher degree, it has been demonstrated that a higher type of research chemist can be obtained by the Institute for a certain remuneration than can be generally secured by manufacturers.

Finally, if the Fellows succeed in a practical way, they receive, through their bonus, a substantial, practical reward, and often the opportunity to become permanently connected with the Company concerned in the agreement.

3—THE UNIVERSITY

The University, under the agreement, fulfils its function in increasing the sum of knowledge; the fact that it is useful knowledge does not make it any less valuable. Furthermore, the right, after a reasonable time, to publish such knowledge is assured to the University. The University also obtains a highly trained staff of specialists as a faculty for a School of Chemistry and Chemical Engineering. Then, too, the University undoubtedly feels the stimulating influence of having in its midst a large body of trained investigators engaged in research work.

4—THE PUBLIC

The public is also advantaged through this system. No discovery can go to the public as a useful actuality of achievement except through some company, and every useful and significant fact developed by a company is a permanent asset to the human race.

The agreement provides for the publication of the results of a Fellowship for the benefit of the public

at the expiration of three years from the time of termination of the agreement, provided that publication at that time does not unduly injure the interest of the donating company. However, many of the by-paths which appear in every investigation yield results of scientific interest and a number of papers detailing results of work of this character have been published by the Institute from time to time.[1]

### INDUSTRIAL RESEARCHES IN PROGRESS

A list of the twenty-three Fellowships in operation at the time of the dedication of the new building (February 26, 1915), together with the men appointed for them, follows.

#### 0—CRUDE PETROLEUM

September 22, 1911—$10,000, 1st year; $10,000, 2nd year; $10,000, 3rd year; $10,000, 4th year, including apparatus fund.

BONUS: Collective interest, 10 per cent.

FELLOWS: Benjamin T. Brooks, Ph.D., University of Göttingen, SENIOR FELLOW. Clinton W. Clark, A.M., Ohio State University—*Work completed.* Lester A. Pratt, M.S., New Hampshire College—*Work completed.* Hugh Clark, A.M., Ohio State University—*Work completed.* Arthur H. Myer, A.M., Leland Stanford, Jr., University—*Work completed.* Frederick Padgett, M.S., University of Pittsburgh. F. W. Bushong, Sc.D., Emporia College—*Work completed.* I. W. Humphrey, M.S., University of Kansas. George W. Stratton, Ph.D., Ohio State University—*Work completed.* Harold Hibbert, D.Sc., Victoria University. Harry Essex, Ph.D., University of Göttingen.

#### 18—BAKING

May 12, 1913—$6,000 a year for two years, and $500 apparatus fund.

BONUS: $10,000.

FELLOWS: Henry A. Kohman, Ph.D., University of Kansas, SENIOR FELLOW. Charles Hoffman, Ph.D., Yale University—*Work completed.* Truman M. Godfrey, B.S., University of Kansas. Lauren H. Ashe, B.S., University of Pittsburgh.

#### 19—ALUMINUM

May 12, 1913—$5,000 a year for two years, including apparatus fund

BONUS: $10,000.

FELLOWS: Hugh Clark, Ph.D., University of Pittsburgh. Lester A. Pratt, Ph.D., University of Pittsburgh. Frank D. Shumaker, B.S., University of Pittsburgh.

#### 20—GLUE

May 12, 1913—$1,500 a year for two years and $300 apparatus fund.

FELLOW: Ralph C. Shuey, B.S., University of Kansas.

#### 21—SOAP

May 12, 1913—$1,500 a year for two years and $300 apparatus fund.

FELLOW: Ben H. Nicolet, Ph.D., Yale University.

#### 22—GLASS

July 14, 1913—$1,500 a year for two years and $300 apparatus fund.

BONUS: $3,500.

FELLOW: R. R. Shively, Ph.D., University of Pittsburgh.

#### 23—RELATION OF ELECTRICAL POTENTIAL TO CATALYTIC ACTION

July 14, 1913—$1,500 a year for two years and $300 apparatus fund.

BONUS: 5 per cent industrial results.

FELLOW: Frank F. Rupert, Ph.D., Massachusetts Institute of Technology.

#### 25—YEAST

July 14, 1913—$5,200 a year for two years, including apparatus fund.

BONUS: $10,000.

FELLOWS: F. Alexander McDermott, M.S., University of Pittsburgh, SENIOR FELLOW. Ruth Glasgow, M.S., University of Illinois. William Smith, B.S., Scholar, University of Pittsburgh James C. Cuthbert, Scholar, University of Pittsburgh—*Work completed.* Lauren Hewitt Ashe, B.S., Scholar, University of Pittsburgh—*Work completed.*

#### 27—LEATHER

October 22, 1913—$1,000, 1st year, and $200 apparatus fund; $1,650, 2nd year, including apparatus fund.

BONUS: 10 per cent interest.

FELLOW: R. Phillips Rose, M.S., University of Kansas.

#### 28—FERTILIZER

November 1, 1913—$2,500 a year for two years, including apparatus fund.

BONUS: $5,000.

FELLOW: Earl S. Bishop, Sc.D., Queen's University, Ontario

[1] A list of these contributions, 1912–1914, is given in *J. Frank. Inst.*, November, **1914**, pp. 629–32.

#### 30—RADIATORS

November 18, 1913—$2,000 a year for two years, including apparatus fund.

FELLOW: J. C. Ballantyne, B.Sc., University College, London; M.S., University of Pittsburgh.

#### 31—TURBINE ENGINES

September 1, 1914—$1,800 a year for one year, including apparatus fund.

BONUS $3,000.

FELLOW: Rudolph McDermet, M.S. in E.E., University of Illinois.

#### 34—FATTY OILS

July 1, 1914—$2,100 a year for one year, including apparatus fund.

FELLOW: Leonard M. Liddle, Ph.D., Yale University.

#### 35 ORES

June 15, 1914—$5,300 a year for one year, including apparatus fund.

FELLOWS: Charles O. Brown, A.M., Cornell University. James B. Garner, Ph.D., University of Chicago. Clement L. Perkins, B.S., New Hampshire College. E. R. Weidlein, A.M., University of Kansas, SENIOR FELLOW (*advisory*). G. A. Bragg, B.S., University of Kansas (*advisory*). H. D. Clayton, B.A., Ohio State University (*advisory*).

#### 36—FLOTATION

June 15, 1914—$3,200 a year for one year, including apparatus fund.

FELLOWS: Harry P. Corliss, Ph.D., University of Pittsburgh. Clarence L. Weirich, M.S., University of Pittsburgh.

#### 37—ACETYLENE

November 15, 1914—$3,000 a year for one year, including apparatus fund.

BONUS: $5,000, maximum.

FELLOW: George O. Curme, Jr., Ph.D., University of Chicago.

#### 38—DENTAL SUPPLY TRADE PROBLEMS

July 1, 1914—$3,200 a year for one year, including apparatus fund.

FELLOWS: Clarence C. Vogt, Ph.D., Ohio State University. H Edmund Friesell, D.D.S., Pennsylvania Dental College (*advisory*).

#### 39—FAT COMPOUNDS

October 1, 1914—$2,500 a year for one year, including apparatus fund.

FELLOW: Edmund O. Rhodes, M.S., University of Kansas.

#### 40—STONE

October 26, 1914—$1,800 a year for one year, including apparatus fund.

FELLOW: H. C. Holden, M.S., New Hampshire College.

#### 41—COPPER

November 1, 1914—$6,000 a year for one year, including apparatus fund.

FELLOWS: E. R. Weidlein, A.M., University of Kansas, SENIOR FELLOW. H. D. Clayton, B.A., Ohio State University. G. A. Bragg, B.S., University of Kansas.

#### 42—GLASS

December 3, 1914—$1,800 a year for one year, including apparatus fund

FELLOW: John F. W. Schulze, Ph.D., Clark University.

#### 43—LAUNDERING

February 1, 1915—$1,800 a year for one year, including apparatus fund.

FELLOW: Harvey G. Elledge, B.S., University of Kansas.

#### 44—LAND DEVELOPMENT

February 1, 1915—$1,000 a year for one year.

FELLOW: Will E. Vawter, B.S., University of Kansas.

### THE SCHOOL OF SPECIFIC INDUSTRIES

The new building of the Mellon Institute was especially designed to afford ample accommodation for a Graduate School of Specific Industries; and, as this is altogether a new idea in education, an explanation of its purpose is in order.

As the Industrial Fellowships which constitute the basis of the system in operation, are constantly increasing in amounts subscribed by the industrialists for their maintenance, and, as well, in their importance, it is, of course, obvious that the seventy researchers thus provided for will number among them men of national or international importance, to say nothing of the fact that, as a class, they are carefully chosen

as picked men from the best institutions of learning and from the greatest industrial organizations in this country. Such a corps of workers will, therefore, be of the highest potential value as an educational staff for students fitted to receive such instruction. Enthusiastic young chemists who have received a thorough training in the fundamentals of the science and who desire to make their life-work in a certain industry, may thus become thoroughly familiar with the application of chemistry to that particular industry—by being in intimate contact with those who are devoting their whole time to the problems of that specific industry. Thus, for example, the man who wishes to become an expert in *glass* will work in the laboratory and in the glass factory with those who have, for a long time, been devoting themselves to the problems of the glass industry and who are in the forefront of that industry.

The young man just out of school, going directly into the factory, is apt to encounter many conditions so discouraging that, unless he is of very exceptional calibre and receives more than ordinary encouragement from those in charge of the business, he may lose his enthusiasm and degenerate into a routine man, and, perhaps, never be able to contribute anything to the upbuilding of that particular industry. American factories, as a rule, do not have adequate laboratory facilities for research, and too many American business executives do not appreciate the time and difficulties involved in prosecuting successful research. Many lines of business are so full of tradition and prejudice that serious obstacles are often deliberately put in the way of the young chemist by misguided workmen and superintendents to prevent his experiments from turning out successfully. Another point of considerable importance in this matter has to do with the organization of many American factories. While the higher executives of the company may thoroughly appreciate difficulties of research and the time often necessary for its successful prosecution, in the actual factory organization the chemist is very often placed immediately under and must report to some man who does not have such breadth of view. This man is often the factory superintendent, who may be chosen primarily because of his ability as a driver of men. The factory superintendent may tell the chemist to undertake a certain piece of research. In a few weeks —or sometimes even in a few days—he comes around to find out the result obtained. If no result is available, very often the chemist is shifted to other problems; or it may be that something unusual, which has just arisen, seems of pressing importance and the chemist is asked to drop everything else to take up the new matter. The net result is that after a few attempts by the young chemist to do big things, unsuccessful because the necessary uninterrupted time was not allowed, the factory superintendent reaches a conclusion that nothing can be gained by the research of the chemist, and the chemist himself, especially if young and inexperienced, may lose his ideals of research.

Under the system of Industrial Fellowships in operation at the Mellon Institute, both the Institute and the Fellow have the sympathy and hearty coöperation of the higher officials of the corporation concerned; and yet in his work the Fellow is, to a considerable extent, independent of that corporation, as he is under the immediate control of the administration of the Institute. The Institute is thus able in many cases to push through to a successful conclusion large-scale experiments in the factories of the corporation which could hardly be accomplished by the company's own chemists. The young student entering the School of Specific Industries learns the difficulties which must be overcome in successful large-scale work, not only on the purely scientific and experimental side but also on the human side, and finds that by proper and tactful methods these human difficulties can be met; so that, instead of losing his first rush of enthusiasm, he gains by actually seeing ideas and theories grow into commercial realities. Lectures are given on the problems of chemical industry, the methods employed in their attack, and on the design, erection and equipment of chemical plants; and specific problems of industrial importance are assigned to the student, who follows the steps preparatory to the solution thereof, from the laboratory to the unit plant stage. The Institute is especially well equipped for such instruction.

Mention may be appropriately made here of the Institute's "large-scale equipment." When a process, developed during the course of a fellowship, demands apparatus of a new type, which is not available in the factory, a unit plant is built. This plant is of such a size and is built in such a way that, when it is running smoothly, the manufacturer will feel justified in taking over its plan and spending such money as will be necessary to put in a very much larger unit or, it may be, several units. I might say that the companies which are using the Institute have, during the past year, spent approximately $55,000 in building small unit plants to develop the processes which have been worked out in the laboratory. This does not include many processes which were adapted to the factory equipment already on hand. In no case was any of this money for plants provided for in the original foundation of the Fellowship, but in every case, after conference, the company felt that the progress of the work and the results obtained appeared promising enough to justify them in the expenditure of this money for further development. In the case of a number of these small plants in which processes have been developed, and where the processes have now gone into the commercial scale of operation, the plants are still available, being located in small, temporary buildings around the Institute; such unit plants can often be adapted to the study of other new processes. The Institute is thus gradually acquiring what might be called a "large-scale equipment" that is undoubtedly unique in American laboratories.

Such, in brief, is the idea of the School of Specific Industries. It is not the intention to go out after students for this School, nor is it the intention ever to have very many students in the School, but it is believed that the proper sort of young men will seek its instruction.

# WILLIAM H. NICHOLS MEDAL AWARD

The Nichols Medal, awarded by the New York Section of the American Chemical Society for the best original contribution to the publications of the Society during the year 1914, was conferred upon Dr. Irving Langmuir, of the General Electric Company Research Laboratory, in recognition of his distinguished researches on chemical reactions at low pressures, at the regular meeting of the Section, March 5, 1915.

The medal was presented by Professor Allen Rogers, Chairman of the Section. The addresses of presentation and acceptance are printed below, together with Dr. Langmuir's abstract of his paper on "Chemical Reactions at Low Pressure," presented in accordance with the rules for the award of the medal.

The Nichols medal was founded in 1902, and the eleven impressions made to date have been awarded as follows:

| | |
|---|---|
| E. B. Voorhees | 1903 |
| C. L. Parsons | 1905 |
| M. T. Bogert | 1906 |
| H. B. Bishop | 1907 |
| W. H. Walker | 1908 |
| W. A. Noyes and H. C. P. Weber | 1908 |
| L. H. Baekeland | 1909 |
| M. A. Rosanoff and C. W. Easley | 1911 |
| Charles James | 1912 |
| M. Gomberg | 1914 |
| Irving Langmuir | 1915 |

—[Editor]

IRVING LANGMUIR—WILLIAM H. NICHOLS MEDALIST, 1915

## PRESENTATION ADDRESS

By Allen Rogers[1]

We are assembled this evening to do honor to a man whose wonderful achievement along scientific lines has very largely attributed to the developments in the high-efficiency tungsten lamp. We can hardly realize, as we enjoy our present day illuminations, that only a few years back our fathers read by the light of the tallow dip. It is such men, however, as Dr. Irving Langmuir, who by their untiring efforts have made this lighting system possible, and to them we owe a debt of gratitude which can never be repaid.

Dr. Langmuir was born in Brooklyn, New York, January 31, 1881. His early education was obtained in the public schools of that city which he attended until June, 1892, at which time his parents went to Paris; there he studied under French teachers for three years. Returning to the United States in the fall of 1895, he entered Chestnut Hill Academy at Philadelphia, and the following year found him in Brooklyn again, attending Pratt Institute. On completing his course at Pratt Institute he entered the School of Mines at Columbia University from which he was graduated in 1903 with the degree of metallurgical engineer. On finishing his course at Columbia we next find him doing post-graduate work at the University of Göttingen under Prof. Nernst, carrying out investigations on the kinetics of chemical reaction and on the dissociation of water vapor and carbon dioxide. In January, 1906, the degrees of M.A. and Ph.D. were awarded to him by the University of Göttingen, his major subject having been physical chemistry.

Returning to America Dr. Langmuir became instructor in chemistry at the Stevens Institute of Technology, where he taught until July, 1909. At this time he entered the research laboratory of the General Electric Company at Schenectady, since which time he has been engaged mainly in investigations on tungsten lamps and also to some extent in work on electric heating devices. Dr. Langmuir has been a frequent contributor to the various scientific journals, and on several occasions has appeared before this section. Some of his contributions are the following:

"Thermal Conduction and Convection in Gases at Extremely High Temperatures."

"A Chemically Active Modification of Hydrogen."

"Chemical Reactions at Very Low Pressures—The Clean-up of Oxygen in a Tungsten Lamp."

"Chemical Reactions at Very Low Pressures—The Clean-up of Nitrogen in a Tungsten Lamp."

"Laws of Heat Transmission in Electrical Machinery."

"Conduction and Radiation of Heat."

"Dissociation of Hydrogen into Its Atoms."

To Dr. Langmuir:

Dr. Irving Langmuir, on behalf of the New York Section of the American Chemical Society, as a slight token of the appreciation and esteem in which you are held by your brotherworkers in the field of chemistry, I take great pleasure in presenting to you the William H. Nichols Medal and sincerely hope that your future efforts will be as fruitful as your undertakings have been in the past.

[1] Chairman New York Section of the American Chemical Society.

Pratt Institute, Brooklyn

## ADDRESS OF ACCEPTANCE

By Irving Langmuir

Mr. Chairman: I deeply appreciate the honor that has been conferred upon me by the New York Section of the American Chemical Society, and I thank you for the kind words you have spoken.

The credit for the work upon which this award is based, should really be shared by many. In the first place, these investigations would never have been possible if it had not been for the active encouragement given by Dr. Whitney and for the wonderful spirit of coöperation and enthusiasm which he has instilled into the research laboratory.

In the second place, the work is the result of the very unusual ability of my assistant, Mr. Sweetser, who has carried out fully 90 per cent of all the experiments. Mr. Sweetser has made a quantitative study of a very large number of chemical reactions and other phenomena, and the data are preserved in the form of about 3000 large pages of notes which record all the details of the experiments. These data constitute a veritable mine of information on low pressure reactions. The results of only about one-fifth of the material have been published thus far. Gradually, I am working through the remaining four-fifths, trying to analyze the results and trying to develop theories of the phenomena observed. Besides Mr. Sweetser, there have been many other members of the laboratory who have actively contributed to this work. Among these I would mention especially Mr. Mackay and Mr. Rogers.

## CHEMICAL REACTIONS AT LOW PRESSURES

By Irving Langmuir

If small quantities of almost any gas are introduced into an evacuated bulb containing a highly heated tungsten filament, it is found that the gas gradually disappears. In the great majority of cases this action proves to be of a purely chemical nature.

A large number of reactions have been studied quantitatively in this way, using many different gases and several different filament materials. In each case the actual rate was determined at which the gas disappeared, under given conditions of pressure, filament temperature and bulb temperature. Pressures ranging from 0.0001 to 0.05 mm. of mercury were employed.

The phenomena observed were studied from the view-point of the kinetic gas theory, and in this way it has been possible in the majority of cases to draw some more or less definite conclusions as to the mechanism of the reactions involved. In particular, the statistics of the reactions have been determined wherever possible. Thus, in a reaction between a gas and a solid body, the question is raised: Out of all the molecules which strike the surface of the body, what fraction enters into reaction with it? Similarly, in a reaction between gases, the question becomes: Among all the collisions between molecules of the two gases, what fraction results in combination?

The reactions occurring between heated filaments and the surrounding gases are heterogeneous. Reactions of this type have often been investigated in the past and several theories of the mechanism of such reactions have been advanced. The theory that has met with most favor is that of Bodenstein and Fink, according to which the velocity of the reaction is limited by the rate at which the reacting substances can diffuse through an adsorbed film of gases on the surface. The rate of diffusion is inversely proportional to the thickness of this film and the thickness of the film is in turn dependent on the partial pressure of the gas from which it is formed.

As a result of several years of study of heterogeneous reaction between solids and gases at low pressures, the writer concludes that under the conditions of these experiments, Bodenstein and Fink's theory does not apply. A new theory, which may be termed the "theory of molecular films," is proposed and is found extremely useful in all the low pressure reactions.

According to the "theory of molecular films" the velocity of heterogeneous reactions is in general limited by the rate at which the gas molecules can come into contact with the *active portion* of the surface.

The fundamental conception back of this theory is that the number of gas molecules which strike a given surface per second, according to the kinetic theory, is strictly limited at any given pressure. Thus, in a gas of molecular weight M at a pressure $p$, and absolute temperature T, the total number, $n$, of molecules which strike a sq. cm. of the walls per second is

$$n = 2.652 \times 10^{19} \frac{p}{\sqrt{MT}}$$

Here $p$ is expressed in bars (dynes per sq. cm.). For air at room temperature and atmospheric pressure, this corresponds to about $2.9 \times 10^{23}$ molecules per second; (in other words, 13.8 grams, or 12 liters of air per second).

Although this rate seems extremely high, yet if the *active surface* of the solid is very small the actual rate at which the gas is able to come into contact with it may also be small.

The portion of the surface which is active in a given reaction is in general determined by the *extent* to which the surface is covered by a layer of adsorbed gas. In some cases, the active surface is in the uncovered portion of the surface, while in others it may be the covered portion. The adsorption film is thus looked upon as a layer of molecules, usually only one molecule deep, which covers the surface more or less completely. This film is not thought to be a layer of highly compressed gas, as in

The William H. Nichols Medal

the usual theory of adsorption, but is considered to be a layer of molecules held on the surface by the same kind of forces as those that hold the atoms of a solid body together.

The adsorption film is taken to be in a state of kinetic equilibrium with the gases around it. Thus it is assumed that the majority of gas molecules striking the bare surface of a filament do not rebound from the surface by elastic collisions, but are held by cohesive forces until they *evaporate* from the surface. According to this view-point, which has been based on much experimental evidence, the rate of formation of the adsorption film is proportional to the pressure of the gas and also to the area of that part of the surface remaining uncovered. On the other hand, the rate of evaporation of the adsorption film is a function of the temperature and is proportional to the extent of the surface covered by the film. In a steady state the rate of formation and the rate of evaporation must be equal.

According to this theory, the adsorption film is in a state of constant change. One by one, the molecules are evaporating and thus exposing the bare surface of the metal of the filament. Other molecules then soon fill up these gaps, but at any given instant there will always be a certain small fraction of the surface exposed.

This theory of "molecular films" has been in good quantitative agreement with the experiments in all the cases studied thus far. In fact, examination of the published data on the velocity of heterogeneous reactions at ordinary pressures, makes it appear probable that even at these higher pressures this theory is more

nearly in accord with the experimental facts than is the theory which postulates that the velocity is limited by the rate of *diffusion through* an adsorption film.

The application of this theory to particular cases will be considered more in detail in connection with the experimental results.

The experiments on the clean-up (disappearance) of gases by heated filaments have shown that there are many advantages in studying heterogeneous reactions at very low pressures.

In the first place, at low pressures convection currents in the gas are entirely absent and diffusion takes place so rapidly that the reaction products moving away from the filament, do not in any way interfere with the movement of the reacting gases towards the filament. In fact, at very low pressures the collisions between gas molecules become relatively so infrequent that one may consider the gas to consist merely of a swarm of totally independent molecules which move in straight lines between different points on the bulb and filament.

Under these conditions the temperature of the gas is determined by that of the bulb and there is no temperature gradient in the gas, in the ordinary sense, even very close to the filament. Thus the filament may react with a gas at a totally different temperature from itself—a thing impossible at ordinary pressures. A study of the effect on the reaction velocity, of the separate variation of gas temperature and filament temperature, opens up a new and powerful method for arriving at a better understanding of the mechanism of such reactions.

Another advantage in working at low pressures lies in the fact that the molecules of the products of the reaction, after once leaving the filament, do not return to it again until after having made many collisions with the walls of the bulb. If the bulb is maintained at such low temperature that the products condense, it is possible to prevent these products from coming into contact with the filament at all, except at the moment of their formation.

The reactions that have been observed in the clean-up of gases at low pressures may be divided into four classes:

1—The filament is attacked by the gas.

2—The gas reacts with vapor given off by the filament.

3—The filament acts catalytically on the gas, producing a chemical change in the gas without any permanent change in the filament.

4—The gas is chemically changed or reacts with the filament as the result of electrical discharges through the gas. These may be termed electrochemical reactions.

In this paper only a few examples of the first three types of reactions will be given. The consideration of the fourth type is reserved for a future paper.

### 1—DIRECT ATTACK OF THE FILAMENT

CLEAN-UP OF OXYGEN BY A TUNGSTEN FILAMENT—Even at very low pressures, oxygen attacks tungsten at high temperatures to form $WO_3$, which distils off the filament, leaving the surface clean and bright. A study of the rate of clean-up under various conditions and an analysis of the results from the viewpoint of the "molecular film theory" has led to the following picture of the mechanism of the reaction:

A large fraction (certainly over 15 per cent) of all the oxygen molecules striking the *bare* surface of tungsten sticks to the surface or is adsorbed, forming a layer which is probably only one molecule deep. This layer exists in two modifications which are in chemical equilibrium with each other. One of these modifications is *active* and reacts immediately with oxygen molecules which may strike it, to form $WO_3$, while the other is *inactive* and cannot so react with oxygen. For example, it may be that the oxygen is first adsorbed by the metal as $WO_2$, but that this reacts with more tungsten to form 2 WO, so that these two substances are in equilibrium with each other on the surface. Oxygen molecules striking WO would react to form $WO_3$, while those striking $WO_2$ would not react. The $WO_3$ distils off as fast as formed, but the rate at which the adsorption film evaporates is small, compared to that at which it is removed by combining with more oxygen.

This theory is in splendid quantitative agreement with the results of the experiments.

REACTIONS BETWEEN OXYGEN AND CARBON—At 1200° K.[1] part of the oxygen reacts with carbon to form $CO_2$ but another part gradually forms an extremely stable adsorption film which greatly retards the progress of the reaction that leads to the formation of $CO_2$.

At 1700° K the adsorption film slowly, and at 2100° K rapidly, decomposes in vacuum giving off CO. Thus when oxygen acts on a filament at 1700°, which has previously been heated in vacuum at a high temperature, at first only $CO_2$ is formed, but gradually, as the adsorption film grows, more and more CO is produced.

The adsorption film may also be formed by heating the carbon in $CO_2$. In this case the volume of CO liberated is equal to the $CO_2$ consumed, showing that half of the oxygen is retained by the carbon to form the film. Carbon monoxide, on the other hand, is not absorbed by the carbon at any temperature, showing that although the adsorption film gives up carbon monoxide on heating it cannot be formed from this gas.

There are good reasons for believing that this adsorption layer consists of oxygen atoms chemically combined with the carbon atoms forming the surface layer of the filament. These carbon atoms in turn form endless *carbon chains* or lattices with all the other carbon atoms of the filament.

According to this view-point it is not possible to assign a chemical formula to the oxygen "compound" on the surface. It is thought probable that the adsorption of oxygen by a tungsten filament at high temperatures is to be explained in a similar manner.

### 2—REACTION WITH VAPOR FROM THE FILAMENT

CLEAN-UP OF NITROGEN BY TUNGSTEN—It has been previously shown that nitrogen does not combine with solid tungsten, but that *every* collision between an atom of tungsten vapor and a molecule of nitrogen, results in the formation of the compound $WN_2$. In this case the temperature of the bulb is without effect on the velocity of the reaction.

CLEAN-UP OF NITROGEN BY MOLYBDENUM—A study of this reaction shows that nitrogen does not combine with solid molybdenum, and that *every* collision between an atom of molybdenum and a molecule of nitrogen results in the two "sticking" together, *sometimes* in the form of a stable compound $MoN_2$, but in other cases as an unstable "adsorption compound," which breaks up again when it strikes the bulb. The relative proportions of the *stable* and *unstable* compounds is dependent on the relative velocity of the nitrogen molecules and molybdenum atoms at the moment of their collision. The lower the relative velocity (lower temperature), the greater is the proportion of the stable modification.

CLEAN-UP OF CARBON MONOXIDE BY TUNGSTEN—With the bulb at room temperature this reaction follows exactly the same mechanism as the reaction between nitrogen and tungsten and leads to the formation of a compound WCO. On the other hand, *when the bulb is cooled below —70° C., the CO actually attacks the tungsten filament* and forms an adsorption film of this compound on the surface of the filament. The rate of attack of the filament is thus limited by the rate at which the compound can distil off, and is independent of the pressure of the CO or the bulb temperature (provided this remains below —70° C.). This is an interesting example of a chemical reaction having a reaction velocity with a negative temperature coefficient.

CLEAN-UP OF OXYGEN BY PLATINUM—This case is analogous

[1] K (Kelvin) is used to denote absolute temperatures.

to that of the clean-up of nitrogen by tungsten, but at higher pressures of oxygen (over 1 mm.), the oxygen in addition to combining with the vapor from the platinum, also attacks the platinum at a rate that increases with the pressure.

3—CATALYTIC REACTIONS

DISSOCIATION OF HYDROGEN INTO ATOMS—This has been fully described in recent papers in the *Journal of the American Chemical Society*.[1]

DISSOCIATION OF CHLORINE INTO ATOMS—A highly heated tungsten filament in chlorine at low pressures dissociates this largely into atoms. This leads to some interesting results. For example, consider two tungsten filaments mounted side by side in a bulb containing chlorine at low pressure. If one of the filaments be heated to a high temperature, while the other is kept cold, the *cold filament* gradually grows thinner and may finally disappear, while the hot filament may grow in size by the decomposition of the vapor of the $WCl_6$ formed by the attack of the cold filament by the atomic chlorine.

REACTION BETWEEN OXYGEN AND CARBON MONOXIDE IN CONTACT WITH PLATINUM—It is found that this reaction takes place only when carbon monoxide molecules strike oxygen molecules which are present in an adsorption film on the surface. At low temperatures the carbon monoxide adsorbed on the surface prevents the oxygen molecules from being adsorbed. As the temperature is raised, the carbon monoxide evaporates more rapidly and thus exposes the bare surface of the platinum. The oxygen and the carbon monoxide molecules then compete with each other to reach these bare spots. If oxygen strikes such a spot it is adsorbed and thus reacts with the next CO molecule which strikes it.

At higher temperatures the CO and $O_2$ distil off more rapidly and finally a point is reached where the velocity of the reaction decreases with further rise in temperature because the oxygen adsorbed on the surface distills off before the CO molecules have a chance to react with it.

The experiments at all temperatures and pressures are in good quantitative agreement with this theory.

REACTION BETWEEN OXYGEN AND HYDROGEN IN CONTACT WITH PLATINUM—The mechanism of this reaction is very similar to that of carbon monoxide and oxygen.

RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK

# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

## GAS PROGRESS IN THE UNITED STATES

In a speech before the convention of the "Investment Bankers' Association of America" on "The Modern Gas Company as Security for Bonds" (quoted in the *J. Gas Lighting*, **129** (1915), 212), Rufus C. Dawes of Chicago outlined the growth of the gas industry in this country.

As early as 1835 there were at least six gas plants in the largest cities of the United States, and the business may be considered as well established at that time. The oldest tradition of the business is to maintain an uninterrupted supply of gas. It was a proud advertisement made by the Consolidated Gas Company that "New York City's gas supply has never failed in eighty-seven years." But it is substantially true of all gas companies. This determination to establish a dependable service has had no small part in the development of the business, for the gas business has, from the start, had many things to contend against. The inventive genius of mankind has exhausted itself in an effort to supply some substitute for the service it has rendered; but, in spite of many obstacles and contrary to many fears, the gas industry has steadily grown. The obstacles have been overcome. The fears have subsided. The industry has entered a new era, and has more than doubled its volume of business in the last decade. Invention now works for, not against, its future growth. The price at which its product has been sold has steadily declined. In New York City, for instance, the price in 1826 was $10; in 1846, $6; in 1866, $3.50; in 1886, $1.25; in 1906, $0.80. Each reduction in the selling price of gas has opened up new fields for its use.

Gas carries heat units in a form more available for use than any of its competitors. Whenever a new field is invaded, the genius of inventors perfects the methods of burning gas; and the demand for such inventions has only recently been felt. The response is most encouraging, and the double effect of lower prices and more efficient burners has already been apparent, and supports the strongest confidence for further success in the heating field. Herein lies our future; and we are not so far as some have supposed from our great goal the use of gas exclusively for domestic heating.

Bonds issued by modern gas companies are secured by a natural monopoly in the sense that their property is the only one capable of supplying exactly the same service. Moreover, under present legal adjustments, which provide for regulation and control with due regard to the protection of money invested, such property can never be duplicated or abandoned, but must be devoted to supplying this service, exclusively and perpetually. Yet these companies are engaged in the greatest of competitions—the competition of fuels. At least we have at last learned to conduct our business in this conviction; and we do believe that we can deliver the elusive and highly prized heat units in safer, cheaper, and more available form than our competitors, for an annually increasing number of purposes.

In support of our confidence, I may submit some statistics compiled by Mr. John W. Lansley, from a United States Government report relating to the gas industry. These figures are the best available, and appear to be substantially correct:

| Year | Plants | Capital | Annual product |
|---|---|---|---|
| 1850 | 30 | $ 6,674,000 | $ 1,921,746 |
| 1890 | 742 | 258,772,000 | 56,987,000 |
| 1900 | 877 | 567,001,000 | 75,717,000 |
| 1910 | 1,296 | 915,537,000 | 166,814,000 |

Between 1890 and 1900 the increase in capital appears, from these statistics, to be 119 per cent, while the increase in annual gross income appears to have been only 33 per cent. Between 1900 and 1910, on the contrary, capital appears to have increased 60 per cent and the annual gross income 120 per cent. The increase in the amount of capital between 1890 and 1900 was about the same as between 1900 and 1910, but the increase in income between 1900 and 1910 was five times that between 1890 and 1900. This increase in gross annual income was brought about by a reduction of 32 per cent in the price at which the product was sold. In other words, a gradual reduction of 32 per cent in the price of the product resulted in ten years in an increase of 120 per cent in the gross annual revenue of an industry eighty years old, and necessitated an increase of only 60 per cent in capitalization.

The most interesting incident in this extraordinary accomplishment is the increase in the consumption of gas for fuel purposes. It is difficult to determine these proportions accurately, but the United States Geological Survey gives figures from which it may be estimated that in 1900 the proportion of gas used for fuel was about 20 per cent of the total, and in 1910 about 50 per cent. From these conditions and these tendencies

[1] Langmuir and Mackay, *J. A. C. S.*, **36** (1914), 1708; and Langmuir, *Ibid.*, **37** (1915), 417.

may it not be safely predicted that the future of the gas industry is secured?

As a basis for bonds, the modern gas company offers, then, these conditions: A stable income for the supply of a public necessity, an increasing income, physical property exceptionally high with relation to income and permanently devoted to public service, moderate and not extortionate profits, a long record, excelled by none, and a present condition of growth never before experienced.

## LOW-TEMPERATURE COAL DISTILLATION

In his second Cantor Lecture, on "Oils, Their Production and Manufacture," before the Royal Society of Arts [*J. Gas Lighting*, **129** (1915), 260], Dr. F. Mollwo Perkin referred to the hopes which have been expressed from time to time, of obtaining large quantities of motor spirit from coal by low-temperature distillation.

Those who have designed retorts for this purpose, he said, have been extravagant in their anticipations; and there has been too much loose talk of phenomenal yields of motor spirit. The fact is that methods of distillation have not been sufficiently studied, with the result that crude products have been spoken of as if they were purified products. Coal owners and others who have subjected their minerals to distillation in various retorts have consequently been considerably disappointed. Personally, he believed in a very great future for low-temperature distillation, but care should be taken not to exaggerate. Many of the enormous claims made out for the production of motor spirit in this way could, on examination, be reduced to one-third.

The best-known processes for producing motor spirit of this kind are the Coalite, the Del Monte, and the Tarless Syndicate —one of the objects being the production of a smokeless fuel. There is not always a good market for this kind of fuel, but there is an increasing market for the other products of the processes—*viz.*, various oils and sulfate of ammonia.

One drawback of the Del Monte process originally was that the retort quickly became blocked up if a caking coal was used, but a form of retort has now been designed in which any kind of coal could be used. Results with a Scottish cannel coal, which contained some 31 per cent of volatile matter, showed a yield of 37 gallons of crude oil per ton—the smokeless fuel remaining behind containing 9 per cent of volatile matter. The crude oil on fractionation gave 1 gallon of motor spirit, 3 gallons of fuel oil, 16.9 gallons of heavy oil, 3 lbs. of wax, and 124 lbs. of pitch. This showed how purification reduced the quantity of oil available for motor purposes.

The Tarless Syndicate's process works on a totally different principle, and produces a good smokeless fuel. Caking coals can be used very readily. With this process, a Yorkshire coal containing $29^1/_2$ per cent of volatile matter gave 18 gallons of crude oil per ton, which, on purification, yielded 3 gallons of motor spirit, $2^1/_4$ gallons of intermediate oil, $8^1/_2$ gallons of fuel oil, 8 lbs. of paraffin wax, 50 lbs. of pitch, and 22 lbs. of sulfate of ammonia. It is possible, with the smokeless fuel from this process, to light a fire without any ordinary coal, which is not the case with all smokeless fuels.

## BRITISH OIL IMPORTS

In a recent issue the *J. Gas Lighting* [**129** (1915), 181] comments editorially on data of British oil imports in 1914 published by the *Petroleum Review*. Far from the war having adversely interfered with the petroleum trade it appears to have beneficially affected it. Last year Great Britain imported not less than 459,744,780 gallons of various petroleum products, exclusive of the large amounts absorbed by the British Government, which may be calculated to aggregate about 200 million gallons. The European war has, of course, interrupted supplies from certain eastward fields. Owing to this fact, owing also to important Continental countries being closed to outside trade, America has taken advantage of its free way to this country, and has made the most of its opportunity; and it is easy to agree that, had it not been for the amplitude of the American supplies, England long ere this would have been in a very unfortunate position. The gas oil trade is now almost exclusively with America; and there is indication of the large revival of carbureted water-gas manufacture, after the shutting-down of plants, due to oil costs, in 1912 and the first part of 1913, when it is learned that the gas and solar oil imports from America last year established a new record—amounting in the aggregate to 83,000,000 gallons. This figure is in the neighborhood of 20,000,000 in excess of the total for 1912, and 18,000,000 in excess of the total for 1913. Notwithstanding the growth of the prepayment gas-meter system, the illuminating oil trade has still very large proportions, though the constant inroads upon it are causing its bulk gradually to dwindle. When one sees that the imports of illuminating oil during the past twelve months amounted to 146,600,000 gallons (which was some 10 millions less than in 1913), it suggests that (not forgetting the use of oil for illumination in other directions) the prepayment gas-meter has still an extensive field to conquer. The *Petroleum Review* admits that during recent years the tendency has been towards a diminished consumption of oil for illuminating purposes. "But now that kerosene can be so advantageously employed for heating and cooking purposes, and its use as an illuminant under modern conditions is regaining favor, there is no doubt that a steady increase will be shown in the illuminating oil imports for many years to come." There is good confidence, says the editorial, in saying that such a messy method as cooking and heating by oil will not gain much headway with cleanly, convenient, labor-saving, and economical gas opposing. Of course, there is an increasing use of oil for internal combustion engines. Motor spirit imports also showed an enormous gain during the past year. Altogether 120 million gallons were imported, or about 18 millions more than in 1913. So long as the gas industry continues to make headway, it can afford to congratulate a companion industry upon its successes, even though that industry may be largely competitive.

## PETROLEUM OUTPUT OF ROUMANIA[1] IN 1913

| Total Output (Metric Tons) in 1913 | 1,885,225 Metric tons | |
|---|---|---|
| Exports | 1912 | 1913 |
| Crude petroleum | 27,498 | 28,622 |
| Residues | 283,594 | 341,912 |
| Mineral oils | 7,351 | 9,543 |
| Gasoline | 353,563 | 418,622 |
| Benzine | 173,817 | 237,168 |
| Paraffin | 600 | 579 |
| Total Exports | 846,423 | 1,036,446 |

| Exports to | Metric tons 1912 | Metric tons 1913 |
|---|---|---|
| Germany | 84,041 | 126,295 |
| Great Britain | 214,195 | 232,880 |
| Austria Hungary | 86,013 | 77,184 |
| Belgium | 11,907 | 25,136 |
| Bulgaria | 10,358 | 13,149 |
| Denmark | 4,500 | 13,893 |
| Egypt | 142,418 | 121,642 |
| France | 163,679 | 151,402 |
| Holland | 26,036 | 44,947 |
| Italy | 25,921 | 118,643 |
| Norway | 11,343 | 8,186 |
| Russia | 1,210 | 9,114 |
| Tunis | 7,053 | 8,204 |
| Turkey | 53,549 | 64,682 |
| Sweden | ..... | 4,190 |

## COAL TAR IN RUSSIA

The supply of coal tar in Russia has, says a Petrograd correspondent in the *J. Gas Lighting* [**129** (1915), 184], become a very acute question since frontier communications between Germany and that country have been closed. The only gas-works that hitherto has made a feature of distilling its own coal tar for chemical purposes to any extent has been that of Warsaw. Moscow had realized the importance of directly utilizing the residuals of gas production, and had entered into a contract with a German house to supply a plant for the recovery of

[1] *Chem. Ztg.*, **39** (1915), 28.

ammonia. But difficulties having supervened in consequence of the war, there is said to be a probability that, in the event of some home house not being found capable of carrying out the work, the contract will ultimately be confided to a firm in England or in a country on friendly terms with Russia. A good deal more coal tar could be obtained by the Russian gas-works, were the industry more alive to the value of using up the raw material that lies close at hand. But hitherto either the raw material itself or its derivatives—such as aniline dyes—have been obtained almost entirely from Germany. The present crisis is forcing attention to what the gas-works can do for the country; and it is believed the result will be a much larger call on these establishments for coal tar and other by-products of value in the chemical industry.

## ACTIVITIES OF THE BRITISH BOARD OF TRADE

Shortly after the outbreak of hostilities, the Commercial Intelligence Branch of the British Board of Trade issued a series of pamphlets dealing with the exports and imports of Germany and Austria-Hungary, and comprising extracts from Consular reports bearing on the articles of industry of which statistics were given. Much of the matter was old, but the reissue of it has helped to focus the attention of the manufacturer on the items which concern him individually.

ARTICLES WANTED BY BRITISH FIRMS

| | | |
|---|---|---|
| Glass artificial fruit | Aniline or pulp dyes | Permanent magnets for magnetos |
| Bakelite | Sulfur black | Gold metal foil |
| Brushes, misc. | Electrical insulating materials (such as ambroin, stabilite, aetna material, etc.). | Zinc sheets (nickel-plated and polished on one side) |
| Celluloid substitute | Milk powder | Solid drawn steel tubes about 2 in. internal diam. and 24 ft. long |
| Cement and plaster | Galalith | Lanoline (anhydrous) |
| Cellulose acetate | Galalith substitutes | Asbestos fiber jointing |
| Salicylic acid | Glass cylinders for vacuum flasks | Japanese toilet paper |
| Bichromates of soda and potash | Presses for stamping thin sheet metal | Imitation Mother-of-Pearl paper |
| Antimony | Machinery for winding fine wires on bobbins, and for twisting wire around gut musical strings | Waterproofing paste and solutions |
| Barium peroxide | | Zinc dust |
| Manganese dioxide | | |
| Sodium salicylate | | |
| Bisulfite of soda | | |
| Hydrosulfite of soda | | |
| Aceto-salicylic acid | | |
| Eau de cologne | | |
| Alizarine substitute | | |
| Aniline | | |

ARTICLES WANTED BY NON-BRITISH FIRMS

| | | |
|---|---|---|
| Balata belting | Copper sulfate | Chinese wood oil |
| Corozo and imitation buttons | Protosulfide of copper | Degras |
| Horn and bone buttons | Aniline colors | Earth wax |
| Celluloid sheets | Dyewood | Linseed oil |
| Chromic and muriatic acids | Indigo | Paraffin |
| Arsenic | Rotary kilns for making Portland cement | Turpentine |
| White lead | Machinery for cutting leather boot laces | Cinnabar |
| Sodium citrate | Machinery for making pins, hair pins, hooks and eyes, and similar articles | Fluorspar |
| Naphthalene | | Talc |
| Formalin | | Dividivi |
| Antimony | | Extracts (especially liquid quebracho, oak and chestnut) |
| Quicksilver | Aluminum sheets | Mangrove extract |
| Ammonium nitrate | Cellular zinc sheets, for making perforated cylinders for seed cleaners | Quebracho |
| Sodium oxalate | | Tannin |
| Red lead | | Zinc |
| White zinc oxide | | Zinc dust |

In connection with this campaign undertaken by the Board of Trade to assist manufacturers and merchants to secure trade formerly in the hands of German or Austria-Hungarian firms, a series of lists are being published weekly, dealing with inquiries for articles which inquirers desire to purchase. The February lists are given above.—[E. GEDDES ANDERSON]

## THE PURIFICATION OF PETROLEUM

According to *The Petroleum World* (Vol. No. 173), the sulfuric acid method for the purification of petroleum is generally regarded as being expensive, and unsatisfactory in some respects, and chemists have spent much time and money in the endeavor to find a more efficient and less troublesome method. A new method in which the mineral bauxite replaces the sulfuric acid is described, and it is stated that the Burmah Oil Co., Ltd., are using this bauxite method, with success, at their refineries at Rangoon. The description goes on to state: "The Indian varieties of the ore are particularly efficient, and many experiments carried out with petroleum products from all parts of the world, including waxes from oils, show this variety of bauxite to be as effective as it has been with the Burmah oil products. The bauxite must be graded in the same way as is fuller's earth, and this is best done by the supplier. The bauxite in its natural state has little effect on coloring matter, or other purifying action, until the water of combination has been driven off at about 500° C. To accomplish this the bauxite is calcined in any suitable furnace, and is then ready for use in the filters. By filtration it will be apparent that the wax or oils may be graded into several degrees of colors; that passing first through the bauxite is colorless, whereas that passing through later is slightly tinged, increasing in color until the bauxite is exhausted. By grading the wax or oils, the process can be carried on, and the full efficiency of the medium used up. After the decolorizing power is completely exhausted, the bauxite containing a certain amount of the wax or oil is extracted in any suitable extraction plant, steam-dried and ignited, when it is again ready for use. There is not much mechanical loss in these operations, although much depends upon the physical nature of the original mineral, some varieties being very soft and easily powdered. It is best to select a variety possessing a good degree of hardness.—A.

## METER-TESTING IN CANADA

A Canadian Blue Book which has lately been issued furnishes particulars in regard to the testing of gas-meters in the year ending March 31, 1914. The number presented for verification was 88,133, of which 23,641 were correct, while 16,253 were fast and 47,400 slow within the legal limit. Altogether 87,295 meters were verified and 838 rejected.

## THE AMERICAN LOCOMOTIVE INDUSTRY

Figures relating to recent locomotive construction in the United States are of rather peculiar interest at the present time, according to *Engineering*, 99 (1915), 146, in view of the efforts made in some quarters to hold Great Britain and the action of our Fleet responsible for the business depression on the far side of the Atlantic. In 1914 there were built in the United States only 1265 locomotives, compared with 5332 built in the previous year. It is very clear from these figures that, supposing no engines to have been built after the outbreak of war, the industry was badly depressed throughout the first half of the year. England cannot have had much to do with causing a depression which was really serious before the international complications of the latter half of the year. Its real cause is rather to be found in the country itself, and so far as the railways are concerned, is due largely to the harassing manner in which they have been treated in recent years. The effect of disturbing the purchasing power of so large an industry as the railways is felt, of course, throughout the country.

## THE GERMAN IRON-UNION NEGOTIATIONS

The different branches of the German iron industry have just been holding a number of meetings in order to discuss the present position and the outlook [*Engineering*, 99 (1915), 183]. As regards the plate-rolling mills, it was held that it was necessary to raise the quotations, on account of the increasing cost of manufacture. No definite arrangements, at least as far as inland sales go, were, however, arrived at, but the works agreed that during the war, and in the meantime until the end of June, all sales abroad should be made jointly through one bureau—that of the Shipbuilding Steel Bureau, at Essen, which was formed after the dissolution of the former heavy-plate union. The report that the bar-iron works had arrived at an understanding on the basis of the former bar-iron union agreement is not correct. At the meeting of the steel works the market position of the "B" products was gone into, more especially with reference to bar iron, and the opinion was generally ex-

pressed that higher prices would have to be insisted upon, and for the first quarter of 1915 a price of 112½ marks net, Oberhausen, was suggested, and for the second quarter a price of 115 marks. No binding arrangement, however, was arrived at, and there is no question of anything like a substitute for the old bar-iron syndicate having come into existence. There has been a discussion about price agreements concerning the three leading "B" products, bar-iron, plates, and tubes as a kind of intermediate step to the contemplated proper syndicate. It appears at present questionable whether such an arrangement can be arrived at on account of the dislike for conventions of this kind which prevails in many industrial circles. The plate-rolling mills, in any case, as has already been mentioned, have decided not to go beyond an arrangement about the export business, which cannot be of much importance at present; for bar-iron syndicate negotiations may be said not to have commenced yet

## THE "SENFROT" CHEMICAL INJECTOR

An interesting piece of machinery for introducing a fixed ratio of chemical solution (as, for example, a coagulant like aluminum sulfate) into a water supply system under pressure is the "Senfrot" injector invented by the English engineer R. C. Parsons. It will work with water under any pressure [*Engineering*, **98** (1914), 699].

The accompanying figure is a section through the two pump cylinders and the main into which the solution is to be introduced.

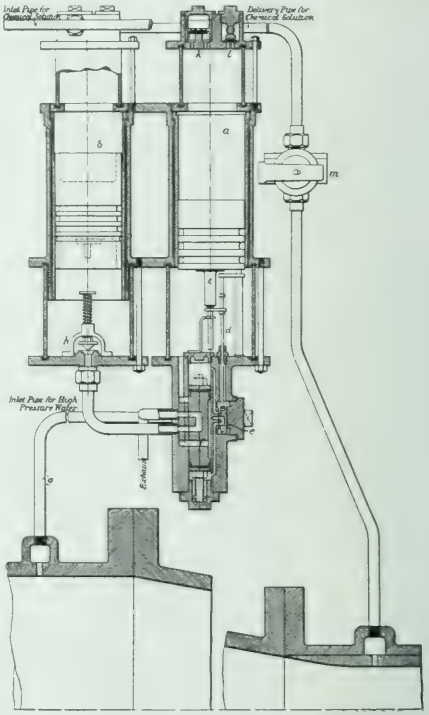
The cylinders are of equal diameter, and are always full of water, or of water and the chemical solution which is to be injected into the mains. Each cylinder contains a solid piston, made of material slightly heavier than the liquid displaced. The pistons, which have wide circumferential grooves, move quite freely in their cylinders. A valve-gear, which controls the admission and exhaust of the water from both cylinders, is situated below the cylinder *a*. It is operated by a fork carried by a rod, *c*, attached to the bottom of the piston of the cylinder *a*. This fork engages the tappet-rod *d*, which has adjustable tappets, and by means of it moves the slide-valve *e* each time the piston completes a stroke in either direction. The operation of this slide-valve *e* controls the movements of a second slide-valve *f*, by admitting pressure-water above or below it. The casing of the valve *e* has a connection to the pressure-main through the pipe *g*, and a further connection to exhaust.

Slide-valve *f* is cylindrical, and in that sense is a piston-valve; but it has ports only on one side, like a slide-valve. The object in using the cylindrical construction is to enable the valve to operate like a piston and to move up or down as pressure water is supplied below or above it by the movement of the valve *e*. The movement of the valve *e* admits water alternately to each end of the valve *f*, and simultaneously puts the other end to exhaust. The ports in the valve *f* are so arranged that, as it moves up and down, it alternately supplies pressure-water to the cylinders *a* and *b*, and at the same time connects the other cylinder to exhaust. In addition to the valves *e* and *f*, there is a further controlling valve, *h*. This is fixed at the bottom of the cylinder *b*, and is kept open by means of a spiral spring, except when it is forcibly closed by the piston, in its lower position, coming down on top of the spindle. There are further valves fixed in casings at the top of the cylinders which control the chemical to be injected into the water-main. The valves of the two cylinders are similar, and in the figure the arrangement for the cylinder *a* is shown in cross-section; the inlet and outlet valves are respectively marked *k* and *l*. All the valves consist of thin discs of pure soft rubber.

The solution to be injected into the main is stored in a tank above the apparatus, connected to the upper valve boxes of the cylinders by the pipe shown in the figure. The delivery pipe from these valves to the main has in it a valve *m* with a diamond-shaped orifice which does not alter its form when opened or closed so that a practically constant coefficient of flow is maintained.

Another essential part of the apparatus is a Venturi tube in the main, indicated by two broken parts at the bottom of the figure. The delivery pipe for the solution enters this at the point of least pressure, while the supply pipe for working the pumps is attached at the point of maximum pressure.

In action the water raises the pistons on the up-stroke because of the difference in pressure above and below, due to the Venturi Throat, and the down-stroke is caused by the relief of pressure from opening the exhaust pipe to the atmosphere. In the




cycle the valve *s* controls the movements of the valve *f* exactly as the slide valve of a steam engine controls the piston; *f* in turn controls the flow of water to the cylinders.

The stroke of the piston *a* is constant, while that of *b* depends on the rate at which the injector is working.

An apparatus with cylinders 3 in. in diam. × 4 in. stroke can inject 70 gallons an hour against any pressure. The apparatus as described is accurate with a range of flow in the main from 1 to 13 and in the injected solution from 1 to 10. Since, however, variations in flow in the main of from 1 to 30 are not in practice, a variable Venturi tube has been designed to allow for this. This device and other auxiliaries are described in detail *loc. cit.*

## IRON PRODUCTION IN NORWAY

A leading Norwegian technical journal strongly advises Norway to take up the manufacture of iron on a sufficiently large scale to supply her own wants according to *Engineering*, **99**

(1915), 208. The belligerent countries—England, France, Belgium, Germany—when the war is finished, will require immense quantities of all kinds of metals, especially iron, for which much ore will have to be imported from abroad, with sundry freight and transport expenses, before it reaches the works. It certainly used to be an accepted maxim that ore should be conveyed to the coal deposits, and not *vice versa*, but a different view now begins to prevail, and modern iron works started in the ore districts have recently shown more rapid development than where the reverse plan has been adopted. Norway has immense deposits of iron ore. The South Varanger concentrate contains 65 per cent iron, and is considered one of the world's finest ores; and good Swedish ore can, of course, also be obtained at an advantageous price. As these are too rich to be used without addition of poorer ores, some of Norway's deposits of this type may become useful. Of limestone, there is sufficient in the country, as is also the case regarding materials for lining the furnaces. The mining of coal at Spitzbergen is likely to develop greatly, and a large coking plant is under consideration in Northern Norway. Discarding for the present electric ore-smelting, the adoption of the ordinary blast furnace of up-to-date design, and with coke, is recommended. Iron ore will be cheap wherever in Northern Norway the iron works are placed, at Norvick, or perhaps further north. The installation should be on a comparatively large scale, as the consumption of iron is rapidly increasing, from 40 lbs. per individual in 1870 to 117 lbs. in 1900, at which date the consumption in Germany already exceeded 220 lbs. per inhabitant A production of 100,000 tons of pig iron per annum is considered the minimum, of which quantity half might be used for foundry purposes, and the other half at steel works. Apart from the home market, one might reckon with the neighboring countries—Sweden, Russia, Finland, and Denmark. An installation of two blast furnaces, with a capacity of 50,000 tons each, is suggested, and, in addition, basic Martin furnaces or Bessemer, rolling-mill, etc., besides power-station and quay accommodation on the railway. The cost is calculated at about $1,750,000, but it is confidently prophesied that this outlay will bear good fruit, and enhance Norway's independence industrially.

## GLASS AND PORCELAIN FOR LABORATORY USE IN GREAT BRITAIN

At a recent meeting of the Society of Chemical Industry, an exhibition was held of laboratory apparatus, formerly mainly produced abroad, but now being manufactured within the United Kingdom. After the inspection an opportunity was given for discussion. It was stated that the difficulties in connection with the production of laboratory glass were very great but that the British Laboratory Association, after some months of labor, were now able to submit a glass which they hoped within the next six or seven weeks to be able to put on the market at a very reasonable price and equal to Jena glass for laboratory purposes. The same remarks applied to porcelain. The materials before being put on the market would be subjected to severe tests and Dr. Cope of Cambridge and other Cambridge university professors had offered their services in regard to the testing of the materials. The question of optical glass was raised and it was pointed out that this was now being worked on.—A.

## PICRIC ACID EXPLOSION

A report, by the Chief Inspector of Explosives, upon an explosion of picric acid at the factory of Ellison, Ltd., at Heckmondwike, has been issued by the English Home office. The inspector is of the opinion that the ignition of the picric acid occurred in the sifting shed, and was probably due to the accidental presence in the grinding mill of a nail, stone, or other hard foreign substance and that the resultant explosion was not owing to the presence of a picrate, nor to the inherent properties of the picric acid, but was rather an explosion of carbonaceous dust, rendered more than usually violent because it contained within itself all the elements necessary to form an explosion. He attaches no blame to Messrs. Ellison, but in consequence of the accident he has requested all licensed manufacturers of picric acid in the United Kingdom to discontinue the process of dry grinding and adopt some method of dealing with abnormally large crystals in a wet state, and further to take preventive methods as far as practicable against the formation of fine dust during the operation of sieving.—A.

## GOLD FOIL AND GOLD LEAF

According to *The Paper Maker* (**49**, No. 2) the manufacture of gold foil and gold leaf for the embossing of book covers, etc., has largely if not entirely been a German monopoly, but a Manchester firm which does a large business each year in embossing, etc., has now obtained the sanction of the Board of Trade for the entire use of a German patent for the manufacture of these two requisites.—A.

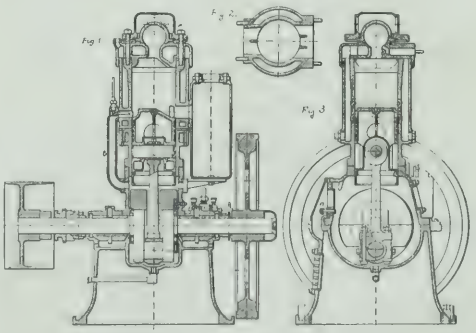
## INDIGO CONFERENCE

At a meeting of the Supreme Legislative Council of India Revenue Minister replying to a question said: "Natural indigo has undoubtedly suffered severely from competition with the synthetic product, and the Government of India are at present considering to what extent, and in what manner assistance can be rendered to growers of indigo. A conference has been arranged to be held at an early date at Delki, to consider the question."—A.

## TWO-CYCLE DIESEL ENGINE

A type of two-cycle Diesel engine built in units as small as 9 H. P. at 475 r. p. m., designed for heavy duty such as agricultural and shop work, is described in *Engineering*, **99** (1915), 187. In appearance the engine is simple and workmanlike.

The scavenging air is drawn in through a grid in the base, passes through the passage *a* to the crank case, where it is compressed, and at the end of the stroke expands through *b* into the cylinder and finally into the muffler. The piston is of the long trunk type with five rings and a heat-insulating air chamber which protects the gudgeon pin from overheating. The governor



is contained in the belt pulley and acts on the fuel supply by altering the throw of the eccentric driving the fuel pump, the eccentric working on a skew cylinder on the shaft.

The cylinder and head are interesting. The head is fixed to the cylinder but fits over the jacket walls, with which the joint is made by means of a rubber ring, as in the jacket of gas

engines. Thus independent expansion of the cylinder and jacket is provided, and only one metal-to-metal joint between the cylinder casting and head has to be made. The head is water-jacketed. It contains a moderately wide neck, opening out for the bulb, which is a separate dome-shaped casting. The hot bulb is not bolted down, but is held down by the cover, which forms a ring pressing evenly all round on the flange of the hot bulb. These features have contributed very considerably to the complete elimination of hot-bulb failures, so common an occurrence in some engines of the two-cycle type. Another interesting point often overlooked is the desirability of placing the scavenging and exhaust-ports in line with the crank-shaft. It will be seen from our illustrations that this is done in the engine under notice. Often they are placed on a line at right angles to the shaft, and therefore reduce the area of the wearing-face provided in the cylinder for the piston at a point where the thrust is severe. Fig. 3 is a section taken across the ports.

The engine illustrated in the figures thus far referred to is, as already stated, of 9 brake horse-power capacity. Two other single-cylinder engines of this type are built—*viz.*, 16 and 25 as brake horse-power. The former has a cylinder 9 in. by 11 in. and the latter one $10^1/_2$ in. by $12^1/_2$ in. The speed of the former is 375, and of the latter 300 revolutions per minute. These two engines are similar to that described in general details, except that they have outside pedestal bearings, the fly-wheel being keyed to an extension shaft bolted to the main shaft by flanged couplings. There is an 18 horse-power engine of the twin-cylinder type, with fly-wheel on a shaft extension and pedestal bearing. The whole is mounted on a separate base-plate. The two cylinders are 7 in. by 8 in., and the speed 475 revolutions per minute.

## NITRO-CELLULOSE

A Government white paper recently issued states that Mr. J. M. Thomson and Mr. W. F. Thomson, respectively the manager and chemist of the Royal Gunpowder Factory, have been awarded a sum of L. 2,850 for improvements brought about in the manufacture of nitrocellulose.—A.

## KELP INDUSTRY

The British Board of Agriculture are at present taking up the question of the revival and extension of the kelp industry in Scotland. A deputation from the North of Scotland was received at the offices of the Board of Agriculture, and the matter was discussed. It was put forward that the main difficulty of stimulating an industry carried on under the conditions in which kelpmaking was carried on, was the actual organization of the industry, and it was proposed to form a joint association of those who might be interested in the production of kelp, with a view to securing fair prices for the commodity.—A

## BRITISH AND GERMAN REFRACTORY MATERIALS

In the course of an article on "Refractory Materials and the War," in a recent number of the English *Journal of the Royal Society of Arts*, Dr. A. B. Searle says: "Retorts for the manufacture of coal gas cannot now be imported from Germany, so that gas engineers are compelled to use the home-made products. There is much divergence of opinion as to the relative values of British and German retorts; and it has not been unusual to find German engineers importing British retorts, while some British engineers have preferred to purchase German ones. Here again British manufacturers are trying to meet the demands as far as they are able. The chief difference between British and German refractory materials may be traced to the difference in the ownership and management of the firms. In this country refractory materials are chiefly made by men who have worked themselves up from a small beginning, or the descendants of such men, their chief characteristic being that of a workman whose knowledge and experience have been gained almost entirely in the workshop, and whose theoretical knowledge—whether of chemistry, physics, or mechanics—is almost negligible. The German manufacturers of refractory materials, on the contrary, have almost invariably had a sound training in chemistry and engineering. They approach the manufacture from an entirely different point of view—*viz.*, that of the user turned manufacturer. Consequently they are more impressed with the needs of the user, while the British manufacturer is chiefly impressed with the difficulties of manufacture and the limitations imposed by his material. If once this bias could be overcome—and the only remedy is the better education of the manufacturers—there is no question that better refractory goods can be made in Great Britain than can be obtained from the Continent for the same price."

## GERMAN IRON AND STEEL

According to a statement by the Union of German Iron and Steel Industries quoted in *Engineering* [99 (1915), 204] the production of pig-iron within the German Customs Union for December, 1914, amounted to 853,881 tons, against 1,611,250 tons for December, 1913, or not very much more than half, while there was an improvement as compared with November, 1914, for which the figure was 788,956 tons. The production of pig iron has been as follows:

| 1914 | Tons per day | District | Tons Total |
|---|---|---|---|
| August | 18,925 | Rhineland-Westphalia | 395,600 |
| September | 19,336 | Siegerland, Wetzlar, and Hessen-Nassau | 52,172 |
| October | 23,543 | Silesia | 61,166 |
| November | 26,299 | North Germany | 14,830 |
| December | 27,545 | Central Germany | 25,299 |
| Foundry pig | 148,881 | South Germany and Thuringia | 15,473 |
| Bessemer pig | 8,778 | Saar district | 53,554 |
| Thomas pig | 542,808 | Lorraine | 124,464 |
| Steel, etc | 128,317 | Luxemburg | 111,323 |
| Puddle | 25,097 | | |

More especially in the last three districts the production shows a considerable increase of late.

The aggregate production for the last two years was:

| Tons | 1913 | 1914 |
|---|---|---|
| Foundry pig | 3,657,326 | 2,494,527 |
| Bessemer pig | 368,840 | 237 988 |
| Thomas pig | 12,193,336 | 9,289,989 |
| Steel, etc | 2,599,887 | 1,996,786 |
| Puddle | 489,783 | 370,257 |
| Total | 19,309,172 | 14,389,547 |

The reduction in the production was, as might be expected, most marked in Lorraine, with Luxemburg, and next in Rhineland and Westphalia, while less pronounced in Silesia. The figures were:

| Tons | 1913 | 1914 |
|---|---|---|
| Rhineland and Westphalia | 8,209,157 | 6,610,119 |
| Lorraine and Luxemburg | 6,417,727 | 4,267,573 |
| Saar district | 1,370,980 | 954,738 |
| Silesia | 994,604 | 853,957 |

The Essen Pig-Iron Union, according to the present arrangement, is to go on until the end of the year 1917 (*vol. cit.*, p. 146). The allotment of 1912—*viz.*, 2,788,000 tons—was raised on account of some additional works joining, the figures of allotment for last year being 2,840,796 tons, which aggregate also holds good for the present year, whereas the figures for 1916 and 1917 were fixed, respectively, at 2,955,796 tons and 2,985,796 tons. It now remains to be seen how the war will affect the actual output. The increase is not brought about by a proportionate general rise, but is rather confined to comparatively few concerns, and some few works have dropped out, or are disappearing, at the end of the current year. Thus the Haigerer Hütte and the Bochumer Union do not figure in the list for 1916, the former withdrawing, and the latter having sold its allotment to the Gelsenkirchener concern, while a couple of works disposed of their allotment to the Pig-Iron

Union at a price of 3 marks per ton. Including these, the original list for the current year comprises thirty-eight concerns, of which the largest allotments (in tons) for 1915 are those of:

| | | | |
|---|---|---|---|
| Gelsenkirchener Co..... | 234,483 | Van der Zyppen-Wissen Co | 106,592 |
| Lübeck Blast-Furnace Co.. | 167,500 | Buderussche Iron Works.. | 105,000 |
| German Luxemburg Co.... | 163,000 | Gutehoffnungshütte..... | 101,197 |
| Kraft Kratzwieck Co..... | 160,000 | North German Iron Works, Bremen..... | 100,000 |
| Kraft Nether Rhine Co.... | 158,600 | East German Pig-Iron Syndicate..... | 100,000 |
| Iron Works Meiderich..... | 157,009 | | |
| Fried. Krupp..... | 150,211 | | |

All the other allotments are of less than 100,000 tons, the lowest on the list being: Geisweiler Iron Works, 12,000 tons.

The East German Pig-Iron Syndicate only figures with 75,000 tons for 1916 and 1917, while the North German Iron Works in Bremen advanced from 100,000 tons in 1915 to 150,000 for the following two years, etc.

There are numerous special arrangements; the allotment of the Gelsenkirchener concern, the figure for which increases 43,000 tons for 1916 and 1917, only refers to the company's production at the blast furnaces of the Schalker section (Gelsenkirchener and Vulkan-Duisburg), and it does not comprise the same company's production in Luxemburg and Lorraine. The Gelsenkirchen concern, it will be seen, comes second to the aggregate of the two Kraft companies.

There is, perhaps, no more striking example of the German disposition to establish and maintain system and method in the prosecution of commerce, industry, of everything in fact, than their immense structure of kartels and combines, the formation and working of many of which have entailed endless labor and the most patient perseverance.

# NOTES AND CORRESPONDENCE

## THE KJELDAHL-GUNNING-ARNOLD METHOD FOR NITROGEN

The possibilities—in point of rapidity—of the Kjeldahl-Gunning-Arnold method of determining nitrogen appear not to be fully realized. Trescot[1] and Jensen[2] seem to imply that the digestion should be an hour and a half at least—in some cases two and a half hours. It is to be regretted that they did not try the method out with shorter periods. The following results are presented with a view to inducing experimenters to test the method for short periods of digestion—a quarter of an hour up. The quantity of substances taken in these determinations was 0.7 gram. The periods of digestion—one quarter, one-half, one and a half, and three and a fifth hours—represent the total time that heat was applied. The digestion was very vigorous throughout. The flasks (500 cc. long neck Jena) were set down against full (or almost full) flame of Bunsen burners at the start. The percentages are for nitrogen.

In the case of short periods of digestion (one-fourth to one-half hour), the acid must, of course, be brought quickly to vigorous boiling, in order that the acid vapor may quickly reach

KJELDAHL-GUNNING-ARNOLD NITROGEN DETERMINATIONS (PERCENTAGES)

| No. | Periods of digestion | ¼ Hr. | ½ Hr. | 1½ Hrs. | 3 Hrs.-23 Min. | |
|---|---|---|---|---|---|---|
| 5416 | Dried blood | 14.18 | 14.28 | | 14.22 | |
| | | 14.12 | 14.36 | | 14.22 | |
| | | 14.14 | | 14.26 | 14.24 | (3 hrs.) |
| | | 14.04 | | | | |
| 5417 | Calcium cyanamide | 16.86 | 16.90 | | 16.88 | |
| | | 16.88 | 16.92 | | 16.70 | |
| 6656 | Cottonseed meal | | 6.12 | 6.06 | | |
| 6672 | Cottonseed meal | | 6.64 | 6.58 | | |
| 6674 | Cottonseed meal | | 6.12 | 6.18 | | |
| 6675 | Cottonseed meal | | 6.56 | 6.54 | | |
| 6676 | Cottonseed meal | | 6.12 | 6.10 | | |
| 6678 | Cottonseed meal | | 6.76 | 6.68 | | |
| 6660 | Cottonseed meal | | 6.08 | 6.16 | | |
| 6659 | Cottonseed meal and hulls | | 3.82 | 3.86 | | |
| 6655 | Shipstuff | 2.46 | | 2.44 | | |
| 6671 | Shipstuff | | 3.04 | 3.00 | | |
| 6673 | Shipstuff | | 2.74 | 2.74 | | |
| 6662 | Red dog | 2.30 | 2.32 | 2.36 | | |
| 6661 | Peanut bran | 3.02 | 2.96 | 3.00 | | |
| 6663 | Ground corn and cob | 1.52 | 1.46 | 1.46 | | |
| 6657 | Ground corn and cob | 1.46 | 1.48 | | | |
| 6669 | Corn screenings | | 1.86 | 1.94 | | |
| 6668 | Cracked corn | | 1.50 | 1.46 | | |
| 6670 | Molasses feed | | 1.40 | 1.38 | | |
| 6658 | Wheat bran | 2.54 | | 2.56 | | |

the entire nterior of the flask, and bring every particle of substance quickly and completely under the full influence of the reagents. It has fallen to the lot of the writer to make many thousands of nitrogen determinations. He regards a half hour—start to finish—of vigorous boiling as ample for determining organic nitrogen by the Kjeldahl-Gunning-Arnold method. Following the lead—if he remembers correctly—of the late Professor Atwater, he alkalizes, and alkalizes strongly, by adding the sodium hydroxide and potassium sulfide as a mixture. This saves one manipulation and precludes the releasing of hydrogen sulfide. There will be no bumping if a little (50 or so mg.) of No. 80 granulated zinc is added. If a large excess of zinc is added, this, besides being a waste of material, releases so much mercury that some of it (mercury) will be carried over into the distillate, where it manifests itself as minute spheres floating on the surface of the distillate. But the presence of this mercury never, so far as the writer ever observed, affected the results of the determination.

[1] THIS JOURNAL, **5** (1913), 914.
[2] *Ibid.*, **7** (1915), 38.

STATE DEPARTMENT OF AGRICULTURE
RALEIGH, N. C., March 12, 1915

J. M. PICKEL

## ON SHORTAGE OF DYES IN THE UNITED STATES

*Editor Journal of Industrial and Engineering Chemistry:*

In view of the long-maintained complaint of a dyestuff shortage the following based upon the "Monthly Summary of the Foreign Commerce of the United States" published by the Department of Commerce for January 1915 are not without present interest.

| IMPORTS FOR JANUARY | 1914 | 1915 | Increase | Ratio 1915 to 1914 |
|---|---|---|---|---|
| Alizarin and alizarin dyes | $ 33,400 | $ 459,266 | $425,866 | 1375 : 100 |
| Anilin oil | 19,872 | 9,872 | —10,000 | 50 : 100 |
| Anilin dyes | 611,350 | 1,086,570 | 475,220 | 178 : 100 |
| Indigo | 77,123 | 183,082 | 105,959 | 237 : 100 |
| TOTALS | $741,745 | $1,738,790 | $997,045 | 235 : 100 |

| IMPORTS FOR THE 7 MONTHS ENDING JAN. | 1913 | 1914 | 1915 |
|---|---|---|---|
| Alizarin and alizarin dyes | $ 833,715 | $ 425,150 | $1,222,093 |
| Anilin oil | 192,741 | 131,143 | 79,320 |
| Anilin dyes | 4,230,730 | 4,199,823 | 4,278,797 |
| Indigo | 680,359 | 660,493 | 862,021 |
| TOTALS | $5,937,545 | $5,416,609 | $6,442,231 |

That is, in the seven months ending January, 1915 (during six of which the European War was going on), the imports of coal-tar dyes were $1,025,622 greater than for the corresponding seven months ending January, 1914 and $504,686 greater than the corresponding period ending January, 1913. Or, the 1915 values are 119 per cent of the 1914 values and 109 per cent of the 1913 values.

With the equally insistent complaint of slow business in colored textiles is there not some room for the suspicion that somebody is hoarding dyes? If there be hoarding, *is* there a shortage in the true sense of the word?

90 WILLIAM STREET, NEW YORK
March 23, 1915

BERNHARD C. HESSE

## THE NORMAL CHLORINE CONTENT OF SURFACE WATERS OF WESTERN FLORIDA

Determinations of chlorine in surface waters of western Florida, made by using the Volhard and Mohr methods yielded the following conclusions and results.

A comparison of chlorine determinations in surface waters by

the Volhard and Mohr methods showed that 0.01*N* ammonium thiocyanate and the 0.01*N* silver nitrate solutions are too dilute to obtain sharp color changes at the end of the reactions. Careful manipulation with a 0.1*N* solution yields as accurate results as the use of more dilute solutions.

Comparing the Volhard and Mohr methods, using 0.1*N* solutions, the former yielded more satisfactory, concordant and accurate results, although requiring more time.

Many determinations on 24 samples of surface water from Leon County in western Florida, about thirty miles inland from the Gulf of Mexico, showed that they contained from 7 to 24 parts per million of chlorine, the average being 12 parts per million. Rain water in this locality, one determination, was found to contain when concentrated to one-tenth of its volume 0.9 part per million of chlorine, equivalent to 1.4 parts per million of sodium chloride. At the Dry Tortugas[1] the chlorine content is 2.9 parts per million corresponding to 5 parts per million of sodium chloride. A few chlorine determinations on surface waters from Pensacola, on the Gulf, in Escambia County, showed from 21 to 42 parts per million of chlorine.

CHEMICAL LABORATORY
FLORIDA STATE COLLEGE FOR WOMEN
TALLAHASSEE, March 1, 1915

C. A. BRAUTLECHT
B. N. LANGLEY

## ACTION OF THE NEW ENGLAND DYE COMMITTEE

The New England Section of the Society of Chemical Industry having requested the Northeastern Section of the American Chemical Society to join with them in appointing a committee to consider the manufacture of dyestuffs in the United States, it was voted that the President of the Section be authorized to appoint such a committee.

The representatives of the two sections were as follows:

| NEW ENGLAND SECTION S. C. I. | | NORTHEASTERN SECTION A. C. S. | |
|---|---|---|---|
| Eugene Barry | F. G. Stantial | John Alden | C. L. Gagnebin |
| A. A. Claflin | C. A. West | W. B. Nye | Grinnell Jones |
| W. D. Livermore | S. W. Wilder | W. K. Robbins | J. Russell Marble |

On January 29th, at a joint meeting of the New England Section of the Society of Chemical Industry and the Northeastern Section of the American Chemical Society, the Joint Committee on Dyestuffs presented its report through its Chairman, Mr. S. W. Wilder. After a lengthy discussion, Prof. H. P. Talbot offered an amendment to the report which was accepted by the committee, and the following amended report was unanimously passed.

"In the opinion of this committee there is no insuperable chemical or physical obstacle to the establishment of a coal-tar industry in this country, but we believe this is an economic question on which it is outside the provinces of these societies to make a recommendation.

"The subject is one of great importance to the chemical industries of the United States, and should be investigated by Congress.

## TO CHANGE THE SPECIFIC GRAVITIES OF SOLUTIONS

*Editor of the Journal of Industrial and Engineering Chemistry:*

As students are constantly required to alter the specific gravities of solutions for reagent purposes, it would seem that simple arithmetic would be as often applied as the hydrometer, But such is not the case and when the hydrometer is misplaced, trouble very often begins. The following formula will suffice in such a case.

If $X$ = Volume of water (sp. gr. 100) to be added to original solution
$S$ = Specific Gravity of original solution
$V$ = Volume of original solution
$S_1$ = Specific Gravity of required solution

Then

$$(S \times V) + (X \times 1.00) = (V + X) S_1$$

whence,

$$X = \frac{(S - S_1) V}{S_1 - 1}$$

As the quantities S, $S_1$ and V are known, substitution in the last equation gives the desired information.

U. S. RECLAMATION SERVICE
SAN FRANCISCO, January 25, 1915

P. F. BOVARD, *Chemist*

## PLATINUM THEFT

A professional platinum thief has stolen about $100 worth of platinum from me. He answers the following description: age about 35, prominent nose, peculiar eyes, red hair, freckled face, Boston accent, two large X-Ray burns on his left arm. Height about 5 feet 10 and weight about 180. This note is intended as a warning to other owners of platinum.

HAHNEMANN MEDICAL COLLEGE
PHILADELPHIA, March 3, 1915

W. A. PEARSON, *Dean*

## HYDROMETALLURGICAL APPARATUS—CORRECTION

In my article under the above title, which appeared in THIS JOURNAL, **7** (1915), 119, the following corrections should be made in addition to those already noted on page 261 of the March issue:

In Table I, page 121, the first heading under "Sand" should be + 100, and not + 200 as given.

Table III, page 124, under remarks in connection with the Porcupine-Crown, Ontario, the figure 83 should read 73 per cent solids.

Page 127—The results of the calculation dealing with the Continuous Counter-Current Decantation flow sheet, Fig. 11, are not quite accurate, owing to the value of "Z" not having been carried out far enough. The results should be:

V = 2.673, W = 1.173, X = 0.298, Y = 0.079, Z = 0.039.

Page 129—The value of Z should be "2.1164 lbs.," instead of "2.7164 lbs.," which means that "2–Solution wasted with the residue, Z, contains 0.1 per cent copper, or 2.1 lbs. per ton of ore."

30 CHURCH STREET, NEW YORK
March 15, 1915

JOHN V. N. DORR

# PERSONAL NOTES

The 2nd annual meeting of the chemical engineers of the University of Kansas was held on March 12th. The program was as follows: Opening Remarks, by Dean P. F. Walker and Prof. W. A. Whitaker; "The Technology of Clay Refractories," Mr. Paul Teetor, clay investigator, University of Kansas; "Rock Salt Mining in Kansas," Mr. Sam. Ainsworth, mining engineer, Lyons, Kansas; "Chemical Process Control," Mr. William J. Kee, Jr., supt., National Zinc Co., Kansas City, Kansas; "The Chemist in Commerce," Mr. Rudolph Hirsch, chemist, Ridenour-Baker Co., Kansas City, Missouri; "Manufacture of Portland Cement," Mr. Chris Goll, chemist, Bonner Portland Cement Co., Bonner Springs, Kansas; "The City Milk Problem," Mrs. George H. Hoxie, Consumers League, Kansas City, Missouri, Mrs. Joseph W. Murray, former food analyst, State Laboratories, Dr. F. H. Billings, prof. of bacteriology and Dr. E. W. Burgess, assistant professor of sociology, University of Kansas. In the evening a "chemical smoker" was given in Eagles' Hall.

Prof. R. W. Thatcher, chief of the division of agricultural chemistry of the University of Minnesota, has been elected president of the Minnesota Section of the A. C. S. The section will hereafter hold regular meetings on the third Friday evening of each month at various laboratories in the Twin Cities.

[1] U. S. Geol. Survey, *Bull.* **319.**

Dr. A. F. Gilman, head of the chemistry department of Ripon College, has returned for the second semester's work after a half year's leave of absence spent in study and travel.

The U. S. Civil Service Commission announces an examination for assistant in agricultural geography, for men only, to fill a vacancy in this position in the Office of Farm Management, Bureau of Plant Industry, Department of Agriculture, Washington, D. C., at a salary ranging from $1,800 to $2,000 a year. The duties of this position will be to assist in investigations being carried on in the above office concerning the development of agricultural enterprises under the influence of geographic conditions, such as topography, climate, soil, location, etc.

Mr. John W. Hornsey, who has been located, for the past two and one-half years, at Trona, Cal., engaged in the development of a method for the separation of potash, borax and soda from the Searles Lake salt deposits, will return to New York at an early date and resume his practice as a consulting chemical engineer, with temporary headquarters at the Chemists' Club.

Mr. Arthur G. Weigel, a graduate assistant in chemistry at the Massachusetts Agricultural College, has accepted a position as chemist in the Experiment Station at Stillwater, Oklahoma.

Dr. Horace Grove Deming, for the past three years associate professor of chemistry in the Philippine College of Agriculture has been appointed professor of chemistry and chief of the department in the University of the Philippines. This is to fill the vacancy occasioned by the death of Dr. Paul Caspar Freer.

The Washington Academy of Sciences will give a series of five illustrated public lectures during March and April. Among these was an address, April 1st, on "High Explosives and Their Effects," by Prof. Charles E. Munroe, of George Washington University.

The subject for the April meeting of the Cincinnati Section of the A. C. S. is "The Manufacture of Soaps and Glycerine."

A factory for the extraction of radium is being erected at Balloch, in the western part of Scotland. The enterprise is under the control of Mr. J. S. MacArthur.

The Rochester Section of the A. C. S. has just issued a booklet which contains a new directory of its members and a programme of its meetings.

The Northern Chemical Engineering Laboratories, of Madison, Wisconsin, announce the adoption of the shorter name "C. F. Burgess Laboratories." The new name implies no change in management or ownership.

The W. Beckers Aniline & Chemical Works of Brooklyn, N. Y., have purchased, in the outskirts of Brooklyn, a tract of about 15 acres bounded by East 83rd, East 84th and East 85th Sts., Ditmas Ave. and the New York Connecting Railroad, where a large-sized chemical plant, consisting of 23 separate buildings, will be erected. Last November the old plant of this concern was destroyed to a large extent by fire, followed by several explosions, killing two chemists and injuring 36 workmen. Three buildings of the new plant are finished, the railroad siding is being laid and the foundations for the boiler house and chimney have just been started.

The department of chemistry of the College of the City of New York announces the following public lectures during the Spring semester, 1915: *March 19th*—"White Lead: Its Manufacture and Use," Dr. G. W. Thompson, chief chemist of the National Lead Co. *March 25th*—"Glass and Its Manufacture," Prof. Alexander Silverman, director of the department of chemistry, University of Pittsburgh. *April 16th*—"Vitamine—A New Food Principle," Dr. F. E. Breithut, of the department of chemistry, College City of New York. *May 7th*—"Crystal Growth and Other Educational Subjects," Mr. Seldon G. Warner, expert in the Edison laboratories.

The Rochester Section of the A. C. S. met on March 15th in conjunction with the Rochester Electroplaters' Society; electroplating problems from the standpoint of the electroplater and the chemist were discussed.

The March meeting of the New York Section of the American Electrochemical Society was held on March 12th in joint session with the New York Section of the American Institute of Electrical Engineers. The electrochemists were represented on the program by Frank B. Washburn, who spoke on "The Cyanamid Process." The electrical engineers were represented by Leland L. Summers, whose subject was the "Fixation of Atmospheric Nitrogen."

The following papers will constitute the program for the April 9th meeting of the New York Section of the A. C. S.: "Contribution to the Structure of Primary and Secondary *p*-Aminophenylmercuric Compounds," by Walter A. Jacobs and Michael Heidelberger, of the Rockefeller Institute for Medical Research; "A New Test for Copper," by W. G. Lyle, L. J. Curtman and J. T. W. Marshall, of the College of the City of New York; "Refining Vegetable Oils," by Chas. Baskerville, of the College of the City of New York; "A Rational Process of Fractional Distillation," by M. A. Rosanoff, Mellon Institute of Industrial Research, Pittsburgh.

The 22nd annual convention of the National Fertilizer Association will be held at The Homestead, Hot Springs, Va., July 13 and 14, 1915. It is altogether probable that the Southern Fertilizer Association will hold their annual meeting on Monday, July 12th, at the same place. The Middle West Soil Improvement Committee of the National Fertilizer Association will meet at the same place on July 16th and 17th. With July 15th devoted to special committee meetings and the National Association golf tournament, practically the entire week at The Homestead, Hot Springs, will be of interest to the fertilizer manufacturers and the allied trades.

Dr. Pierre de P. Ricketts announces the dissolution of the firm of Ricketts & Banks by mutual consent on March 1st. Dr. Ricketts will continue his practice as a consulting chemical and metallurgical engineer, under the name of Ricketts & Company, with offices and laboratories at 80 Maiden Lane. The new business will be continued on a coöperative basis with departments for industrial research, general analytical work and metallurgical engineering.

The Pittsburgh Section of the A. C. S. met on March 18th in the new building of the Mellon Institute, University of Pittsburgh. Prof. M. A. Rosanoff, of the Mellon Institute, addressed the meeting on "A Rational Process of Fractional Distillation." The Section were the guests of the Institute, and following Dr. Rosanoff's lecture the new building was inspected, and a social evening and "smoker" were enjoyed.

Edwin F. Hicks, chief chemist, Victor Talking Machine Co., Camden, N. J., spoke on the "Responsibilities of the Analytical Chemist," at the meeting of the Chemical Society of Drexel Institute on March 2nd.

On March 19th, Professor A. H. Gill addressed the Detroit Engineering Society on "Lubricating Oils: Essentials and Characteristics."

The 7th semi-annual Meeting of the American Institute of Chemical Engineers will be held in San Francisco, August 25th to 28th. An itinerary is being arranged so that the natural scenery of the west may be seen and also some of the more important mining operations as well as the typical chemical industries of California.

The department of chemistry of the Iowa State College, Ames, Iowa, is now installed in the new building which replaces the one destroyed by fire in March, 1913. The initial cost of the new building was $200,000. It covers a space 244 ft. x 162 ft., is three stories high, has a usable basement, is constructed entirely of brick, stone and concrete and is as nearly fireproof as possible.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### DEPARTMENT OF AGRICULTURE

**Utilization of the Fish Waste of the Pacific Coast for the Manufacture of Fertilizer.** J. W. Turrentine. Department Bulletin 150, from the Bureau of Soils. 71 pp. Paper, 15 cents. This bulletin discusses the utilization of the waste, particularly of the salmon canning industry, indicating the commercial conditions to a sufficient extent to make clear the source, character, methods of disposal, and amount of the waste. Analyses are given of the materials available not only from the salmon industry but also from the other similar packing industries, and there is included an estimate of the cost of installing and operating a plant for this work. The use of fish scrap with kelp to produce a mixed fertilizer is also discussed.

**Cactus Solution as an Adhesive in Arsenical Sprays for Insects.** M. M. High. Department Bulletin 160, from the Bureau of Entomology. 20 pp. Paper, 5 cents. This bulletin describes the use of cactus solution with the various kinds of arsenic-containing spray solutions and indicates the various preservatives which can be used to prevent decomposition of the cactus extract. A considerable number of analyses of cactus plant ash and extract are given.

**A Field Test for Lime-Sulfur Dipping Baths.** Robert M. Chapin. Department Bulletin 163, from the Bureau of Animal Industry. 7 pp. Paper, 5 cents. This bulletin describes a portable testing outfit for estimating the strength of lime-sulfur baths used in the dipping of sheep and includes tables indicating the proper change in the bath to restore to normal concentration.

**Field Test with a Toxic Soil Constituent: Vanillin.** J. J. Skinner. Department Bulletin 164, from the Bureau of Soils. 9 pp. Paper, 5 cents. The effect upon plant growth of vanillin is demonstrated by pot and field tests.

**Ability of Colon Bacilli to Survive Pasteurization.** S. Henry Ayers and W. T. Johnson, Jr. Journal of Agricultural Research, **3** (1915), 401–10.

**Organic Phosphoric Acid of Rice.** Alice R. Thompson. Journal of Agricultural Research, **3** (1915), 425–30.

### PUBLIC HEALTH SERVICE

**Purity and Strength of Household Remedies, Variations in Purity and Strength of Widely Used Drugs and Preparations; a Possible Source of Danger to the Patient.** Martin I. Wilbert. Public Health Reports, January 29th. Also obtainable as a reprint.

**The Limitations to Self-Medication.** Martin I. Wilbert. Public Health Reports, **30**, 470–73. Also obtainable as a reprint. The uses and abuses of proprietary preparations and household remedies are discussed with suggestions as to what drugs form acceptable remedies and what are objectionable in self-medication.

**Hypochlorite Treatment of Water Supplies.** H. A. Whittaker. Public Health Reports, **30**, 608–18 (February 26). Also available as a reprint. This article describes a portable plant and field equipment for its administration in caring for water supplies in time of emergencies and epidemic.

### HYGIENIC LABORATORY

**Examination of Drinking Water on Railroad Trains.** Richard H. Creel. Part 2 of Bulletin 100. 72 pp. Paper, 10 cents.

### BUREAU OF MINES

**Metallurgical Smoke.** Charles H. Fulton. Bulletin 84. 90 pp. Paper, 20 cents. This bulletin describes the commercial methods utilized in prevention of smoke and fume nuisances in various classes of metallurgical work. The general aspects of the smoke problem are discussed both from the standpoint of vegetation and public health and the standpoint of economy in plant operation. The character of smoke and fume from different processes is pointed out and the methods and machinery used for elimination or retention of the fume are described in detail. The bulletin is a general review of the subject, not on a report of the experimental work.

### GEOLOGICAL SURVEY

**The Calcite Marble and Dolomite of Eastern Vermont.** T. N. Dale. Bulletin 589. 67 pp. "The object of this bulletin is twofold—to locate definitely and describe accurately the marbles and dolomites of eastern Vermont with a view to setting forth their possible economic uses and to discuss whatever features of scientific interest they may present." The deposits are described in considerable detail by locations which include the most productive regions contributing to the marble industry of the United States.

**Structure of Fort Smith-Poteau Gas Field, Arkansas-Oklahoma; Glenn Oil and Gas Pool and Vicinity, Oklahoma.** Carl D. Smith. Bulletin 541-B. 25 pp. and two maps.

**Deschutes River, Oregon, and Its Utilization.** Several articles by F. M. Henshaw, J. H. Lewis, E. J. McCaustland and Others. Water Supply Paper 344. 200 pp. and 38 maps. Paper, 50 cents. Prepared in coöperation with the State officials of Oregon.

### DEPARTMENT OF COMMERCE

**List of Publications.** The 11th edition of the list of publications of the Department of Commerce which are available for distribution is dated January 1, 1915. 73 pp. Free.

### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Pineapple Canning Industry of the World.** J. Alexis Shriver. Special Agents, Series 91. 43 pp. Paper, 5 cents. This publication incorporates the results of an investigation of all the pineapple-canning centers of the world, with special emphasis on superiority of Hawaiian methods over those of older pineapple districts of the Far East.

### COMMERCE REPORTS—FEBRUARY, 1915

Special Supplements issued in February include: Persia 57*a* and Honduras 31*a*.

The present status of the **beer, porcelain and dye industry** in Japan are discussed. (P. 450.)

Plans are being made to increase the **soap industry** of Manchuria, using **soya-bean oil.** (P. 452.)

The regulations regarding **monazite** mining in Brazil are stated. (P. 475.)

Mr. Thomas H. Norton, formerly U. S. Consul at Chemnitz, Germany, is engaged in a special investigation for the Department of Commerce, of the **chemical and dyestuff industries** in the United States. (P. 490.)

A summary is given of the **mineral production** of the world for 1912, as published in the British Mines and Quarries Report. (P. 498.)

The German Potash Syndicate is selecting a means to "denature" **potash salts**, *i. e.*, prevent their use for ammunition or military purposes while permitting their use as **fertilizers**.

The **gold mining** industry of the Philippines is flourishing. (P. 530.)

**Camphor** is now being obtained in the Philippines from a shrub "Blumea balsamifera." (P. 589.)

The German **paper industry** has been very seriously crippled, owing to a shortage in raw materials, previously imported. (P. 613.)

In Italy the oil obtained from tomato seeds is used for **soap**, and is also said to be edible. (P. 615.)

The supply of Turkish **gum tragacanth** is very short, owing to scarcity of labor to gather it. (P. 625.)

A special licensing committee exists in England to regulate shipments of **rubber** to the United States. (P. 633.)

The **iodine** production of Chili is restricted by a controlling organization. The normal output could be doubled if desired. (P. 644.)

A market for **infusorial earth** is desired by Chili. (P. 647.)

The **bergamot-oil** industry of Catania, Italy, is described. (P. 652.)

The **tin plate** industry of Wales has suffered not only because of reduced market but also on account of the increased cost of tin. (P. 660.)

Japan is now supplying China and India with **sheet glass** formerly imported from Belgium. (P. 663.)

Various provinces in China are purchasing **smokeless powder** from American firms. (P. 677.)

The details of the scheme of the British Government for fostering the **dyestuff** industry have been materially changed, with special reference to the needs of the users of dyes. A stock company with a capital of £1,000,000 is to be established to which the Government will loan an equal amount for 25 years at 4 per cent. In addition the Government will grant £100,000 per year for 10 years for research work. (P. 678.)

The **sulfur** output of Hokkaido, Japan, is increasing, due partly to difficulty in securing Italian sulfur for America. (P. 687.)

The United States import statistics for **fertilizer materials** include the following articles: Kainite, potassium chloride, potassium sulfate, "manure salts," sodium nitrate, ammonium sulfate, bone dust, guano, apatite, calcium cyanide, crude phosphates, and basic slag. (P. 694.)

British **oil mills** are increasing their demand for Philippine **copra**. (P. 702.)

A company with a capital of £5,000,000 is being organized in Russia to develop the **dyestuff industry**. (P. 729.)

The exportation from Germany of **kainite** containing less than 20 per cent of potash, is now permitted. (P. 737.)

The Chinese people are urged to plant the **indigo** plant wherever the poppy has been previously grown. (P. 784.)

A preliminary report on the **dyestuff** situation in the United States submitted to the United States Senate by the Secretary of Commerce, after analyzing the conditions, suggests the need of "anti dumping" legislation to prevent unfair foreign competition. (Pp. 786–9.)

A company in India has just erected plants for the manufacture of **cement** by the wet process in rotary kilns, and also of tile, fire brick, drainage pipes and other **clay products**. (P. 804.)

STATISTICS AND INFORMATION REGARDING EXPORTS FROM VARIOUS LOCALITIES IN THE UNITED STATES

PHILIPPINES—441
Copra

BRAZIL—453
Rubber

MEXICO—489
Crude oil

CHINA—519
Antimony

PERSIA—Sup 57*a*
Gums

PARIS—701
Hides
Soap
Wines

PORTUGAL—750
Argols
Cork
Hides
Rubber
Sulfur ore (pyrite?)
Wolframite

GERMANY—626
Dextrin
Thorium nitrate
Glue
Enamel ware
Chinaware
Dyestuffs
Fats
Oils
Linoleum
Arsenic
Sugar-beet seed
Paints
Platinum
Zinc dust
Potash
Bronze powder
Tungsten

HONGKONG—664
Tin

DENMARK—682
Casein
Chemicals
Dextrin
Flint pebbles
Glycerine
Hides
Safety matches
Condensed milk
Pottery
Rags
Rennet
Scrap rubber
Soya bean oil

HONDURAS—Sup 31*a*
Hides
Rubber
Sarsaparilla

RECENT DEMANDS FOR AMERICAN GOODS ON ACCOUNT OF THE WAR CONDITIONS

FRENCH WEST INDIES—455
Chinaware
Earthenware
Glassware
Fertilizers
Ammonium salts

ECUADOR—561–586
Soap
Hides

ITALY—598
Starch
Brandy
Cottonseed oil
Leather
Glycerine
Zinc

Benzine
Gasoline
Lubricating oils
Paraffin
Dyestuffs
Bronze
Caustic soda
Chemicals
Fertilizers
White zinc
White lead
Steel plate
Tallow
Tin
Copper

GERMANY—705
Phosphate rock

COSTA RICA—508
Portland cement in steel drums

PERSIA—Sup. 57*a*
Petroleum
Sugar
Rubber goods
Matches
Paints
Dyes
Soap
Candles
Paper
Glassware
Galvanized iron
Enameled ware

The **soya-bean** industry of Manchuria has been hampered by lack of transportation. (P. 809.)

The plant is to be erected in Yucatan to make **paper pulp** from "henequen" (a variety of sisal) stalks and waste. (P. 814.)

### BUREAU OF STANDARDS

**Regulation of Electrotyping Solutions.** Circular 52. 13 pp. This is the first printed edition of this circular; see announcement of preliminary edition, THIS JOURNAL, **6** (1914), 1043.

**A Wheatstone Bridge for Resistance Thermometry.** C. W. WAIDNER, H. C. DICKINSON, E. F. MUELLER AND D. R. HARPER, 3d. Scientific Paper 241. 20 pp. "The Wheatstone bridge described in this paper was designed with special reference for flexibility of use in measurements with resistance thermometers. The bridge is adapted to use with either the Siemens type or Callender type of resistance thermometer, or with the potential terminal type of thermometer by the use of the Thomson double-bridge method. The instrument is also arranged so that it may be completely self-calibrated.

The accuracy attainable with the bridge is such that resistances of 1 ohm or more can be measured to an accuracy of 1 part in 300,000 in terms of the unit in which the calibration is expressed. This corresponds to an accuracy of about 0.001° for measurements with the platinum resistance thermometer."

# BOOK REVIEWS

**Coal Gas Residuals.** By FREDERICK H. WAGNER, M.E. New York: McGraw Hill Book Co. 1914. xi + 179 pp., with diagrams. Price, $2.00.

The title of this book would indicate a rather general survey of the nature of the residuals secured in gas manufacture, or perhaps the various methods of obtaining same, but the reader does not progress far before he finds that in reality the book aims to set forth primarily the process invented by the late Walther Feld of Lin-am-Rhein. To be more descriptive of the contents, the title might better read "Coal Gas Residuals by the Feld Process." The theories of this process are so very interesting by themselves and so revolutionary, if the dreams of the talented inventor could all be realized, as to deserve by themselves a book even more ample than the present.

In the introductory chapter is given a brief survey and in the later chapters a more detailed description of the ambitious plan of the complete Feld system, which aims to take the coal gas directly from the gas retorts or coke ovens and pass it continuously through a series of eleven Feld centrifugal spray washers of an interesting and very effective design, in which the gas is successively freed from Pitch, Heavy, Middle and Light Oils, Ammonia, Sulfur, Cyanogen, Naphthalene and Benzol, and all of these products are recovered in merchantable form. The gas engineer naturally opens his eyes on being assured that instead of recovering coal tar more or less contaminated with ammoniacal liquor, which tar must later be worked up in a separate distillation process, he is to draw pitch continuously from one washer and as many and such fractions of tar oil from succeeding washers as he desires. Still further he pricks up his ears when he reads on page 31, as a presumably typical example, that instead of selling tar at $5.00 per ton, the Feld washers whizzed this ton of tar into products sold for $16.00. And when later in the book it is set forth how comparatively simple it is to recover, direct from the gas, sulfur for use in converting Ammonia into Ammonium Sulfate without the outside purchase of expensive Sulfuric Acid, and the enormous returns to be secured from Benzol, etc., the gas engineer sees gold dollars of profit shining even more brilliantly than the famous coal tar colors and inquires how long he has been asleep, why he has not been awakened earlier, and where he can go to see all this in working order.

The gas engineer, however, is naturally thorough and sets to work to analyze the plan and figures, and he finds that as yet the complete process is a very ingenious and attractive theory, of which so far only certain parts have been imperfectly worked out in practice. He finds further that the Feld patented centrifugal washer is a very effective piece of apparatus and that *if* he can deliver his crude gas to the washers under reasonably uniform conditions of quantity, temperature, pressure and composition, the theory may perhaps be worked out in practice to a considerable extent. But he finds, also, that if it could be worked out in practice, the mere fractional condensation of tar into pitch and oils does not and never did turn $5.00 into $16.00, nor anything like it. This statement as to values is absolutely misleading and since it stands out so prominently as indicating what may be expected, the author should have been more careful to get the facts. We have no doubt that here, as in many other places, he was copying from European reports of Feld without knowing sufficiently about the tar industry to appreciate how gross was such error and how it throws in doubt his other claims.

We used above the important word "if" to indicate that there is considerable doubt in the minds of many whether the necessary uniform conditions can be secured in practice. The reader must keep in mind that this process is not like the continuous fractional condensation of a uniform gas or vapor from a single source, but that he is dealing with the gas from perhaps seventy-five or more large coke ovens, or an even greater number of small gas retorts in different stages of carbonization and consequently giving off different gases. Theoretically, perhaps, suitable rotation in operation will be secured so that at all times there is a certain average condition, but this will not be found by any means easy to practice. We should hesitate greatly before saying that it cannot be worked out in practice, and we expect to see excellent progress along these lines, but in the few plants (mostly in Germany) which have tried the Feld process there has been small promise that all of the condensation products will be secured in merchantable condition direct from the centrifugal washers, as the book would have us expect.

There seems more reason to expect success in working with Ammonia and Cyanogen than with the coal tar, for the reason that in the former cases we are dealing with definite chemical compounds which, though elusive, have certain fixed characteristics, whereas tar consists of perhaps over one hundred and fifty distinct and different chemical substances, all mixed together in varying forms and proportions, depending on the coal being carbonized, the temperature and stage of carbonization, the shape and size of the retort and the length of travel of the gases while exposed to relatively high heat either in the retorts or ovens or mains leading to the washers. Reports from some of the European experiments show what may be expected from the complex conditions; instead of securing uniform pitch of a given melting point, the product from the pitch washer would be pitch at one moment, thin tar at another, constantly fluctuating, so that instead of securing merchantable pitch and oil products, they secured, in fact, in some cases, products less merchantable even than the ordinary tar, because less uniform. There seems little reasonable expectation of securing by direct condensation pitch of sufficiently uniform consistency and of the grade and quality required to meet American conditions, as these are far more complex and much further developed than is the pitch business in Germany, notwithstanding the well-known German superiority in the chemical end of the coal tar industry.

Without attempting to go into detail, the book contains many statements and tabulations of figures which the author should be sure are checked carefully before another edition. We comment on one or two inaccuracies.

On page 8 is an obviously incorrect statement that the "free carbon" in coal gas tar contains "about 85 per cent volatile matter of an oily, rather heavy nature." The percentage would hardly ever exceed 10 per cent.

On page 29 it is stated that at a plant in Upper Silesia they obtained 5500 lbs. of thin soft pitch from a Feld plant handling the gas from 395 tons of coal in twenty-four hours. This Silesian coal would probably average a yield of at least 3 per cent of tar, equaling at least 23,700 lbs. of tar in twenty-four hours, and such tar would contain at least 14,000 lbs. of soft pitch. There is a little discrepancy between this quantity and the 5500 lbs. reported recovered.

Also on page 32 in Table VIII is included "Carbon Content (Anyline, Pyridine, Methane) 0.23 and 0.32 percent." "Anyline" should evidently read "Aniline," and even with this correction the item would not be intelligible to a gas engineer, who might easily suppose that Aniline, Pyridine and Methane were the carbon compounds and the only ones secured, whereas we interpret it to indicate the percentage of the so-called "Free Carbon" in the tar obtained by washing the same with Aniline and Pyridine by the Kramer Spilker extraction method.

At the end of the chapter on Naphthalene (page 42) reference is made to a possible source of revenue to the gas producer from the sale of Naphthalene as a fuel for internal combustion engines. The authority apparently overlooked the fact that this possible outlet in Europe is not likely to materialize in the United States which is blessed with large supplies of comparatively cheaper and much more convenient petroleum oils.

In this review especial attention has been given to the tar end of the Feld process, as this is the greatest departure from existing methods and other new processes being developed, but there is much to be worked out yet in the other operations of the system before they will be seriously considered, even by themselves, for American conditions of gas and coke industries. It is to be noticed that in the chapter on Ammonia and Benzole the author outlines more fully a number of the other processes besides that of Feld. Also in the appendix are given a number of useful tables. It is to be regretted that in Table XXX many items are missing which should, if available, be included later to make this complete.

In conclusion, it is to be hoped that the excellent inventive work of Feld will not be brought to an abrupt close by his untimely death. It may be that later one of his co-workers, Jahl and the author of this book, will be able to develop many parts of the theory into workable practice within the limits reasonably obtainable. R. P. PERRY

**The Preservation of Structural Timber.** By HOWARD F. WEISS, Director, Forest Products Laboratory, U. S. Forest Service. New York: McGraw-Hill Book Co., 1915 viii + 312 pp., with illus. Price, $3.00 net.

All who are interested in the preservation of timber will welcome Mr. Weiss' book as one peculiarly adapted as a volume of reference to the subject of which it treats. It is largely a compilation of the various circulars and bulletins issued by the U. S. Forest Service and other government bureaus during the last eight years, supplemented with extracts from the proceedings of such widely known organizations as the American Wood Preservers' Association and the American Railway Engineering Association. It will prove a great convenience to all who need to refer frequently to these scattered publications.

The contents of the book are well indicated by the chapter headings. Chapter I, an Introduction to the Subject, defines wood preservation, its importance, the present state of the industry in the United States, and its effects on the conservation of our timber, with something as to the history of the subject.

Chapter II, Factors which Cause the Deterioration of Structural Timber, describes their relative importance, decay insects, mechanical abrasion, fire, soil characteristics and birds.

Chapter III, The Effect of the Structure of Wood upon Its Injection with Preservatives.

Chapter IV, The Preparation of Timber for Its Preservative Treatment, referring to the season of cutting and to the seasoning of timber by various methods.

Chapter V, Processes Used in Protecting Wood from Decay—The author does not seem to be aware of the fact that the Creo-Resinate Process of wood block treatment has practically been abandoned, or that the Vulcanizing Process of the Old New York Vulcanizing Company is in a similar state.

Chapter VI, Preservatives Used in Protecting Wood from Decay—Here the author does not indicate with sufficient clearness the fact that coke-oven tars and water-gas tars are used for this purpose rather than distillates from the same. He writes of water-gas tar creosote and states that it is seldom sold under its own name. While this may be true of distillates from this tar it is quite the reverse with the tar itself as sold for timber treatment, in regard to which he seems to be uninformed. The Specifications of the National Electric Light Association, which he quotes, are not for water-gas tar creosote but for the water-gas tar itself. There are now in use in the Unites States approximately 500,000 square yards of wood paving blocks treated with this material, and some of this work is seven years old, the results being entirely satisfactory. No mention is made of the Otto Hoffman coke-oven tar distillates which are now upon the market.

Chapter VII, The Construction and Operation of Wood Preserving Plants, is worthy of commendation. It is thorough and accurate and shows that the author is well versed in the requirements of a first-class plant and the methods of its operation. A section of this chapter on the Inspection of Treatments, is particularly fair and intelligent and worthy of consideration by many engineers and inspectors who are all too frequently inclined to be unreasonable in their demands.

Chapters VIII to XV refer to the Prolonging of the Life of Ties, Poles and Cross Arms, Fence Posts, Piling and Boats, the Life of Mine Timber, the Life of Paving Blocks, Shingles and Lumber and Logs.

In the chapter on Prolonging the Life of Paving Blocks the author fails to refer to the use of coke-oven tar as a preservative, nor does he realize that most of the bleeding of blocks under the hot summer sun, to which he refers, is due to the use of such a preservative.

Chapter XVI treats of the Protection of Timber from Fire, and Fire-proofing wood, together with the effect of cresote on its inflammability.

Chapter XVII, The Protection of Wood from Minor Destructive Agents, includes the effects of alkaline soils, birds, sap stain and sand storms.

Chapter XVIII, The Strength and Electrolysis of Treated Timber, refers to the effect of preservatives and the temperature and pressure at which they are applied, upon the strength of the wood, and to the electrical resistance of wood treated with creosote and zinc chloride.

Chapter XIX, The Use of Substitutes for Treated Timber, refers to the use of concrete for this purpose, and the replacing of wood by steel, masonry and concrete for many structural purposes, as in bridges and steel cars.

Chapter XX, Appendices, considers minor wood preserving processes and patented and proprietary preservatives used in the United States, methods of analysis of preservatives and U. S. patents. In the methods of analysis of creosote he fails to give any for determining the presence of acetic acid or acetates, although some specifications still require that the oil shall be free from them.

The list of U. S. patents on wood preservation is extensive and forms a valuable feature of the book.

As a whole, the book fills a field which has not hitherto been covered satisfactorily and it should and will, no doubt, have a wide circulation. CLIFFORD RICHARDSON

**Metallurgy: A Condensed Treatise for the Use of College Students and Any Desiring a General Knowledge of the Subject.** By HENRY WYSOR, B.S., Prof. of Metallurgy in Lafayette College. Second Edition. The Chemical Publishing Co., Easton, Pa., 1914. Price, $3.00.

The first edition was reviewed in THIS JOURNAL, 1 (1909), 49. The book has now been enlarged from 308 to 391 pages, following the same scheme of treatment as the first edition. The first seven chapters of 100 pages deal with the introduction to metallurgy such as the physical properties of metals, fluxes and refractories, combustion, fuels, ore dressing, furnaces and accessory apparatus. Iron and steel are dealt with in 125 pages, the section on electrolytic processes being new. Copper, 42 pages; Lead, 24 pages; Zinc, Tin and Mercury, 15 pages; Silver and Gold, 33 pages; Nickel, Aluminium, etc., 11 pages; Alloys, etc., 20 pages. Prof. Wysor has undertaken to bring the whole

field of metallurgy within this small compass and has done it well, producing a well balanced book.

Some of the mistakes have been changed, but many remain, *e. g.*, Silicon in iron, p. 107; the ideas expressed are vague. We know that two and only two compounds form, $Fe_2Si$ and FeSi. On p. 269, "small percentages of silver lower the melting point of lead and large quantities harden it and raise the melting point." This shows a haziness in the understanding of the difference between melting and freezing points, for silver lowers the melting point of lead to the eutectic temperature and never raises it; p. 288, "silver alloys with zinc more readily than it does with lead; therefore if zinc is melted with lead and silver the zinc upon separating carries most of the silver with it." Again the old and vague ideas are expressed. Modern work on alloys shows that the reason lies in the fact that lead and zinc form two conjugate solutions, whose "partition" coefficient for silver is so great that most of the silver is found in the zinc.

Taken as a whole, the book is to be commended in that it gives us a clear and concise account of the general principles of the metallurgy of the different metals.

The chief criticism to be made is in the section on alloys, Chapter XXIX. This ought to be rewritten and placed after the physical properties of metals at the beginning of the book.

Minor criticisms such as follow are due to the retention of the old ideas, for example "affinity," used both for solubility and for heat of combination. On p. 6 we read, "Some metals, having practically no alloying affinity will, upon cooling from a fused mixture separate more or less completely, into layers according to their specific gravities. This is called liquation and is the opposite of diffusion." On p. 18, Fluxes, "Some substance of the opposite chemical character to the gangue is added and combination ensues with the formation of an easily fusible compound. The substance added is called a flux and the resulting compound is slag." The work of Vogt and of the Geo-Physical Laboratory has upset all our old ideas on the subject of slags by showing us that they are solutions like alloys and behave as such. Most slags owe their easy fusibility to the presence of a eutectic. Page 105, "Iron may be made to dissolve as much as 4.63 per cent of its own weight of carbon." The work of Wittorf shows us that solubility is a function of temperature and alloys beyond $Fe_3C$ (6.67 per cent carbon) are readily formed when the requisite temperature is reached.

In the chapter on wrought iron the long description and illustrations of the Catalan forge and bloomary might be replaced by an account of the charcoal hearth.

W. CAMPBELL

**The Manufacture of Organic Dyestuffs.** By ANDRÉ WAHL, D.Sc. Translated by F. W. ATACK and published by G. Bell & Sons, London, 1914. Size, $7\frac{1}{2} \times 5$. Price, $1.60 net.

This book is a translation of Dr. Wahl's "L'industrie des matières colorantes organiques," which was published as one of a numerous series of volumes of Derômes Bibliotheque des industries chimiques. It is somewhat of the general nature of Benedickt's "Chemistry of the Coal Tar Colors" but as this has now gone out of print and also is rather behind the times in its information, the present volume is a very acceptable contribution to the literature. One feature to be recommended is that it does not take up valuable space in educating the reader in general organic chemistry but goes right at the subject of the coal tar dyestuffs with the supposition that the reader will be sufficiently prepared in organic chemistry to understand the chemical problems with which the book deals. Again, the application of the dyestuffs, that is to say, the practical use of the products in the dyeing of various materials, is not gone into in any detail but is only slightly touched upon, it being considered beyond the scope of the volume; and this is well, for much better information on the application of the dyes can be obtained from other books having this object more in view.

In the first part, this volume takes up the consideration of the raw materials, describing briefly coal tar and the various derivatives to be obtained from it by processes of distillation. This part of the book, however, is too brief to be of any special value and it would have been well if the author had given us more information concerning the preparation of this raw material with the object of the manufacture of dyestuffs in view. The second part of the book deals with the chemical properties and methods of preparation of the so-called intermediate products and describes in some detail the general reactions whereby these intermediate products are made. This includes such reactions as sulfonation, alkaline fusion, nitration, reduction and alkylation. The third part deals with the organic dyestuffs themselves, classified under the generally recognized chemical groups. In this portion of the book a good deal of the general dyestuff chemistry is discussed and a few examples of the manufacture of specific dyes are given.

The book is primarily a text-book for students and can hardly be considered as a book for the study of the practical methods of manufacturing dyes. At the present time, when there is a good deal of interest in this country concerning the possible enlargement of our dyestuff industry, there must be many who are sufficiently interested in the subject to become more familiar with the chemistry of the processes whereby dyestuffs are made, and to them this book will be of considerable value. In my opinion, however, it does not measure up to the same standard as that found in a similar book by Seyewitz and Sisley on the "Chemistry of the Organic Coloring Matters," nor does it have the same scope and detail as Bucherer's "Lehrbuch der Farbenchemie," which has appeared almost simultaneously, but unfortunately it is not as yet available to the American reader in an English translation. However, Atack's translation is a very good one and under the present circumstances is a welcome addition to our rather limited literature in English on this subject.

J. MERRITT MATTHEWS

**The Hydrogenation of Oils.** By CARLETON ELLIS, S.B. New York: D. Van Nostrand Company. 1914. 145 illustrations. x + 340 pp. 8vo. Price, $4.00.

In this work, the author has presented a review of this new and interesting development of the chemistry of fats so far as that industry has been reported and discussed in publications. The literature of the subject is well presented and it would seem from an examination of the work as though very little of what has ever been written on this subject either in journal publications or in patent records had been omitted.

The different processes are presented to the reader very much as the inventors of the processes themselves describe them and the claims of each worker in this field are fully set forth.

A criticism to which this treatise is fairly subject is that it is lacking in perspective, that is, that the important and the relatively unimportant points are presented to the reader upon a common plane as though they were features of equal magnitude. This, however, is evidently the author's intention, for he states in the preface that he did not think it practicable to carry through a vein of critical comment "at this stage of a young art," and that all he aimed to accomplish was to "array the multitude of processes, formulae proposals and opinions, leaving to the reader the selection of that which should prove of greatest utility."

The work regarded as a review of the literature appears to be excellent; as a guide to direct the reader toward the practical and away from the purely theoretical, it makes no pretenses but since it is the first book of its kind and has the great merit of completeness, it should prove a valuable addition to the library of the modern chemist.

PARKER C. MCILHINEY

# NEW PUBLICATIONS

By JOHN F. NORTON, Massachusetts Institute of Technology, Boston

**Acetylene: Oxy-acetylene Welding and Cutting: including the Operation and Care of Acetylene Generating Plants: and the Oxygen Process for Removal of Carbon.** By C. F. SWINGLE. 16mo. 190 pp. Price, $1.00. Drake, Chicago.

**Assaying: A Text-book of Practical Assaying.** By J. PARK. 8vo. Price, $2.50. J. B. Lippincott Co., Philadelphia.

**Cyanogen: The Chemistry of Cyanogen Compounds and Their Manufacture and Estimation.** By HERBERT E. WILLIAMS. 8vo. 423 pp. Price, $3.50. P. Blakiston's Son & Co., Philadelphia.

**Explosives: Les Poudres et Explosifs. Les mesures de sécurite dans les mines de Nouille.** By L. VENNIN and G. CHESNAU. 8vo. Paris.

**Gas: Gas Works Directory and Statistics, 1914-15.** 8vo. 548 pp. Price, $3.00. Hazell, Watson & Viney, London.

**General Chemistry: Chemistry of Familiar Things.** By S. S. SADTLER. 8vo. 320 pp. Price, $1.75. J. B. Lippincott Co., Philadelphia.

**General Chemistry: Elementary Practical Chemistry for Medical and Other Students.** By J. E. MYERS and J. B. FIRTH. 12mo. 194 pp. Price, $1.25. J. B. Lippincott Co., Philadelphia.

**Inorganic Chemistry: A Text-book of Inorganic Chemistry. Vol. I., Pt. 1. An Introduction to Modern Inorganic Chemistry. Pt. 2. The Inert Gases.** By J. NEWTON FRIEND and others. 8vo. 385 pp. Price, $3.00. J. B. Lippincott Co., Philadelphia.

**Physiology: Directions for a Practical Course in Chemical Physiology.** By W. CRAMER. 2nd Ed. 4to. 102 pp. Price, $1.00. Longmans, Green & Co., New York.

**Sewerage: American Sewerage Practice. Vol. 2. Design of Sewers.** By LEONARD METCALF and HARRISON P. EDDY. 8vo. 564 pp. Price, $4.00. McGraw-Hill Book Co., New York.

**Technology: Lehrbuch der Chemie und chemische Technologie für Handelsakademein.** By A. CHAZEL. 2. 8vo. 231 and 353 pp. Price, $2.00. Wien.

**Vinegar: A Practical Treatise on the Manufacture of Vinegar.** By W. T. BRAUNT, Editor. 3rd Ed. 8vo. 567 pp. Price, $6.00. H. C. Baird & Co., Philadelphia.

**Water: Examination of Water for Sanitary and Technical Purposes.** By HENRY LEFFMAN. 7th Ed. 12mo. Price, $1.25. P. Blakiston's Son & Co., Philadelphia.

**Wood: The Preservation of Structural Timber.** By HOWARD F. WEISS. 8vo. 312 pp. Price, $3.00. McGraw-Hill Book Co., New York.

## RECENT JOURNAL ARTICLES

**Air: Ueber Luftverunreinigung durch Kohlenoxyd, mit besonderer Berücksichtigung einiger weniger bekannter Quellen derselben.** By LEO G. MEYER. *Archiv für Hygiene.* Vol. 84, 1915, No. 2, pp. 79–120

**Alcohol: Some Technical Phases of Alcoholic Fermentation.** By W. L. OWEN. **Sugar,** Vol. 17, 1915, No. 3, pp. 44–6.

**Alkaline-Earths: Ueber die Peroxyde der Erdalkalien.** By E. H. RIESENFELD and W. NOTTEBOHM. *Zeitschrift für anorganische Chemie,* Vol. 90, 1915, No. 4, pp. 371–6.

**Ammonium Chloride: Anlage zur Herstellung von Ammoniumchlorid aus technischen Salmiakgeist odor Konzentrierten Gaswasser.** By G. BARNICK. *Chemische Apparatur,* Vol. 2, 1915, No. 3, pp. 33–4.

**Analysis: Ueber Metalltitrationen mittels Arsensäure.** By J. VALENTIN. *Zeitschrift für analytische Chemie,* Vol. 54, 1915, No. 2, pp. 76–89.

**Apparatus: Bemerkungen über Mischapparate.** By OSKAR NAGEL. *Chemische Apparatur,* Vol. 2, 1915, No. 3, pp. 35–6.

**Atomic Weights: Twenty-second Annual Report of the Committee on Atomic Weights.** By GREGORY PAUL BAXTER. *Journal of the American Chemical Society,* Vol. 37, 1915, No. 3, pp. 407–17.

**Benzol: Gewinnung von Benzol aus Koksofengasen.** By G. BARNICK. *Chemische Apparatur,* Vol. 2, 1915, No. 1, pp. 1–4.

**Blast Furnace: Filling the Blast Furnace.** By J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 3, pp. 161–73.

**Boiler Water: The Purification of Boiler Feed Water.** By EVERARD BROWN. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 3, pp. 156–60.

**Calorimetry: Corrections in Bomb Calorimetry.** By G. NEVILL HUNTLY. *The Analyst,* Vol. 40, 1915, No. 467, pp. 41–8.

**Copper: Die Struktur des Elektrolytisch abgeschiedenen Kupfers.** By A. SIEVERTS and W. WIPPELMANN. *Zeitschrift für anorganische Chemie,* Vol. 91, 1915, No. 1, pp. 1–45.

**Copper: Present Tendencies in Copper Metallurgy.** By E. P. MATHEWSON. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 3, p. 141.

**Cotton: Notes on the Various Methods of Finishing Cotton Goods, with the Most Recent Improvements and Economical Applications.** By RAFFAELE SANSONE. *The Textile American,* Vol. 23, 1915, No. 1, pp. 23–4.

**Dyes: Fortschritte in der Herstellung und Anwendung von Küpenfarbstoffen während des letzten Jahres.** By FRANZ ERBAN. *Färber-Zeitung,* Vol. 26, 1915, No. 3, pp. 32–7.

**Ferrovanadium: The Determination of Manganese in Ferrovanadium.** By WILLIAM W. CLARK. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 3, pp. 155–6.

**Fertilizers: Ueber die chemisch-quantitative Zusammensetzung der Stassfurter Salzablagerungen.** By RÓZSA. *Zeitschrift für anorganische Chemie,* Vol. 90, 1915, No. 4, pp. 377–85.

**Indigo: Einige Bemerkungen über die Erzielung weisser und roter Druckeffekte auf mit Indigo gefärbter Ware.** By G. TAGLIANI und G. AROSIO. *Färber-Zeitung,* Vol. 26, 1915, No. 1, pp. 1–3.

**Knit Goods: Operating Costs and Economies in Knitting Mills.** By C. E. MURRAY. *The Textile American,* Vol. 23, 1915, No. 1, pp. 25–6.

**Lactic Acid: Analysis of Lactic Acid.** By T. A. FAUST. *Journal of the American Leather Chemists' Association,* Vol. 10, 1915, No. 2, pp. 73–8.

**Milk: Condition of Casein and Salts in Milk.** By L. L. VAN SLYKE and A. W. BOSWORTH. *Journal of Biological Chemistry,* Vol. 20, 1915, No. 2, pp. 135–52.

**Milk: The Manufacture of Condensed Milk, Milk Powders, Casein, Etc. Discussion of Methods of Analysis.** By R. T. MOHAN. *Journal of the Society of Chemical Industry,* Vol. 34, 1915, No. 3, pp. 109–13.

**Moisture: A New Chemical Hygrometer.** By ERIC K. RIDEAL and A. HANNAH. *The Analyst,* Vol. 40, 1915, No. 467, pp. 48–54.

**Nitrates: Production of Nitrates from Air, with Special Reference to a New Electric Furnace.** E. KILBURN SCOTT. *Journal of the Society of Chemical Industry,* Vol. 34, 1915, No. 3, pp. 113–26.

**Nitrous Acid: Nachweis und jodometrische Bestimmung der salpetrigen Säure in daniet verunreinigten Wässern.** By L. W. WINKLER. *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel,* Vol. 29, 1915, No. 1, pp. 10–16.

**Oils: Hydrogenation of Oils.** By VICTOR J. LUMBARD *Journal of the American Leather Chemists' Association,* Vol. 10, 1915, No. 2, pp. 80–7.

**Oils: Polymerised Drying Oils.** By R. S. MORRELL. *Journal of the Society of Chemical Industry,* Vol. 34, 1915, No. 3, pp. 105–9.

**Oils: Sind die gehärteten Oele für den menschlichen Genuss geeignet.** By PHILIPP O. SÜSSMANN. *Archiv für Hygiene,* Vol. 84, 1915, No. 2, pp. 121–45.

**Pasteurization: The Ability of Colon Bacilli to Survive Pasteurization.** By S. HENRY AVERS and W. T. JOHNSON, JR. *Journal of Agricultural Research,* Vol. 3, 1915, No. 5, pp. 401–10.

**Phosphorus: An Improved Method for the Estimation of Inorganic Phosphoric Acid in Certain Tissues and Food Products.** By ROBERT M. CHAPIN and W. C. POWICK. *Journal of Biological Chemistry,* Vol. 20, 1915, No. 2, pp. 97–114.

**Radium: The Radium Situation.** By WARREN F. BLEECKER. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 3, pp. 143-5.

**Sea Water: Die Destillation des Meerwassers zur Gewinnung von Trink- und Gebrauchswasser.** By ERNEST GOLZ. *Chemische Apparatur,* Vol. 2, 1915, Nos. 1 and 2, pp. 5–7 and 17–9

**Stock Yards Wastes: Two Years' Tests Indicate Best Treatment for Chicago Stock Yards Wastes.** ANONYMOUS. *Engineering Record,* Vol. 71, 1915, No. 9, pp. 266–8.

**Sugar: Sugar Industry of the Philippines.** By C. W. HINES. *Sugar,* Vol. 17, 1915, No. 3, pp. 31–4.

**Sugar: Ueber die Wirkung der Bleitannatklärung bei der polarimetrischen Untersuchung von Zucker-, Dextrin-, und Stärkelosungen.** By J. GROSSFELD. *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel,* Vol. 29, 1915, No. 2, pp. 51–6.

**Tanners: Tannery Problems for Tanners and Chemists.** By W. R. COX. *Journal of the American Leather Chemists' Association,* Vol. 10, 1915, No. 2, pp. 101–4.

**Textiles: Die Veredlung von Baumwollwaren in Nordamerika.** By EDGAR LANDAUER. *Färber-Zeitung,* Vol. 26, 1915, No. 3, pp. 29–32.

**Textiles: The Mercerization of Textiles.** By H. A. CARTER. *The Textile American,* Vol. 23, 1915, No. 1, pp. 35–8.

**Trade Wastes: Maintenance of Sewers and Disposal Works Demands Treatment of Injurious Trade Wastes.** By W. L. STEVENSON. *Engineering Record,* Vol. 71, 1915, No. 9, pp. 256–60.

**Ventilation: Some Results of the First Year's Work of the New York State Commission on Ventilation.** By C.-E. A. WINSLOW and others. *American Journal of Public Health,* Vol. 5, 1915, No. 2, pp. 85–118.

**Water: On the Action of Lead, Copper, Tin, Nickel, Zinc, and Aluminum on Water. 13. Lead.** By W. P. JORISSEN. *Chemical News,* Vol. 111, 1915, No. 2882, pp. 91–2.

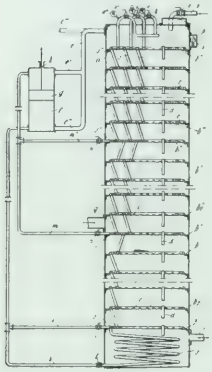
**Wine: Ueber die Trübung von Weinen durch Eisenphosphatverbindungen.** HERMANN WEIL. *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel,* Vol. 29, 1915, No. 2, pp. 60–6.

# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. Parker
Solicitor of Chemical Patents, Washington, D. C.

**Separating Gaseous Mixtures into Their Constituents. R. P. Pictet, Dec. 1, 1914. U. S. Pat. 1,119,312.** This process is primarily intended for the separation of air into oxygen and nitrogen. An upwardly moving stream of air is subjected in the apparatus illustrated, to the action of a descending stream of liquid nitrogen in a succession of liquid layers. This liquid nitrogen dissolves oxygen from the gaseous air and becomes progressively richer in oxygen. The layers of liquid nitrogen are then caused to boil by the action of a succession of streams of nitrogen forced into the apparatus at different heights and passing to the upper end through the liquid layers without mixing therewith. These streams of nitrogen are supplied under such different pressures that the nitrogen just liquefies at the temperature of the mixture of nitrogen and dissolved oxygen at the point of entry of the nitrogen.



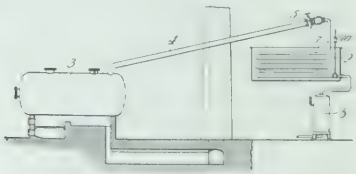
**Carbon-Destroyer. A. A. Saxe, Dec. 1, 1914. U. S. Pat. 1,119,458.** This composition for removing carbon from internal combustion engine cylinders consists of kerosene 5 gallons; benzol 2 gallons; alcohol 3 quarts; and spirits of camphor 1 quart.

**Distilling Petroleum. E. M. Clark, Dec. 1, 1914. U. S. Pat. 1,119,496.** Petroleum is distilled by circulating it forcibly and rapidly in a relatively small stream under confinement and subjecting it to a cracking temperature from and back to a bulk-supply of the liquid, taking off and condensing the resultant vapors and maintaining upon them a pressure of the vapors of about 3 to 7 atmospheres.

**Composition for Laying Road-Dust. C. Ellis, Dec. 1, 1914. U. S. Pat. 1,119,500.** The composition consists of concentrated waste sulfite liquor and a substantially tar-free oil.

**Pure Oxid of Tin. G. Spitz, Dec. 1, 1914. U. S. Pat. 1,119,547.** Pure tin oxid in its most amorphous condition is produced from stannate solutions by removing contaminating metals, precipitating the tin oxid, washing the precipitate with water and calcining it unmixed with acid.

**Distilling Hydrocarbons. R. E. Humphreys, Dec. 1, 1914. U. S. Pat. 1,119,700.** In this process products of low boiling points, such as gasoline, are produced from hydrocarbons of relatively high boiling points by distilling at a pressure of upward of four atmospheres, cooling the vapors while under pressure to condense the heavier fractions, simultaneously returning the condensed heavier fractions to the still for further treatment and leading off and condensing the light vapors.



**Stable Colloidal Solutions of Metals. B. Schwerin, Dec. 1, 1914. U. S. Pat. 1,119,647.** Silicic acid is mixed with a solution of the metal salt to be employed and the metal reduced with hydrazin hydrate.

**Cleaning Compound for Metals. G. D. Feidt, Dec. 1, 1914. U. S. Pat. 1,119,781.** The composition consists of phosphoric acid, alcohol, and carbon tetrachlorid.

**Ink. R. Hochstetter, Dec. 8, 1914. U. S. Pat. 1,119,960.** A pulp color is mixed with a varnish in a partial vacuum and at the same time subjected to a temperature sufficient to vaporize the mixture under the vacuum.

**Hydrocarbon Liquid Suitable for Use in Internal-Combustion Engines. D. R. McArthur, Dec. 8, 1914. U. S. Pat. 1,119,974.** Natural gas is subjected to compression and the heat resulting from such compression and commingled with a higher liquid paraffin in an atomized or vaporized condition. The resultant product condenses in the form of a liquid of lower specific gravity than that of the higher paraffin used.

**Recovering Precious Metals. F. A. Wiswell, Dec. 8, 1914. U. S. Pat. 1,120,175.** Pulverized ore or sand containing precious metals in fine particles is subjected to the action of an aqueous solution of mercuric chlorid in the presence of iron while subjecting the material to the action of an electric current.

**Materials for Generating Hydrogen. S. Uyeno, Dec. 15, 1914. U. S. Pat. 1,120,768.** An amalgam is produced by forming an alloy of aluminum, tin and zinc, rubbing the surface of the alloy with an amalgam of mercury and zinc and heating the resulting product to a relatively high temperature but below the boiling point of mercury.

**Cream of Tartar. J. B. Moszczenski, Dec. 15, 1914. U. S. Pat. 1,120,839.** Material containing potassium bitartrate is subjected to the action of a solution of sodium acetate at a high temperature to dissolve the potassium bitartrate. The solution is allowed to cool and the resulting crystals separated from the mother liquor.

**Caoutchouc Substitute. O. Rohm, Dec. 15, 1914. U. S. Pat. 1,121,134.** A solid acrylic acid ester obtained by polymerization is subjected to vulcanization.

**Soluble Phosphates. J. W. Beckman, Dec. 15, 1914. U. S. Pat. 1,121,160.** Alunite is heated to a reacting temperature with tricalcium phosphate.

**Perborate of Zinc. W. Weber, Dec. 15, 1914. U. S. Pat. 1,121,428.** Sulfate of zinc is melted with sodium perborate, while constantly stirring the mass.

**Recovering Alkalis from Flue-Gases. S. B. Newberry. Dec. 15, 1914. U. S. Pat. 1,121,532.** Flue dust from flued gases of cement kilns is leached with water and the solution caused to move over an extended surface in contact with a current of flue-gases in a direction contrary to the flow of the gases and in such manner that the solution will be concentrated by absorption of salts from the gases and by evaporation by their heat. The resulting concentrated solution is subjected to crystallization, the crystals withdrawn and the mother liquor employed for further contact with the flue-gases

**Hydrogenating Unsaturated Compounds. H. K. Moore, Dec. 22, 1914. U. S. Pat. 1,121,860.** Separate streams of oil and hydrogen are brought into contact with a catalyzer and with each other, and the hydrogenated product separated from the catalyzer.

## BRITISH PATENTS

By D. GEDDES ANDERSON
Chemical Engineer and Patent Chemist, Glasgow, Scotland

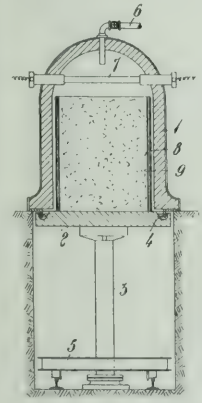
The following abstracts are taken direct from the patent specifications, as soon as these are published by the British patent office. The date given at the end of the abstract is date of acceptance.

**Hydraulic Cementing Material. W. A. Oakley, Application, July 15, 1913. Brit. Pat. 16,243.** Magnesium carbonate is added to hydrochloric acid (1 acid to 2 water), until no more will dissolve. The resulting solution is mixed with kaolin, dried at 120° F., and ground with burnt magnesite.—Accepted Jan. 7, 1915.

**Separation of Metallic Sulfides. L. Bradford, Sept. 18, 1913. Brit. Pat. 21,104.** This process deals in particular with the selective separation of zinc sulfides from lead sulfides. A differentiating medium, consisting of a solution of sodium chloride slightly acidulated is used, and it is found that the galena particles become "wetted," and are not then susceptible to flotation in such a medium. They are left as a high-grade leady residue, while the zinc sulfide (blende) particles are not "wetted" and a float concentrate high in zinc can be obtained.—Jan. 7, 1915.

**Repairing Material for Pneumatic Tires. W. H. Halsall and P. Coulton, May 13, 1914. Brit. Pat. 25,997 of 1913.** Material consists of a thin sheet of vulcanized india-rubber, and applied to one face is a thin layer of unvulcanized but vulcanizable rubber composition consisting of pure rubber 1 lb., sulfur $3^1/_2$ oz., French chalk 1 lb. The heat generated by the friction of the tire on the roadway vulcanizes the repairing material to the air tube.—Jan. 21, 1915.

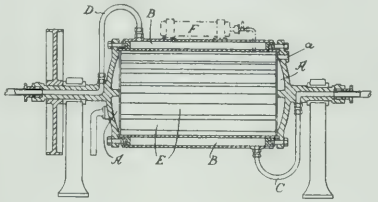
**Furnace for Producing Cyanamides. Dettifoss Power Co., Ltd. and J. H. Lidholm, Dec. 11, 1913. Brit. Pat. 28,629.** This furnace is stated to save time and electrical energy and to diminish labor charges. The furnace is provided with a bottom adapted to be raised or lowered, and on which the charge is placed in a vessel, in such manner that when the reaction is finished the charge may be removed, by lowering the bottom, and immediately replaced by a fresh charge: 2 is the bottom of the furnace lowered or raised by the hydraulic piston 3: 8 is the vessel for containing the charge of carbide, and 6 the inlet for nitrogen. The charge is lowered on to the carriage 5 and replaced by a fresh charge.—Jan. 14, 1915.



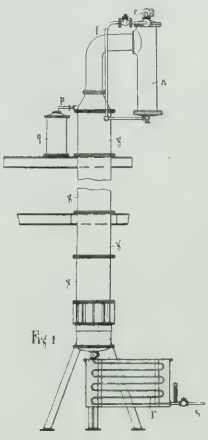

**Recovery of Acid from Acid Sulfates. G. Hunnybun, Dec. 18, 1913. Brit. Pat. 29,254.** One part of sulfur is heated with 2 parts acid sulfate. Sulfur dioxide and acid are evolved and collected in any usual manner.—Jan. 18, 1915.

**Composition for Application to Surfaces Subjected to Friction. A. Elder, Dec. 31, 1913. Brit. Pat. 30,035.** This is a mixture of 70 parts steel dust, 20 parts gutta percha, 5 parts rubber, 5 parts shellac. Mixture is rolled into ribbons and is heated before use. —Jan. 13, 1915.

**Apparatus for Use in Impregnating Oils or Fats with Gases. A. H. Charlton, Jan. 19, 1914. Brit. Pat. 1410.** The cylinder or drum "A" containing the oil and gas is supported on trunnions through which pass the steam inlet "C," and exhaust "D". The cylinder is provided on its inner periphery with a series of scoop-like members which, when the drum is rotated, lift up and throw back the oil. "B" is the steam packet and "F" a gas-containing cylinder.—Jan. 19, 1915.




**Deodorizing Oils. J. T. Bateman, Jan. 6, 1914. Brit. Pat. 367.** The oil flows from preliminary heater "a" into deodorizing chambers "g" where it comes into actual contact with superheated steam. "q" is a separate which collects any oil spray carried up with the steam. The oil passes down through chambers "g" into the cooling coil "y."—Jan. 6, 1915.




**Utilization of Kelp. Boberg, Testrup, and Techno-Chemical Laboratories, Ltd., Jan. 22, 1914. Brit. Pat. 1766.** The kelp is reduced to a pulp and forced under pressure through a heater in which its slimy water-binding constituents are destroyed by heat. The cooled, treated pulp is pressed, and the effluent contains most of the alkali salts and iodine.—Jan. 14, 1915.

**Products from Rubber. F. E. Matthews and E. H. Strange, Jan. 26, 1914. Brit. Pat. 2070.** Liquid sulfur dioxide is added to a cooled benzene solution of the soluble portion of synthetic or natural rubber, and the mixture warmed to a temperature of 40° C. in a sealed vessel. An elastic product is obtained.—Jan. 21, 1915.

**Oil for Internal Combustion Engines. B. O. Jenkins, Feb. 14, 1914. Brit. Pat. 3899.** A mixture of 25 per cent benzol, 70 per cent alcohol, 1 per cent camphoric acid distilled at 80° C. to 160° C. The camphor renders the liquid more volatile.—Jan. 14, 1915.

**Puncture Sealing Composition for Pneumatic Tires. P. W. Owen, April 10, 1914. Brit. Pat. 8753.** Flake mica or a mixture of flake mica and resin, is made into a paste with water and poured into the air tube of the tin through the valve opening. The mica forms an adhering film over the inner surface of the air tube. —Jan. 20, 1915.

**Substitute for Laundry Starch. E. M. Newbery and E. A. Simpson, July 14, 1914. Brit. Pat. 16,774.** Gelatin or other albuminoid is soaked in water and then boiled, and borax, white wax and formaline added. Product forms a stiff mass which can be used exactly as starch.—Jan. 7, 1915.

**Application of Dyestuffs. E. Lodge and J. M. Evans, Sept. 5, 1914. Brit. Pat. 19,473.** A sulfur color is reduced to its leuco compound by an alkaline sulfid in the presence of an alkaline sulfite, and a neutral salt of ammonia is added to the dye bath before the introduction of the material to be dyed. This process avoids strong alkalinity in the dyebath, and animal fibers can be dyed without drying. It is also applicable to the dyeing of artificial silks.—Jan. 28, 1915.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF MARCH, 1915

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid | Lb. | 90 | @ | 95 |
| Acetic Acid (28 per cent) | C. | 1.75 | @ | 2.00 |
| Acetone (drums) | Lb. | 18 | @ | 20 |
| Alcohol, denatured (180 proof) | Gal. | 33 | @ | 35 |
| Alcohol, grain (188 proof) | Gal. | 2.50 | @ | 2.54 |
| Alcohol, wood (95 per cent) | Gal. | 45 | @ | 47 |
| Amyl Acetate | Gal. | 2.60 | @ | 2.70 |
| Aniline Oil | Lb. | 75 | @ | 85 |
| Benzoic Acid | Lb. | 1.10 | @ | — |
| Benzol (90 per cent) | Gal. | 55 | @ | — |
| Camphor (refined in bulk) | Lb. | 41 1/2 | @ | — |
| Carbolic Acid (drums) | Lb. | 1.15 | @ | 1.50 |
| Carbon Bisulfide | Lb. | 6 1/2 | @ | 7 1/2 |
| Carbon Tetrachloride (drums) | Lb | 14 | @ | 15 |
| Chloroform | Lb. | 30 | @ | 35 |
| Citric Acid (domestic), crystals | Lb. | 55 | @ | 57 |
| Dextrine (corn) (carloads, bags) | C. | 2.93 | @ | — |
| Dextrine (imported potato) | Lb. | — | @ | — |
| Ether (U. S. P., 1900) | Lb. | 15 | @ | 20 |
| Formaldehyde | Lb. | 8 1/2 | @ | 9 1/2 |
| Glycerine (dynamite) | Lb. | 20 1/2 | @ | 21 |
| Oxalic Acid | Lb. | 17 1/2 | @ | 18 |
| Pyrogallic Acid (bulk) | Lb. | 1.90 | @ | 2.10 |
| Salicylic Acid | Lb. | 1.50 | @ | 1.60 |
| Starch (cassava) | Lb. | 3 1/4 | @ | 4 |
| Starch (corn) (carloads, bags) | C. | 2.15 | @ | — |
| Starch (potato) | Lb. | — | @ | — |
| Starch (rice) | Lb. | — | @ | — |
| Starch (sago) | Lb. | 2 7/8 | @ | 3 |
| Starch (wheat) | Lb. | 5 | @ | 10 |
| Tannic Acid (commercial) | Lb. | 60 | @ | 66 |
| Tartaric Acid, crystals | Lb. | 37 | @ | 38 |

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lead (brown, broken) | Lb. | 7 1/4 | @ | 7 1/2 |
| Acetate of Lime (gray) | C. | 2.00 | @ | 2.05 |
| Alum (lump) | C. | 2.50 | @ | 3.00 |
| Aluminum Sulfate (high-grade) | C. | 1.50 | @ | 1.75 |
| Ammonium Carbonate, (domestic) | Lb. | 8 1/4 | @ | 9 |
| Ammonium Chloride, (gray) | Lb. | 5 1/2 | @ | 6 1/2 |
| Aqua Ammonia (drums) 16° | Lb. | 2 1/4 | @ | 2 1/2 |
| Arsenic (white) | Lb. | 4 | @ | 5 |
| Barium Chloride | Ton | 55.00 | @ | 60.00 |
| Barium Nitrate | Lb. | 16 | @ | 20 |
| Barytes (prime white, foreign) | Ton | — | @ | — |
| Bleaching Powder (35 per cent) | C. | 1.37 1/2 | @ | 1.50 |
| Blue Vitriol | Lb. | 5 3/4 | @ | 6 |
| Borax, crystals (bags) | Lb. | 4 1/4 | @ | 4 3/4 |
| Boric Acid, crystals (powd.) | Lb. | 7 3/4 | @ | 10 |
| Brimstone (crude, domestic) | Long Ton | 22.00 | @ | 22.50 |
| Bromine (bulk) | Lb. | 40 | @ | 50 |
| Calcium Chloride (lump) | Ton | 11.70 | @ | 12.00 |
| Chalk (light precipitated) | Lb. | 4 1/2 | @ | 5 1/2 |
| China Clay (imported) | Ton | 14.00 | @ | 18.00 |
| Feldspar | Ton | 8.00 | @ | 14.00 |
| Fuller's Earth (powdered, foreign) | C. | 80 | @ | 90 |
| Green Vitriol (bulk) | C. | 30 | @ | 32 |
| Hydrochloric Acid (18°) | C. | 1.15 | @ | 1.65 |
| Iodine (resublimed) | Lb. | 4.20 | @ | 4.50 |
| Lead Nitrate | Lb. | 8 | @ | — |
| Litharge (American) | Lb. | 5 | @ | 5 1/4 |
| Lithium Carbonate | Lb. | 1.00 | @ | 1.10 |
| Magnesium Carbonate | Lb. | 4 1/2 | @ | 4 3/4 |
| Magnesite "Calcined" | Ton | nominal | | |
| Nitric Acid (36°) | Lb. | 3 7/8 | @ | 4 1/4 |
| Phosphoric Acid (sp. gr. 1.75) | Lb. | 28 | @ | 28 1/2 |
| Phosphorus | Lb. | 35 | @ | 95 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate | Lb. | 13 | @ | 15 |
| Potassium Bromide | Lb. | 70 | @ | 80 |
| Potassium Carbonate (calcined), 80 @ 85% | C. | 14 | @ | 14 1/2 |
| Potassium Chlorate, crystals spot | Lb. | 40 | @ | 45 |
| Potassium Cyanide (bulk), 98–99% | Lb. | 22 | @ | 35 |
| Potassium Hydroxide | Lb. | 14 | @ | 14 1/2 |
| Potassium Iodide (bulk) | Lb. | 3.15 | @ | 3.25 |
| Potassium Nitrate (crude) | Lb. | — | @ | — |
| Potassium Permanganate (bulk) | Lb. | 25 | @ | 30 |
| Quicksilver, Flask (75 lbs.) | | — | @ | — |
| Red Lead (American) | Lb. | 5 1/2 | @ | 6 |
| Salt Cake (glass makers') | C. | 55 | @ | 65 |
| Silver Nitrate | Oz | 31 3/4 | @ | 33 1/2 |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash (48 per cent) | C. | 67 1/2 | @ | 72 1/2 |
| Sodium Acetate | Lb. | 4 | @ | 4 1/2 |
| Sodium Bicarbonate (domestic) | C. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate (English) | Lb. | 3 1/2 | @ | 4 |
| Sodium Bichromate | Lb. | 4 | @ | 4 1/2 |
| Sodium Carbonate (dry) | C. | 60 | @ | 80 |
| Sodium Chlorate | Lb. | 16 | @ | — |
| Sodium Hydroxide (60 per cent) | C. | 1.55 | @ | 1.57 1/2 |
| Sodium Hyposulfite | C. | 1.60 | @ | 1.90 |
| Sodium Nitrate (95 per cent, spot) | C. | 2.20 | @ | 2.25 |
| Sodium Silicate (liquid) | C. | 85 | @ | 1.15 |
| Strontium Nitrate | Lb. | 15 | @ | 17 |
| Sulfur, Flowers (sublimed) | C. | 2.20 | @ | 2.60 |
| Sulfur, Roll | C. | 1.85 | @ | 2.15 |
| Sulfuric Acid (60° B) | C. | 85 | @ | 1.00 |
| Talc (American) | Ton | 15.00 | @ | 20.00 |
| Terra Alba (American), No. 1 | C. | 75 | @ | 80 |
| Tin Bichloride (50°) | Lb. | 11 | @ | 12 |
| Tin Oxide | Lb. | 48 | @ | — |
| White Lead (American, dry) | Lb. | 5 | @ | 5 1/4 |
| Zinc Carbonate | Lb. | 8 1/2 | @ | 9 |
| Zinc Chloride (granulated) | Lb. | 4 1/2 | @ | 4 3/4 |
| Zinc Oxide (American process) | Lb. | 5 3/8 | @ | 6 3/8 |
| Zinc Sulfate | C. | 2.50 | @ | — |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax (pure white) | Lb. | 45 | @ | 57 |
| Black Mineral Oil, 29 gravity | Gal. | 12 1/2 | @ | 13 |
| Castor Oil (No. 3) | Lb. | 8 1/4 | @ | 9 |
| Ceresin (yellow) | Lb. | 10 | @ | 25 |
| Corn Oil | C. | 6.26 | @ | 6.31 |
| Cottonseed Oil (crude), f. o. b. mill | C. | 5.53 | @ | 5.60 |
| Cottonseed Oil (p. s. y.) | Lb. | 6 3/4 | @ | 7 |
| Cylinder Oil (light, filtered) | Gal. | 20 | @ | 25 |
| Japan Wax | Lb. | 12 | @ | 15 |
| Lard Oil (prime winter) | Gal. | 92 | @ | 94 |
| Linseed Oil (raw) | Gal. | 55 | @ | — |
| Menhaden Oil (crude) | Gal. | 37 | @ | 39 |
| Naphtha, 68 @ 72° | drums | — | @ | 12 |
| Neatsfoot Oil (20°) | Gal. | 95 | @ | 98 |
| Paraffine (crude, 120 & 122 m. p.) | Lb. | 2 1/2 | @ | 3 |
| Paraffine Oil (high viscosity) | Gal. | 22 | @ | 23 |
| Rosin ("F" grade) (280 lbs.) | Bbl. | 3.55 | @ | 3.60 |
| Rosin Oil (first run) | Gal. | 25 | @ | — |
| Shellac, T. N. | Lb. | 14 | @ | 14 1/2 |
| Spermaceti (cake) | Lb. | 25 1/2 | @ | 26 |
| Sperm Oil (bleached winter), 38° | Gal. | 70 | @ | 71 |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid (double-pressed) | Lb. | 10 | @ | 11 |
| Tallow (acidless) | Gal. | 62 | @ | 63 |
| Tar Oil (distilled) | Gal. | 30 | @ | 31 |
| Turpentine (spirits of) | Gal. | 45 | @ | 46 |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum (No. 1 ingots) | Lb. | 19 | @ | 19 1/2 |
| Antimony (Hallet's) | Lb. | 24 | @ | 28 |
| Bismuth (New York) | Lb. | 2.80 | @ | 2.90 |
| Bronze powder | Lb. | — | @ | — |
| Copper (electrolytic) | Lb. | 14 7/8 | @ | 15 |
| Copper (lake) | C. | 15 | @ | 15 1/2 |
| Lead, N. Y. | C. | 4.10 | @ | — |
| Nickel | Lb | 42 | @ | 45 |
| Platinum (refined) | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | 50 1/2 | @ | — |
| Tin | C | 53.00 | @ | — |
| Zinc | C | 9 3/4 | @ | 10 |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | C. | 3.19 | @ | — |
| Blood (dried) | Unit | 2.65 | @ | — |
| Bone, 4 1/2 and 50 (ground, raw) | Ton | 30.00 | @ | — |
| Calcium Cyanamid | Unit of Ammonia | 2.20 | @ | — |
| Calcium Nitrate (Norwegian) | C. | — | @ | — |
| Castor meal | Unit | — | @ | — |
| Fish Scrap (domestic, dried) | Unit | — | @ | — |
| Phosphate, acid (16 per cent bulk) | Ton | 7.00 | @ | — |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble (68 per cent) | Ton | 2.25 | @ | 2.50 |
| Tennessee (70–80 per cent) | Ton | 5.00 | @ | 5.50 |
| Potassium, "muriate," basis 80 per cent | Ton | 1.15 | @ | 1.25 |
| Pyrites (furnace size, imported) | Unit | 12 1/2 | @ | — |
| Tankage (high-grade) | Unit | 2.65 | @ | 10 |

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# FIFTIETH MEETING AMERICAN CHEMICAL SOCIETY

The Spring Meeting of the American Chemical Society convened in New Orleans, March 31st to April 3rd; the total registration was 256. The formal opening session and the public symposium by the Division of Industrial and Engineering Chemists were held at Tulane University on Thursday, April 1st. The meetings of the Divisions and the General Public Meeting on Thursday evening, took place in the Grunewald Hotel, the official headquarters.

Registration was practically completed on Wednesday. Each member, or guest, was presented with a badge and a watch fob, the design of the seal being a combination of the Louisiana State seal and the A. C. S. insignia. No official meetings took place on Wednesday and the guests made the most of the opportunity for sightseeing, in which they were aided by the Reception and Entertainment Committee.

It was the stated intention of the Local Committees, headed by Mr. W. L. Howell, Chairman of the Local Section, to show the visitors as many of the unique and characteristic features of New Orleans as was possible in the limited time allowed. In this he was ably assisted by his nine committees, including the Ladies' Committee led by Mrs. E. J. Northrup.

On Wednesday afternoon the visiting ladies were treated to a motor trip which whirled them from the Grunewald Hotel through the interesting but fast disappearing French quarter out through lovely tropical parks to the shores of Lake Pontchartrain and back among the newer and more pretentious residence sections of the city to the foot of Canal Street where they joined the rest of the convention in the boat ride on the Mississippi. The steamer "*Sydney*" had been chartered for the occasion by the Local Section; it was decorated with Spanish moss on the outside, and the cabin, lavishly adorned with flowers and vines, presented a truly southern appearance; here the complimentary smoker was held later in the evening. Turtle soup, cold meats, salads, ice cream and cakes, "smokes" of various kinds, beer and punch were served in abundance to 275 members and guests. Music by Anderson's darky band and Walter Coquille's Entertainers, comic songs and real darky dancing helped to promote in an informal way the making of new acquaintances, as well as to relieve the visitors from the strain occasioned by the long railroad journey to New Orleans. The committee in charge deserve the hearty thanks of the Society for providing such a delightful means of beginning the meeting.

The Council met at the Hotel Grunewald on Wednesday evening. The minutes of the meeting appear in full in the May issue of the *Journal of the Society*.

The Society was formally welcomed to New Orleans by Mayor Martin Behrman, and by Dr. Robert Sharp, President of Tulane University. In reply to their cordial greetings and expressions of appreciation of the value of the services of chemists to the whole South as well as to New Orleans, President Charles Holmes Herty spoke for the Society: his address is printed in full below. The formal opening address on "The Industrial Resources and Opportunities of the South," by Dr. A. D. Little, is also presented below. The Symposium on "The Contributions of the Chemist to American Industries," including the address by Dr. Bernhard C. Hesse on "The Chemist's Contribution to the Industrial Development of the United States—A Record of Achievement," appeared in full in the preceding issue of THIS JOURNAL. The entire program of papers is printed elsewhere in this issue.

On Thursday, the Tulane Refectory served a complimentary luncheon to the convention; afterwards an hour was spent in an inspection of the buildings and extensive grounds of the University.

Through the efforts of Prof. Phillip Asher, Chairman of the Publicity Committee, the New Orleans papers had given ample notice of the convention and all public meetings were well attended.

The Abstractors' Dinner was served at the Chess, Checkers and Whist Club on Thursday evening. Editor E. J. Crane emphasized the unusual and pre-eminent importance of our Abstract Journal during the present unsettled period, which will continue, of course, until some time after the close of the European war. Up to the present time the chief aim has been to make Abstracts cover the entire field of chemical and related literatures, completely and promptly, but now that this is practically accomplished, arrangements are being made to materially improve the quality of the Abstracts furnished. Abstractors and users of Abstracts were invited to coöperate towards this end.

The Banquet was held on Friday evening at the Restaurant de la Louisiane, the entire cuisine being Creole. One hundred and nineteen guests enjoyed the unusual and delicious feast. The ladies were presented with huge fragrant bouquets of sweetpeas and ferns and each received a handsome silver souvenir spoon, the design on the handle representing a river scene at the docks of New Orleans. Professor B. P. Caldwell, of Tulane University, acted as Toastmaster and short speeches were made by Prof. Herty, President of the Society; Mr. Howell, Chairman of the Local Section; Dr. Carl Alsberg, Head of the U. S. Bureau of Chemistry; and Dr. Chas. L. Parsons, Secretary of the Society.

The Committee on Excursions had arranged for the inspection of the New Orleans Water Purification Plant and an excursion to the Salt Mine at Weeks Island, 130 miles from New Orleans. Reports of these excursions are given elsewhere in this issue.

In addition to being welcomed at all sessions of the meeting and all social functions, the visiting ladies were entertained by a personally conducted tour through the Vieux Carré and a visit to the Newcomb pottery. All were charmed with the tropical aspects of the city and voiced warm praise of the cordial hospitality of the people of New Orleans.

The Louisiana Section and Tulane University de-

DELEGATES OF THE FIFTIETH MEETING OF THE AMERICAN CHEMICAL SOCIETY AT TULANE UNIVERSITY, NEW ORLEANS

serve the highest praise for the skillfull and efficient manner in which they handled the details of the convention as well as for the many unique and enjoyable features which they added to the purely scientific and business program of the Fiftieth Meeting of our Society.

## PRESIDENT'S ADDRESS

By CHARLES HOLMES HERTY

It is my pleasant duty, in behalf of the members of the American Chemical Society, to express our grateful appreciation of the cordial words of welcome so generously spoken by the people of New Orleans through Mayor Behrman, and by the members of Tulane University through President Sharp.

So hearty and so evidently sincere is this greeting that no other assurance could be required than the gracious words of the speakers. Yet another proof does exist. Ten years ago this Society met in New Orleans and the memories of that delightful week are still keenly alive in the hearts of all who were present at that meeting. It was not a matter of surprise, therefore, that the invitation to meet here again was gladly accepted.

But as I think of the tremendous changes which have taken place in the South during the intervening decade I cannot help but feel that the acceptance of the invitation was prompted also by a desire to get into sympathetic touch with that new spirit whose throbbing can be felt throughout our beloved southland today.

That spirit is not yet entirely freed from the shackles of ultra-conservatism and long-accustomedness, but the thought of the nearness of the day of its full emancipation tempts me beyond resistance to quit the rôle of responding guest and to join with you of New Orleans in welcoming to our midst this group of men whose presence has always proved an incalculable blessing.

Ours is a land lavishly blessed with natural resources —theirs the hands which take these products under closest scrutiny and by patient and laborious research shape them into greater blessings for humanity.

Of what value were the wonderful deep-seated sulfur deposits of this state until the dogged persistence of a Frasch brought this golden material to the surface by an ingenious application of the breadmaker's art, and thereby changed completely the sulfur market of the world. Are we to rest content with supplying this raw material while the methods of changing it into more valuable forms are so well known and are open for use by all?

Again, we fall so easily into the poetic habit of speaking of our "snow-white" fields of cotton, although we well know that when this cotton has been woven into cloth it shows a marked yellow coloration. But the chemist comes to the aid of nature and sets free from its tranquilizing union with sodium that element, chlorine, which gives the perfect bleach, so that a cotton cloth may be made that is pleasing to the eye. Here in your vast deposits of rock salt is stored sufficient chlorine to bleach the cotton crops for years to come. Shall it continue in this idle sleep?

Our esthetic tastes are also exacting; mere white-

ness does not satisfy; variety of color is demanded, and at the outset nature was drawn upon for dyes, successful binding to the cotton cloth being effected by the chemist through the aid of various mordants. Then followed the wonderful development of the coal-tar dye industry, a fascinating chapter in German chemical industry, culminating in the discovery of that group of dyes which need no mordant for attaching themselves firmly to the cotton fiber. In the development of this industry nature has been far surpassed in regard to both shades and durability. So insistent is this demand for colors that many of our laboring class are today threatened with enforced idleness if the artificial dyestuff supply is completely shut off by the complications of the foreign war. Much more will be said upon this subject during this meet- by those far better qualified to speak concerning it.

The chemist brings cotton and nitric acid together and behold a wonderful series of substances, varying from guncotton, that powerful explosive now playing so terrible a rôle in the fate of mankind, through camera and moving picture films to celluloid, to the beautiful artificial silk, and in lighter vein, if you will, to the wigs of straight black hair which have supplanted the anti-kink nostrums so eagerly bought by the more modern of our darker population.

The statutes of Mississippi once imposed a heavy fine for allowing cottonseed to endanger health by its rotting, or for fouling the streams into which it was thrown, but the chemist solved the problem of profitable cottonseed oil manufacture and a new source of wealth was opened to the South. Even today he is changing that oil by a new process into a better lard than ever graced a greasy grunter.

Much use is made of the chemist in this oil industry, but it cannot be considered to be upon a thoroughly rational basis until it pays for its raw product, cottonseed, according to the analytical results as to oil and protein present. Past economic conditions have not justified this, but the present is beginning to show it and the future will surely establish it.

Thanks to the splendid work of Charles M. Hall, the bauxite of my native state, Georgia, finds its way to Niagara Falls for change into the beautiful metal aluminum by the electric current generated there by falling water; yet all around its native home the power of the mountain streams has for centuries been neglected.

Even today shall we rest content with utilizing this power simply for purposes of transportation and illumination while we remain a producer of raw material? This same water power converted into the form of the electric current can set free your chlorine, can make available the nitrogen of the free air for nitric acid, and can isolate your aluminum. Our thoughts for the future development of chemical industries in the South must turn to the better utilization of our now almost neglected water powers.

These are simply types which I have mentioned to you this morning; a host of other illustrations could be given, but I must not go further in this line for the first paper on our program today, by Mr. A. D. Little, will tell the full story. We are especially glad to welcome Mr. Little into our midst, for he has been strongly drawn to the possibilities of our section and his is the clear eye which sees and the steady hand which can point the way to a truly greater future; for there is waste all around us and the development of our resources has scarcely begun.

I cannot close, however, without registering a plea which is not local or sectional in its character—a plea for closer coöperation between business men and the chemists of our technical laboratories and our educational institutions. Chemistry is no "black art;" the days of magic are past; the methods of research are well known. Patience, time, accumulating experience and good training are sure to bring rich results. The accomplishments of chemists in the past are ample proof of this statement. Why should the pioneer be always subjected to scoffing and to ridicule? Cannot the man of finance distinguish between a chemist and a fakir? The earmarks are plain. Our program today contains affirmative testimony on this point from some of the greatest business men of this country. They have been able to make the distinction, and they have no vested right in that ability. Dr. Hesse will tonight summarize this situation in an address which will clear many matters and give inspiration for new hope.

I confidently believe that such a hope is fully justified. The stimulation of this war period and the awakening of our whole people to the need of closer coöperation warrant the belief that, while the South will always remain a great agricultural section, through the blessings of its fertile soil and splendid climate, there will also be developed here industries undreamed of at present. These will convert our raw material into more and more highly finished products, not for the purpose of mere sordid accumulation of wealth, but to relieve in the masses of our people that pinch of hardship and privation which followed the close of our civil war and which for many years has made the struggle for existence paramount to all else. Is there reason for aught but optimism?' Is not the air vibrant with the conviction that a new day is dawning for the South?

What part are we of the South to play in that development? The great discoveries we now make use of are not the products of southern brains. Frasch of Germany developed our sulfur, Hall of Ohio our aluminum, Gayley of Pennsylvania increased the output of our blast furnaces by his dry-air blast, de Chardonnet of France gave us artificial silk, Mercer of England our mercerized cotton, Sabatier of France the reaction by which our cottonseed oil is hardened, Germany the great bulk of our dyestuffs.

What can our young men do? For those whose tastes lead them to chemistry as a profession, I would urge a more thorough training in the methods of research, which can be obtained in our universities. I know that this necessitates a postponement for several years of entrance into active business life, and requires an extra expenditure of funds which many of our

brightest young men do not possess. Here lies the responsibility of our wealthier people—to aid by giving full educational advantages to young men of this type and further to see that their own sons realize and appreciate the great part they may play in this development if properly equipped. Love of country, section, and state, which mean sympathy and acquaintance with those among whom we are to work, constitute a most valuable advantage in the struggle for success when it forms the broad foundation on which is laid a thorough educational training.

Can our young men afford to sit idly by and not do their share in this great development now at hand? My faith in their courage and ability, when once aroused, is unwavering.

CHAPEL HILL, NORTH CAROLINA

## THE INDUSTRIAL RESOURCES AND OPPORTUNITIES OF THE SOUTH[1]

By ARTHUR D. LITTLE

Only those who have stood upon the seashore and there endeavored conscientiously to place the Atlantic Ocean inside a quart bottle by the aid of a teaspoon will appreciate the temerity and difficulties involved in an attempt to present within the compass of a brief address the industrial potentialities of the South. Probably no one but a relative stranger to the South would make the attempt at all. Nevertheless we are all prone to overlook the obvious in our immediate surroundings, and the visitor who looks upon them from a different standpoint with sympathetic interest and keen appreciation may sometimes point out new aspects in them and values before unrecognized. The man who views a mountain range from a distance may even trace its outlines and sense its trend better than those who dwell upon its slopes. So it happens that one whose knowledge of the South is in no way comparable to your own may hope, through your indulgence, to enlist your interest and possibly to turn your thought in new directions.

The awful spectacle of a world in arms which we are forced to contemplate today must recall with a peculiar vividness to many men and women North and South the horrors and desolation of another struggle which was concluded, happily as we all now believe, just fifty years ago. When we consider that the wealth of the whole United States in 1850 was estimated at a little more than $7,000,000,000, and the cost of the war to the South has been conservatively figured at $4,000,000,000, we may gain some faint notion of the material burden under which the South slowly arose to work out her destiny.

The situation she then faced was one to daunt the stoutest hearts. It involved a reorganization of the whole economic and social structure in a land mourning the loss of the flower of its youth and manhood, with broken credit, capital destroyed, industry prostrate, and streams of immigration diverted. To the burdens of the Reconstruction Period were added the paralyzing fallacies of the Greenback issue and the nation-wide disasters and stagnation of the panic of 1873 and the five lean years which followed. Not until 1880 did the South begin to come into its own.

[1] Opening Address, New Orleans Meeting, American Chemical Society, March 31 to April 3, 1915

### EXTENT OF SOUTHERN INDUSTRIES

In 1880 the agricultural capital of the South was $2,762,000,000 and the total value of its agricultural output $756,000,000. The cotton crop was 5,761,000 bales of which the South used 179,000 bales and the North 1,610,000. Only about $330,000,000 were invested in manufactures; the mineral output was $18,000,000; the railway mileage was approximately 25,000, and the population 18,600,000. With these figures in our minds let us attempt the construction of a concept of the industrial South today.

The population of the South in 1912 has risen to 33,475,000, and the railway mileage to 90,930. The population of the whole United States in 1880 was about 50,000,000 and the total railway mileage 93,000. In general it may be said that the South today is in a far stronger position industrially than was the entire country in 1880. It cuts more lumber, mines nearly twice as much coal, produces nearly four times the petroleum, and nearly six times the spelter. It has more looms and spindles and a much larger investment in manufacturing plants. Its agricultural capital is greater and the products of its farms are worth 50 per cent more. It makes nearly as much pig iron and twice as much coke as the whole country produced only thirty-five years ago.

### AGRICULTURE IN THE SOUTH

Agriculture is still and always will be the greatest business of the South and the backbone of its prosperity although even now the value of manufactured products exceeds, by nearly $900,000,000, the revenue from its farms.

As all the world knows, the South affords a peculiarly favorable habitat to the cotton plant and the 36,000,000 acres under cotton produce annually from 14,000,000 to 16,000,000 bales of the fiber, or about 65 per cent of the world's crop. In this connection it may be said in passing that chemists by developing methods for utilizing values in the cottonseed have added from $12 to $14 per bale, or perhaps $200,000,000 yearly, to the value of this single crop, so that the seed alone is now worth nearly as much as the entire crop of 1860. Cotton and seed together constitute about 30 per cent of the total value of southern farm products, excluding live stock. The ultimate products of the cotton plant together constitute 30 per cent of the merchandise exports of the whole United States. The value of staple, linters and seed in 1913 was $911,000,000. Corresponding values for 1914 were $704,000,000, so that the European war may fairly be said to have cost the South, on this one item, over $200,000,000.

Many years ago a certain café in New York attained a cheap but wide-spread notoriety by embedding in the mosaic of its floor a few hundred silver dollars. There are 600,000,000 acres in the South and nearly every one of them carries on its surface more dollars than the floor of that café. Upon 110,000,000 of these acres the South now raises crops valued at more than $3,000,000,000. From 1880 to 1910 agricultural capi-

tal increased from about $2,800,000,000 to nearly $11,000,000,000, or 296 per cent.

In spite of the proud preëminence of cotton in southern agriculture a considerable diversity of crops has already been established. Texas alone has raised 200,000,000 bushels of corn in a single year and the value of the 1913 corn crop in the South was $766,000,000. In that year the value of the hay raised was $111,000,000, wheat $95,000,000, and tobacco $72,000,000, with another $125,000,000 in oats, Irish and sweet potatoes, sugar cane and citrus fruits. Twenty million head of cattle, 25,000,000 swine and 9,000,000 sheep add their values to the wealth of southern farms.

### MANUFACTURING IN THE SOUTH

Strangers to the South do not commonly think of this portion of our country as a manufacturing community. They may therefore well be surprised to learn that already the manufactures of the South greatly exceed in value the products of its farms and reach the stupendous total of more than $4,000,000,000. In the 29 years from 1880 to 1909 the capital invested in the South in manufactures increased 900 per cent and the value of manufactured products 407 per cent. The census survey of the entire country enumerates 262 different lines of manufacture. Of these 236 are already carried on in the South. Sixty-five per cent of the new spindles installed in the United States since 1890 are in place in southern cotton mills which now operate over 12,000,000 spindles and consume nearly 3,000,000 bales of cotton, whereas the northern mills in 1913 used only 2,500,000. Two southern states already manufacture more cotton than they raise. The value of cotton goods produced is nearly $250,000,000. One seldom hears of southern flour and grist mills, yet their product reaches the striking total of $209,000,000.

The factory products of one southern state, Missouri, reached a value of $1,688,000,000 in 1912, which included nearly $50,000,000 in boots and shoes and corncob pipes to the number of 28,000,000: the value of Missouri manufactures today is probably nearly or quite equal to the total value of southern agricultural products in 1880. West Virginia claims the largest pottery and largest glass factory in this country and the largest ax factory in the world.

In nine years, beginning with 1900, eleven southern manufacturing industries, including some of the greatest importance, increased their annual output by amounts ranging from 259 per cent to 2,380 per cent. The total increase in 92 leading industries was from $1,288,000,000 to $2,696,000,000, or 106 per cent. During the same period capital invested in factories rose in Texas from $64,000,000 to $217,000,000.

### SOUTHERN FORESTS AND LUMBER INDUSTRIES

The total forest area of the South is estimated at 259,000,000 acres. That of Germany is about 35,000,000. In 1913 the whole United States cut 38,000,000,000 feet of lumber, of which the South cut over 22 billion, including 15 billion feet of yellow pine. One Louisiana sawmill cuts 1,000,000 feet of this wood a day. Eight years ago the site selected for this mill was in a stretch of virgin forest. Today it stands upon the outskirts of the thriving and unusually attractive little city of Bogalusa with over 10,000 inhabitants and stores, residences and public buildings which would be the pride of many an older community of much greater size.

The outstanding predominance of yellow pine should not cause us to overlook the fact that of more than fifty woods manufactured into lumber in the United States the South cuts over forty. In case of ten of the more important of these fifty woods the cut of individual southern states ranks first.

The annual value of southern lumber is about $350,000,000, but the reported cut excludes so many primary wood products of larger importance that at least another $100,000,000 must be added to represent their value and $25,000,000 more for naval stores.

### COAL, COKE AND IRON

Coal lies at the basis of civilization and its stored-up energy is the present measure of man's command over nature. Excluding lignite, the coal areas of the southern states amount to about 88,000 square miles or over 50 times the coal areas of Germany, seven times those of Great Britain and twice those of all Europe including Russia. The South's present proved reserves of coal are estimated at 530,000,000,000 tons or 25 per cent more than the more thorough exploitation of all European countries has disclosed—and these southern reserves comprise 75 per cent of all the coking coal in the United States. West Virginia alone has a far greater coal area than Great Britain and Germany combined and she has mined less than $1/6$ of one per cent of the 150,000,000,000 tons beneath her surface. Nevertheless her 1912 output of 67,000,000 tons was 50 per cent more than all the bituminous coal mined in the United States in 1880. Alabama already stands next to Pennsylvania in coke production.

With coal, limestone and iron ore closely adjacent within her borders Alabama has already demonstrated her ability to manufacture pig iron more cheaply than any other locality on earth and "he who has the iron will get the gold." Her present output of 2,000,000 tons is merely an earnest of her potentialities. The immediately available southern iron ores are estimated at 2,600,000,000 tons with even greater reserves of ores of lower grade. Together these constitute not less than 50 per cent of the total iron ore reserves of the country.

### PETROLEUM AND NATURAL GAS

It is doubtful if any American product is better known throughout the East than those tins of kerosene which bear the label of the Standard Oil Company. Our automobiles consume an amount of gasoline equivalent in volume to the water supply of a town of 40,000 inhabitants. The range of endeavor of Newfoundland fishermen is determined by its price and the flight of aeroplanes over the battlefields of Europe is measured by its supply. In 1890 the South produced less than 500,000 barrels of petroleum. In 1912 its output was 84,800,000 barrels. Passing by the great deposits of Louisiana and Texas, it may be pointed

out that the oil production of Oklahoma alone in 1911 was 54,000,000 barrels.

Among these bounties of Nature with which the South has been so plenteously endowed few have greater potential values and none have been wasted more recklessly than natural gas. More than 60 per cent of the gas output of the country, or 290,000,000,000 feet, must now be credited to the South. From the standpoint of industrial utilization this is more than 1,000,000,000 feet per working day.

### WATER POWER IN THE SOUTH

The relative cheapness of water power as compared to steam has determined in the North the location and development of many great manufacturing centers like Holyoke, Lowell and Lawrence in Massachusetts, and Rumford Falls and Lewiston in Maine. The application of this power to electrochemical industries has made Niagara Falls the most interesting place on earth to chemists. Cheap water power not only implies but ensures the ultimate development of public utilities and the establishment of manufacturing plants within the radius which it may serve.

Seven years ago the United States Geological Survey estimated the minimum available power in eleven of the streams which have their headwaters in the Southern Appalachian Mountains at 2,800,000 H. P. The estimate for all the streams of the South has been put at about 5,000,000 H. P. Only about one-fifth of this power has been developed and of this amount nearly 800,000 H. P. is in the five states of Alabama, Georgia, North Carolina, South Carolina and Virginia. Georgia alone has available 500,000 H. P.

### SECONDARY MINERAL RESOURCES

The lavishness with which Nature has bestowed her gifts upon the South is nowhere more apparent than in the extraordinary variety and range of what may be termed the secondary mineral resources of this fortunate section of our country. An output of $5,800 worth of diamonds per week of the best South African quality in Pike County, Arkansas, is interesting and promises to become spectacular, but it shrinks to insignificance before many other southern mineral products. The whole country knows of the annual shipment of 8,000,000 boxes of Florida oranges and grape fruit, but relatively few of us give thought to the 3,000,000 tons of the infinitely more important phosphate rock which Florida produces. This is about four-fifths of the country's output, practically all of which now comes from the South.

Portland cement requires for its manufacture an assured supply of limestone and clay or shale adjacent to cheap fuel. Nowhere are these conditions met more fully or more generally than in the South. As a result its development of the manufacture of Portland cement has become one of the industrial miracles of the world. In 1890 the production for the whole United States was less than 400,000 barrels. In 1911 the output of cement in the southern states alone was nearly 11,000,000 barrels.

The South has inexhaustible supplies of clays which exhibit every desirable range of quality. There are clays in any amount desired for the making of common brick and tiles, cheap pottery and drain pipe, terra cotta and paving brick, and prodigal amounts of the finer white plastic clays and kaolins for china and the purposes of paper making. The production of Fuller's earth is almost exclusively a southern industry.

The South is equally fortunate in its endless stores of sand and gravel, road material and building stones. The latter range from the superb Georgia marbles and the granite of Stone Mountain near Atlanta, through every variety and quality, to meet all structural demands.

Immense deposits of gypsum occur in several southern states and ochres, mica, graphite, barytes, and corundum are among the well known mineral products of the South.

The history of industrial chemistry is a record replete with romance, and one of its best known stories is that which chronicles the development of the aluminum industry. In 1855 the metal cost $90 a pound; the Castner process brought the price to $4 in 1889. Then Hall in America and Héroult in Europe simultaneously developed the process which permits its cheap production by electrolyzing alumina in a fused bath of cryolite. Bauxite is an impure alumina and has become the chief source of the metal. Arkansas leads in the production of bauxite, but Georgia, Alabama and Tennessee contribute largely to the growing demands.

Another romance of chemical achievement is that which tells the story of the sulfur mines in Calcasieu Parish, Louisiana. There sulfur in inexhaustible amounts lies 1,000 feet below the surface and under 500 feet of quicksands. An Austrian Company, a French Company and many American Companies had tried in many ingenious ways to work this deposit, but each had failed. Frasch solved the problem by forcing superheated water down a boring, and pumping out the melted sulfur through an inner tube. Today Louisiana holds easily within her hands the sulfur markets of the world and supplies one-half the world's consumption.

Sulfur, as the direct source of sulfuric acid, constitutes the foundation of all chemical industries. The keystone of the structure is common salt. This the South bountifully supplies at Avery's Island, also in Louisiana, and in the salt wells of Oklahoma and West Virginia.

The largest sulfuric acid plant in the world is at Ducktown, Tennessee, but the striking feature of the installation which holds this record is that the acid is made from smelter fume, which commonly in other plants goes only to create a nuisance. The copper production, which is the primary output of the plant, is over 18,000,000 lbs. per year. The largest copper refining plant in the world is at Patapsco, Maryland, with an annual production of 200,000,000 lbs.

In 1911, 42 per cent of the lead output of the country came from the South and 41 per cent of the zinc production. The value of Missouri zinc alone was

$14,000,000. The largest pyrites producing plant in the whole country is in Louis County, Virginia.

There are produced in the United States 57 useful minerals. Of these every one is mined in the South except platinum and borax.

### THE FAILURES OF THE SOUTH

We have reviewed in the most casual and disjointed manner the immediate achievements and demonstrated resources of the South in those things which make for industrial preëminence. All these figures are well known to you. They have been set forth time and again in the publications of the federal government and those of your own states, and reiterated with compelling emphasis and illuminating comment by that apostle of southern achievement and prosperity, the *Manufacturer's Record*. The aggregate of these stupendous figures represents an achievement and a heritage of which any people may well be proud, but the community whose eyes are filled with a vision of the future should take measure not of its successes but of its failures. What are the failures to be charged against the South?

First of all there is the stupendous failure of its agriculture. In 1909 only about 18 per cent of the total area of the South was tilled, whereas 75 per cent is available for tilled crops. What is more to the point, the 110,000,000 acres, which were tilled, were most of them tilled badly. Upon 35,000,000 acres the South raises as a maximum 16,000,000 bales of cotton—less than $^1/_2$ bale per acre. In some localities the yield shrinks even to 132 lbs. per acre. As compared with this, Georgia has raised upon 2500 acres 2700 bales, while as much as 2.38 bales has been raised upon a single acre in Texas. Little more than deeper ploughing and intelligent fertilization is required to double the present cotton crop or to produce the 1914 crop upon half the present acreage, leaving 18,000,000 acres available for corn and other crops. In one southern state 232 bushels of corn have been raised on a single acre; in another 13 acres of lettuce have sold for $12,000, and in a third 5,000 acres of cabbages have yielded $800,000 and 2,000 acres $600,000 worth of cucumbers. In the same state 145 million cabbage plants were started upon 346 acres and exported to other states to complete their growth. A single acre of Florida celery has paid $1,500 in freight to the railroad. North Carolina, which shipped 1,600 carloads of strawberries from Wilmington, in one season, reports 15,000,000 acres within the state upon which no agricultural improvements have been made. Alabama still buys largely of western grain, provisions and even hay, while Arkansas bought $80,000,000 worth of foodstuffs last year.

Next perhaps in importance is the failure of southern lumbering which is one of the most wasteful operations conducted on the whole broad face of the earth. In cutting 15,000,000,000 feet of merchantable yellow pine the South wastes not less than 30,000,000,000 feet, which, if intelligently utilized as raw material, should yield ten times the profit derived from lumbering.

For every ton of coal mined in the South, or for that matter in the country, one-half a ton was wasted or left underground in such condition that it can probably never be recovered.

The most atrocious and unnecessary wastes which have attended the development of any resources of our country have been those which have accompanied the exploitation of natural gas. As to these the South is no more culpable than other portions of our country upon which this extraordinary boon of nature was conferred. Nevertheless it may interest you as southern men who would conserve the resources of your birthright to know that the waste of gas in the Oklahoma fields alone has been as high as 150,000,000,000 cubic feet a year, and is now annually not less than 25,000,000,000 cubic feet. The time is fast approaching when natural gas will have its value determined by the number and value of the synthetic products which chemists are able to derive from its several components. For the present it may suffice to point out that every 100,000,000 cubic feet of natural gas represents on the basis of a ten-hour day 588,000 horse power, if consumed in a fair gas engine on fluctuating load averaging 50 per cent of rated capacity. West Virginia is now the largest producer of natural gas in the country and the especial disability under which the South now labors is exemplified by the fact that a very large part if not the major portion of the gas originating in West Virginia is piped outside the state and used for the generation of heat and light and power elsewhere.

It has already been pointed out that the South contains over 50 per cent of the total iron resources of the country. Nevertheless it produces only 12.5 per cent of the pig iron made and consumes not over 150 lbs. per capita while the whole country consumes 650 lbs. per capita. Here again we have before us the fundamental difficulty which confronts the South. A ton of iron ore shipped as ore returns only $2 and provides less than one day's work for one man. If shipped as stoves it returns $40 and has provided a day's work for ten men. The South has been selling raw materials. It should sell brain values and labor values.

Owing to its later advent as a large producer and its relatively more general introduction of by-products from coke ovens, the South has been less wasteful than the North of the ammonia values in its coal. It will probably never be possible to recover more than a moderate proportion of these values, but the extent of the problem in the whole country may be indicated by the fact that the total volatile ammonia in the coal mined annually in the United States would be worth, at $60 per ton for ammonia sulfate, over $300,000,000. We save less than $4,000,000. In Germany four-fifths of all coke is made in by-product ovens: in the United States only about one-sixth is so made.

In the Florida pebble field the tonnage of phosphate rock wasted is two or three times the total tonnage saved. The waste occurs mainly through the washing away of fine particles by the water used in mining and for cleaning the larger aggregates. In the Tennessee field there is relatively much less waste.

The wastes in zinc mining and smelting constitute another heavy drain upon your resources. Less than

50 per cent of the zinc in the mines ever reaches the form of spelter.

Many other comparable examples of the prodigal use of utter waste of valuable raw material might easily be cited though perhaps to no advantage at this time. There are signs that the era of thoughtless or willful extravagance is passing. Means of production, methods of practice and systems of organization which have been worked out painfully and at great cost elsewhere are being gradually adopted in the South but a more general appreciation of their advantages may well be urged.

An excellent example of intelligent conservation is afforded by the great pulp mill at Canton, North Carolina. Formerly the spent chips from the chestnut extract plants were burned. Now they are boiled in caustic soda and converted into high-grade pulp and paper.

All visitors to the South who have been so fortunate as to partake of the hospitality of southern homes cherish always thereafter a warm appreciation of the grace and courtesy of southern life. The charm of New Orleans is proverbial and the metropolitan aspect and quality of many southern cities like Jacksonville and Atlanta strikes the observer at once. One may nevertheless be permitted to suggest that the South would gain immeasurably by giving to a larger proportion of its smaller towns and country places that atmosphere of trig neatness and comfortable prosperity which characterizes so many of the older villages of Massachusetts and Vermont and reflects the pleasantness of life in them. The South is also greatly handicapped by the general quality of its roads. Only about 60,000 miles out of 850,000 have ever been improved.

### VALUE OF INDUSTRIAL TRAINING FOR NEGROES

One of the greatest of the relatively undeveloped potential industrial assets of the South is undoubtedly the negro. The negro population in the southern states is about 10,000,000, and by the efficiency of the units of that population the prosperity of the South is profoundly affected. Many negro farmers are now raising from 30 to 60 bushels of corn per acre where formerly they raised from 5 to 15 bushels. Where they produced from 150 to 200 lbs. of lint cotton per acre many now secure 250 to 600 lbs. Nevertheless, a demonstration agent of the Department of Agriculture has recently found negroes farming almost entirely by hand. Three persons carried on the planting of the grain: the first would dig a hole for the seed, the second would plant it and the third would cover it. He introduced the use of the plow in this twentieth century.

Scarcely any work carried on in the South today is more truly constructive or fraught with greater ultimate possibilities than that which goes forward at Tuskegee and in those other institutions of which it is the type. Since its foundation approximately 9,000 young negro men and women have received two years of industrial training. They entered with an average earning capacity of about $100 per year. Their earnings after training have averaged $700, which by the way is above the average for doctors and lawyers in Massachusetts. The average length of time that these 9,000 students have been out is 14 years and in that time their estimated earnings have been $88,200,000. Deduct from this the $12,600,000 which they might have earned without their special training and the already accrued value of that training which it cost Tuskegee $1,467,000 to impart is $75,600,000. Is there any more profitable business in which the South can engage?

We have given a brief consideration to the imperial resources of the potential South and have sketched in a few high lights, in an attempt to picture something of the South's amazing progress and achievement. Let us turn our attention to the trend and goal of her development.

### SOUTHERN RURAL LIFE NEEDS ENRICHENING

The first of her problems would seem to be the organization of rural life to make it richer, more satisfying, more profitable and pleasanter. It is bound up with the problem of the reorganization of southern agriculture. The South has really not begun to farm. To prove this thesis one has only to turn to the results secured by agricultural demonstrators, demonstration farms, boys' clubs, the girls' tomato clubs, the McRae experiment in North Carolina and the output of truck farms under scientific control in many southern states. There is not a single southern crop which cannot easily be increased 500 per cent. For 2 per cent of the value of a single potential crop 20,000,000 acres of swamp land in Louisiana could be drained and the South's output of cotton doubled. There are no more fertile lands on earth than the Louisiana lowlands, and Louisiana, which might have been in ages past another Egypt, should become another and a greater Holland, and in Holland lands potentially less productive sell for $500 to $1500 per acre. Tennessee has a swamp area of 1,000,000 acres. Along the Atlantic Coast are 25,000,000 acres of sandy loam ideally adapted to intensive farming. Texas has an area of 170,000,000 acres, greater by 55,000 square miles than either France or Germany, but less than 30,000,000 acres are yet improved. It now carries over 10,000,000 head of live stock while Texas bees are worth $5,000,000 and produce each year honey and comb to the value of $5,000,000. It pays to keep a bee in Texas.

One yields in passing to the temptation to refer to the camphor trees of Florida and Texas and the date palms profitably grown on the islands near the Texas coast. But details and figures merely obscure the broad and basic proposition which is that the agricultural possibilities of the South are almost beyond conception and that in their development can profitably be employed all that enterprise, capital and science can supply for many years. Diversified, intensive agriculture by individual endeavor, corporation farming and community effort under scientific direction and control will find full scope and reap harvests unthought of now.

### CONSERVATION THE SOUTH'S FOREMOST INDUSTRIAL PROBLEM

Foremost among the industrial problems of the South would seem to be the suppression of wastes, the vastly

greater development of labor values in its products and the keeping at home of money now needlessly spent elsewhere. The South has been too generally content with shipping crude materials and primary products and too ready to accept from other sections the things which it might better produce at home.

For gigantic wastes which may immediately be utilized to the enormous profit of the South, no industry is comparable to the lumbering of yellow pine. Our studies have shown that in Louisiana at least, under exceptionally able management, the products of the average yellow pine tree may be classified as follows: Needles and twigs, 2.25 per cent; limbs under 3 in., 2.54 per cent; cord wood, 6.142 per cent; pulp wood, 4.154 per cent; red and rotten, 8.05 per cent; sawdust and shavings, 17.62 per cent; lightwood, 0.61 per cent; stump 6.48 per cent; lath, 1.39 per cent; shingles, 0.06 per cent; and finally lumber and box shooks, 31.97 per cent.

Two-thirds of the tree is at present wasted either as litter in the field or as mill waste; and $3 a thousand is a good profit on lumber.

While northern paper mills are paying on the average $18.37 for the wood to make a ton of paper the South is throwing away tens of thousands of cords of pulp wood every day, only a cord and a half of which is needed to make a ton of Kraft paper worth $70. The ultimate development of a vast paper industry in the South is assured, but as a recent editorial in the New Orleans *Item* pointed out "Great industries do not spring from great opportunities. They result from the initiative of some individual. The captain of industry may create an industrial empire in a desert and bring his materials hundreds of miles from spots far more favored by nature than is their destination. We in Louisiana lack industrial empire because we lack captains of industry."

The recently culminating discoveries in a century long research have proved that 20 gallons of 95 per cent ethyl alcohol, that is, not wood alcohol, but the alcohol commonly produced from grain, may be obtained from a cord of yellow pine sawdust or hogged waste. From a bushel of corn worth say 80 cents only $2^1/_4$ gallons are obtained. Such difficulties as have attended the initial large scale operation of this process are certain to be overcome, and have in fact for the most part already been surmounted. Cheap industrial alcohol made in enormous volume from yellow pine waste and available for motor fuel, lighting, heating and a thousand miscellaneous applications in the arts is a certainty of the future.

In Georgia a great plant for the production of naval stores is shut down, primarily, it is claimed, because the annual loss of solvent represented 23 per cent of the entire plant investment. New processes promise a solvent loss of less than 2 per cent.

Several types of gas producer are now operating profitably on wood waste. New methods of controlled distillation have been developed and applied to wood and it has been proved both by the Forest Service and our own laboratory that turpentine and rosin may be profitably extracted from stumps and lightwood by processes which permit the manufacture of paper from the extracted chips. The production of lumber in the South will ultimately become a mere incident in the business of lumbering. No longer then will logging tramways be pulled up the moment the saw logs on the tract have been removed. They will stay until the tract is cleared of cord wood, pulp wood, lightwood, stumps and saw logs. The cleared land will be devoted to grazing or to farming under the stimulus of demonstration farms or corporation management, and the lumber mill will become the center of a whole group of highly profitable industrial activities.

### PRESENT MANUFACTURING LIMITED

Less than 30 per cent of the lumber produced in any southern state receives any further industrial handling in the state of origin. Cottonseed oil is shipped to Chicago, Berlin, and New Hampshire, to be hydrogenated and converted into lard and butter substitutes. Bauxite is sold for $5 a ton to be subjected elsewhere to the purifying treatment which raises its value to $60. The South will one day benefit enormously by a cheap process of producing alumina direct from clay. It will give new values to southern clay beds and to southern water powers and transfer the aluminum industry to this section. It does not appear, however, that any effort is being made in the southern states to develop such a process.

There are at Webster, N. C., millions of tons of low-grade nickel ore awaiting only a commercial method of extraction. Thus halloysite in large quantities occurs on Taylor's Mountain, near Gore, Ga. It contains 30 to 35 per cent of alumina, said to be soluble in dilute sulfuric acid to form a clean white alum cake almost wholly free from iron and silica. If these claims can be established there is the basis for a large industry. A single northern paper company consumes 12,000,000 lbs. of alum a year.

No locality in the United States and perhaps none in the world presents such advantages for the establishment of the great basic chemical industries as Louisiana. Here in close juxtaposition are found cheap salt, even cheaper sulfur, gas, oil, rosin, turpentine and wood waste while near-by are the coal and minerals of Arkansas and Alabama.

### SMALL NUMBER OF CHEMISTS IN THE SOUTH

It is noteworthy in view of the extraordinary opportunities for chemical development presented by the South that in the southern states are to be found only about 10 per cent of the chemists of the country as represented by the membership of the American Chemical Society. The Society has 7180 members, of whom only 746 are in the entire South whereas New York has 1186 members, Pennsylvania 659, Massachusetts 511. What one chemist can do for the South has been shown by Frasch in Louisiana, by Wesson wherever cottonseed oil is made, and by our distinguished president, Dr. Herty, in the conservation of turpentine and increase of yields.

### CONCLUSION

Fragmentary and utterly inadequate as this attempted presentation of southern resources has proved

to be it will have served its purpose if it has brought freshly home to some of you who live in this supremely favored section of our country the responsibility for individual initiative imposed upon you. Opportunity implies responsibility. Gentlemen, you are heirs to an imperial inheritance and its responsibilities are yours.

93 Broad St., Boston

# ORIGINAL PAPERS

## ELECTROPLATING WITH COBALT[1]

By Herbert T. Kalmus, C. H. Harper and W. L. Savell

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In 1842, Professor Boetger pointed out that dense and lustrous deposits of nickel could be obtained, which, on account of their resistance to oxidation, great hardness and elegant appearance, were capable of many applications. The outcome of this has been that during the last 20 years commercial plating with nickel has developed to an industry of very great magnitude. On the other hand, no plates of cobalt or of its alloys have ever been in extended commercial use. No doubt part of the reason is because of the difficulty of obtaining a supply of cobalt metal at an attractive price. On the other hand, for commercial plating, where labor, overhead charges, the preparation of the surface to be plated, the difficulty of maintaining the bath, the amount of buffing, the current efficiency, and particularly the speed with which the work may be run through the baths, are so considerable a fraction of the cost of the finished work, the price of the metal to make up the anodes and the salts is by no means alone the determining factor in the choice of that metal. Moreover, the speed of plating largely determines the hardness and other physical properties of the plate, which in turn determine the weight of metal required for satisfactory commercial tests.

A great many technical points in connection with the plating of cobalt have not been investigated; the corresponding investigations for nickel have been comparatively thorough. Before platers can adopt cobalt for many purposes, on a considerable scale, a number of questions must be definitely answered by experiments, such as:

1—Can cobalt be plated on iron, steel, brass, tin, German silver, lead, etc., to yield as uniform, as adhesive, and as satisfactory a finished surface as nickel?

2—Is cobalt plate harder than nickel plate?

3—Is cobalt plate less corrosive than nickel plate under ordinary atmospheric action?

4—What bath is most suitable for the deposition of cobalt where a heavy protective coating, which may be buffed to a superior finish, is required to be deposited in a minimum of time?

5—Can a satisfactory cobalt bath be maintained at such an increased concentration as compared with the nickel bath, that plating from it may proceed with greater speed?

6—Is the cobalt bath more or less troublesome than the nickel bath as regards crystallization, etc.?

7—Should alkali, acid, or neutral baths be used for cobalt plating?

8—Is the nature of the deposit improved by hardeners such as boric acid, citric acid, magnesium salts, etc.?

9—How does the maximum current density at which cobalt may be deposited commercially compare with the maximum current densities used in the commercial deposition of nickel?

10—What electromotive force had best be used for cobalt plating, using the bath found most suitable for a given class of work?

11—How do cobalt anodes compare with nickel anodes as regards solubility, under the conditions of the plating bath?

12—What are the relative current efficiencies of cobalt and nickel plating under the best conditions?

13—How do the electrical conductivities of satisfactory cobalt and nickel plating solutions compare?

14—Can cobalt be deposited to considerable thicknesses from any solution in accordance with commercial practice?

15—What is the relative cost of cobalt and nickel plating?

Although numerous statements have been published in the past with regard to cobalt plating, the conclusions to be drawn from a survey of the existing literature and patents would lead one to be very skeptical as to the advantages of cobalt plating over nickel plating. It is noticeable, however, that the conditions for the production of good cobalt plates, as given by different authors, vary tremendously among themselves. Not only are the conclusions often diametrically opposite, as shown below, but likewise the data from which these conclusions are drawn.

Consider alone the question of the relative maximum current densities with which cobalt and nickel may be successfully plated. There is little or nothing in the literature relating to the solutions of cobalt which we have found in this laboratory to be most suitable for fast plating. If it can be shown to be practically feasible to plate cobalt from a bath at several times the speed possible for nickel, other things being equal or in favor of the cobalt, this greater speed of turning out the work, with attendant economics, might offset a very considerable difference in the initial cost of the anodes and salts of the two metals. It must certainly appeal to anyone that if cobalt-ammonium sulfate, because of its very much higher solubility than nickel-ammonium sulfate, or for other reasons, may be used as a plating bath at very much higher current densities, that with such a bath the plater might turn out cobalt plates more economically than nickel plates. Moreover, plating at greater speed means a harder and denser plate with consequent less weight of metal required.

[1] Authors' abstract of report under the above title to the Canadian Department of Mines, published by permission of the Director of Mines, Ottawa, Canada. This publication is one of a series on the general investigations of the metal cobalt and its alloys, particularly with reference to finding increased commercial usage for them, now being conducted at the School of Mining, Queen's University, Kingston, Ontario, for the Mines Branch, Canadian Department of Mines. See also This Journal, **6** (1914), 107 and 115; **7** (1915), 6.

This paper is concerned with the presentation of a large amount of experimental data on cobalt plating. It attempts to record data, to summarize, and to draw conclusions with reference to practical cobalt plating and its application in the industries. Theoretical considerations concerning the explanation of the results are reserved for a separate publication.

A large number of plating experiments were undertaken at this laboratory in the study of the questions outlined above. Numerous types of cobalt baths were used and various concentrations of each solution. The object of this paper is to set forth the data of these experiments and the conclusions to be drawn therefrom.

LITERATURE ON ELECTRODEPOSITION OF COBALT

Langbein, in his well-known work, "Electro-Deposition of Metals,"[1] devotes nearly 175 pages to the deposition of nickel, and a scant 2 pages to the deposition of cobalt. With regard to cobalt, Langbein remarks:[1] "For plating with cobalt, the baths given under 'Nickeling' may be used by substituting for the nickel salt a corresponding quantity of cobalt salt. By observing the rules given for nickeling, the operation proceeds with ease. Anodes of metallic cobalt are to be used in place of nickel anodes.

"Nickel being cheaper and its color somewhat whiter, electroplating with cobalt is but little practiced. On account of the greater solubility of cobalt in dilute sulfuric acid, it is, however, under all circumstances, to be preferred for facing valuable copper plates for printing.

"According to the more or less careful adjustment of such plates in the press, the facing in some places is more or less attacked, and it may be desired to remove the coating and make a fresh deposit. For this purpose Gaiffe has proposed the use of cobalt in place of nickel, because the former dissolves slowly but completely in dilute sulfuric acid. He recommends a solution of one part of chloride of cobalt in ten of water. The solution is to be neutralized with aqua ammonia, and the plates are to be electroplated with the use of a moderate current."

From our experiments we find in general that the substitution of cobalt for nickel in Langbein's baths, as recommended by him, does not do justice to the metal cobalt. These baths have been primarily worked out for nickel, whereas cobalt, being in many instances of far greater solubility, requires a much more concentrated bath than that recommended for the fastest and best plating. Some of our best cobalt solutions are not included at all in Langbein's list.

MacMillan,[2] Watt,[3] and others report that cobalt deposits are harder than the corresponding nickel deposits. Brochet[4] says: "Cobalting has been proposed in place of nickeling when a deposit of greatest hardness is desired."

On the other hand Langbein,[5] Wahl[6] and others say that cobalt plates are softer than the corresponding nickel ones.

S. P. Thompson[7] finds that articles plated with cobalt are less corroded in the atmosphere of London than either silver or nickel plate, while Stolba[1] reports that cobalt salts treated like nickel salts yield metallic deposits of a steel-gray color, less lustrous than nickel and more liable to tarnish.

While some authorities report that it is practically impossible to obtain a deposit of cobalt more than a few hundredths of a millimeter in thickness, Bouant[2] says: "Electrolytic deposits of cobalt are easily obtained even of a very great thickness, so that electrodeposition of cobalt is as easy as that of copper."

A review of much of the literature on the electrodeposition of cobalt was presented at the meeting of the American Electrochemical Society, at Atlantic City, in April, 1913, by O. P. Watts. A consideration of Watts' paper emphasizes the diversity of opinion with regard to cobalt plating above mentioned.

Watts mentions about fifty solutions of cobalt which have been used with greater or lesser success. Some of these are similar to ones used by us in our experiments, but several of our best solutions are not included in the list. Many of these baths are recommended only for very weak currents, others are more or less indefinite, and there is much contradiction among them. For example, the first solution in Watts' list is—"Becquerel's solution, 37.5 grams of cobalt chloride neutralized by ammonia or potassium hydroxide, gives a brilliant, white, hard and brittle deposit; a very weak current must be used." Later, quoting from Watts, Isaac Adams says in a patent application: "I have found that a solution made and used in the manner described in the books will not produce such a continuous and uniform deposit of cobalt as is necessary for the successful and practical electroplating of metals with cobalt. * * * I have found further that the simple salts of cobalt, such as are recommended by Becquerel and others, are not such salts as could be used in practical electroplating with cobalt. * * * * * "

Even in a matter so immediate and important to the practical plater as the acidity or basicity of his plating bath, there is no general agreement among the authorities even for nickel solutions, much less for cobalt. Dr. Langbein[3] writes: "All nickel baths work best when they possess a neutral or slightly acid reaction * * an alkaline reaction of nickel baths is absolutely detrimental; such baths deposit a metal dull and with yellowish color and do not yield thick deposits." Bennett, Kenny and Dugliss, in a paper read before the American Electrochemical Society at New York City, April, 1914, state as two of their seven general conclusions the following: "A good deposit of nickel may be obtained from the double sulfate if the solution at the surface of the cathode is kept alkaline. * * * Since alkalinity is necessary for good efficiency, it is very probable that in acid solutions nickel is deposited only when impoverishment of the hydrogen ions has caused the solution to become alkaline and given the conditions under which nickel may deposit."

[1] Dr. Geo. Langbein, "Electro Deposition of Metals," 6th Edition Revised, Henry Carey Baird and Co., Philadelphia, p. 318.

[2] MacMillan, "Electro-Metallurgy," **1901**, p. 227.

[3] Watt-Phillips, "Electro-Plating and Electro-Refining of Metals," **1902**, p. 360.

[4] "Manuel Pratique de Galvanoplastie," **1908**, p. 313.

[5] "Electro-plating of Metals," 6th Edition, p. 319.

[6] Watt-Phillips, "Electro-Plating and Electro-Refining of Metals," **1902**, p. 360.

[7] *Journal of Institute of Electrical Engineers*, **1892**, p. 561.

[1] *Electrical Review*, Nov. 18, **1887**, p. 503.

[2] Bouant, "La Galvanoplastie," **1894**, p. 294.

[3] Langbein, "Electro-Deposition of Metals," 6th Edition Revised, p. 251

These are but a few of many contradictory statements to be found in the literature.

SUBDIVISION AND ARRANGEMENT OF EXPERIMENTS

A very large number of plating experiments were conducted by us at this laboratory for the purposes outlined above, in connection with which some sixteen different types of solution or baths were employed and studied, as noted below:

| SERIES | SOLUTIONS |
|---|---|
| I | Cobalt-ammonium sulfate. |
| II | Cobalt-ammonium sulfate, with an excess of ammonium sulfate |
| III | Cobalt-ammonium sulfate, ammonium sulfate and citric acid. |
| IV | Cobalt-ammonium sulfate and ammonium chloride. |
| V | Cobalt chloride with ammonium chloride. |
| VI | Cobalt-ammonium sulfate and boric acid. |
| VII | Cobalt-ammonium sulfate, cobalt carbonate and boric acid. |
| VIII | Cobalt sulfate, potassium citrate and ammonium chloride. |
| IX | Cobalt phosphate and sodium pyrophosphate. |
| X | Cobalt-ammonium sulfate and magnesium sulfate. |
| XI | Cobalt sulfate, neutral ammonium tartrate, and tannic acid. |
| XII | Cobalt sulfate, potassium tartrate and tartaric acid. |
| XIII | Cobalt sulfate, sodium chloride and boric acid. |
| XIV | Cobalt sulfate, ammonium sulfate, magnesium sulfate and boric acid. |
| XV | Cobalt-ethyl sulfate, sodium sulfate and ammonium chloride. |
| XVI | Cobalt sulfate, ammonium sulfate, ammonium chloride and boric acid. |

Each set of plating experiments with a definite group of principal components in the bath has been given a series number. Variations in concentration or changes in the relative proportions of the components or additions to a bath, have been designated by the use of letters, A, B, C, etc. Also, where a nickel bath has been used, analogous to a given cobalt bath, the data for the experiments on it are noted under the corresponding cobalt series.

There were two distinct series of plating experiments, one set conducted at this laboratory and one in the plating department of the Russell Motor Car Co., Toronto.

METHOD AND ARRANGEMENT FOR LABORATORY PLATING EXPERIMENTS

ARRANGEMENT OF ELECTRICAL CIRCUIT—Power was taken from three storage batteries connected in series, yielding approximately 6 volts. The various baths were connected independently across the 6 volt terminals of this storage-battery set, with appropriate resistance in series with each. In this way the potential across the electrodes of each was cut down to the desired value. A 5 volt range Weston voltmeter, reading to 0.01 volt, was connected directly across the electrodes of each bath. A Weston milliammeter, 600 milliampere scale, was connected in series with each bath.

PLATING TANK AND COMPUTATION OF EFFECTIVE ELECTRODE SURFACE—The plating tanks used were of glass, rectangular in shape, and of approximately the following internal dimensions: 12 in. × 6 in. × 6 in., though some were deeper.

In general, if the bath is not large in cross-section in comparison with the area of the electrodes, the results obtained will not be reproducible. We tried experiments using a tank not much larger in cross-section than the electrodes. In that case the voltage required for a given current density, with electrodes 10 cm. apart, is very much greater than with a tank of considerably larger cross-section, other conditions being the same. This is largely due to the fact that with the smaller cross-section of tank the available solution between the electrodes is diminished.

For the most part, our electrodes were approximately 3 in. × 2 in. in surface, placed from 10 to 20 cm. apart, in the center of the rectangular plating tank above mentioned. If the electrodes were kept in place, the tank lowered away from them and substituted by a very large tank of the same solution, we found that the electromotive force across the electrodes for a given current density diminished by nearly 20 per cent. The leads of the electrodes were coated with a layer of insulating asphaltum, as described in the paragraph on electrodes. In the case of these experiments, therefore, the effective electrode area is something like 20 per cent less than the exposed surface.

Again, instead of submerging electrodes of the above size in the middle of the tank, in some of our experiments the electrodes were lowered into a tank to such a depth as to be just covered by the solution. It is obvious, in this case, as we found by test, that the electromotive force across the electrodes would diminish if the height of the bath around them were raised. This is true even though no greater area of electrode is thereby covered with solution, and although the leads are insulated with asphaltum. The reason is that, with the level of solution just covering the top of the electrodes, the electrical field between the upper portion of the electrodes was limited by the surface of electrolyte, as compared with what it was with the electrodes immersed in the center of a large body of electrolyte.

Consequently had our experiments been performed in an ideally large tank, the electromotive forces would have been smaller for the same current densities. We preferred to use a bath approximating to the conditions of plating practice, and have in all cases noted, in the tables to follow, the values of current density, electromotive force, etc., just as observed, without correction.

Good practice for commercial nickel plating with many solutions, is to have about eight gallons of solution for each sq. ft. of anode surface. In our experiments we have not departed widely from this value, although we find different solutions require a somewhat different magnitude of this ratio for the best results.

THE PLATING EXPERIMENTS—The plating experiment itself consisted in noting changes in appearance of the solution and electrodes as the deposition progressed, as well as making a record of milliammeter, voltmeter and time readings at frequent intervals. The concentration of the bath was measured from time to time, and the physical properties of the resulting plate were studied. Wherever current efficiencies were desired, milliammeter readings were made at intervals at not more than two minutes. These readings were very constant in all cases, so that more frequent readings were not necessary. Also the cathode was carefully dried and weighed before and after the deposition. Precautions were taken so that conditions of weighing of the electrode before plating and after plating were identical.

Advantage was taken of the well-known fact, for

the deposition of nickel and other metals, that the deposit is more adhesive when struck on initially at a higher potential than is to be used throughout the greater part of the plating run. Our practice was to diminish the resistance in series with the bath, so that an initial electromotive force of about 6 volts was used, sending very considerable currents through the bath during approximately the first thirty seconds of the run. The effect of this was uniformly satisfactory in causing the plates to adhere firmly.

After a sufficient plate had been deposited on the cathode it was removed from the bath, immediately washed in cold water, and then rinsed in boiling water until it came to a uniform temperature, after which it was dried in hot sawdust. This procedure was practiced throughout the plating experiments.

BUFFING AND FINISHING COBALT PLATES—The cathode after being removed from the plating bath and dried, is, in general, white and metallic, and requires but little buffing to produce a satisfactory mirror surface. Our practice has been to employ a large buffing wheel rotating at high speed which will "color" the work in one operation. Cobalt plates color more readily than nickel, and for commercial purposes should not require cutting with Tripoli, etc.

## PREPARATION AND USE OF ELECTRODES

ANODES—Both cast and rolled anodes were used for these experiments, the cobalt employed analyzing as follows:

| Lab No. | Anodes Made No. | Size—Inches | Percentage Analyses of Anodes Co | Ni | Fe | As | C | S | P | Si |
|---|---|---|---|---|---|---|---|---|---|---|
| H 218 | 2, cast | $3\frac{1}{2} \times 2 \times \frac{1}{4}$ | 95.70 | 0.80 | 2.10 | ..... | 0.040 | 0.043 | 0.004 | 0.050 |
| H 219 | 4, cast | $3\frac{1}{2} \times 2 \times \frac{1}{4}$ | 98.00 | 0.75 | 1.35 | ..... | 0.060 | 0.042 | 0.007 | 0.067 |
| H 221 | 4, rolled | $3\frac{1}{4} \times 2 \times \frac{1}{4}$ | 95.63 | 0.75 | 3.72 | 0.048 | 0.052 | 0.029 | 0.005 | ..... |

The cast anodes were poured in sand and smoothed down with an emery wheel to a finished surface.

The rolled anodes were made from ingots about 8 in. long and 1 sq. in. in cross-section, which were rolled down to plates of $\frac{1}{4}$ in. thickness, from which the anodes were finished.

IMPURITIES IN ANODES—Nickel anodes, as sold in the market, frequently contain in the neighborhood of 92 per cent nickel and $7\frac{1}{2}$ to 8 per cent iron. The iron is cast in the anode because pure nickel is not corroded rapidly enough under most conditions to furnish the necessary metal to the bath. Iron is a cheap material and has a solution tension enough greater than nickel to make it effective for the end in view. The greater solution tension of cobalt in the plating baths, as compared with nickel, renders practicable the use of a lesser amount of iron, or of no iron at all. Very pure cobalt anodes were readily dissolved in the solution under the conditions of many of our best plating tests. The freedom of the cobalt anode from iron no doubt has much to do with the diminished corrosion of the cobalt plate as compared with the nickel plates.

ROLLED *vs.* CAST ANODES—Cast anodes of both nickel and cobalt go into solution much more readily than the rolled anodes. With a number of each in a nickel or cobalt bath, the proportion between the two may be so chosen that the composition of the electrolyte remains constant as the anodes go into solution. If too large a proportion of cast anodes is used, the anodes dissolve with too great readiness and the bath may become alkaline. Conversely, if too large a proportion of rolled anodes is used, the solution of the anodes may not take place with sufficient readiness, and the bath may become acid and depleted in metal. The greater solubility of cobalt anodes in a number of the plating baths described in this paper, as compared with nickel anodes in the corresponding nickel bath, renders the use of a larger proportion of rolled anodes possible in the case of cobalt than is customary at present with nickel in the nickel plating trade. The greater solubilty of the cobalt anode is distinctly in its favor for practical plating purposes.

CATHODES—The cathodes for these experiments were of brass, iron or steel, and were usually $3\frac{1}{2}$ in. $\times$ 2 in. $\times$ $\frac{1}{4}$ in. in size. One side was given a high polish with emery and buffing wheels, and the other was covered with a thin coat of asphaltum varnish.

It is of the utmost importance in all plating work that the cathode be absolutely smooth and thoroughly cleansed from particles of dust, grease, etc. This was accomplished by the following procedure: Brass, steel or other stock, as required, was first machined down to the required size, after which it was smoothed down with an emery wheel and finished with an appropriate buffing wheel to a mirror surface. This left the surface with a certain amount of grease and adherent buffing material, which was removed by scrubbing with "Kalye" caustic solution. After thorough rinsing with water the electrode was immersed in dilute hydrochloric acid, or in dilute potassium cyanide solution and again thoroughly rinsed with water. It was then ready for use in the bath.

In addition to smooth plane cathodes, a number of them were prepared by cutting patterns and depressions on one side. These were used in the same manner as the smooth ones after cleansing and buffing as described.

## PREPARATION OF SALTS

The ammonium sulfate, ammonium chloride, boric acid, citric acid, potassium citrate, tannic acid, sodium sulfite, sodium phosphate, ammonium tartrate, and magnesium sulfate used for these experiments were Merck's chemically pure, purchased from a supply house, as were the reagents used in the preparation of the cobalt salts.

All cobalt compounds used for these experiments were prepared at this laboratory, and the method of preparation of each is given as follows:

COBALT SULFATE was prepared by dissolving $Co_3O_4$ in HCl and adding an equivalent of $H_2SO_4$. The solution was then evaporated to drive off HCl and crystallize $CoSO_4.7H_2O$. The crystals were collected in the usual manner and heated in the presence of $H_2SO_4$ until $SO_3$ fumes disappeared and the salt became dehydrated. Or the collected crystals were recrystallized in the usual manner where dehydrated salt was not desired.

COBALT-AMMONIUM SULFATE was prepared by mixing hot solutions of cobalt sulfate and ammonium sulfate containing molecular proportions of each of the salts. As the cobalt ammonium sulfate is less soluble than either of the single salts,

most of the crystallization was effected in the hot mixed solution. The crystals were collected and washed with alcohol.

COBALT CHLORIDE was prepared by dissolving $Co_3O_4$ in HCl, and after filtering off the excess $CO_3O_4$, crystallizing the salt and collecting and washing the crystals in the usual manner.

COBALT ETHYLSULFATE—Ethyl alcohol and concentrated, sulfuric acid were heated together to form ethyl sulfuric acid. This was then neutralized with calcium carbonate and the calcium ethyl sulfate crystallized by evaporation of the solution after filtering off precipitated calcium sulfate. The crystals were re-dissolved and the calcium precipitated as calcium sulfate by adding sulfuric acid in molecular proportion, reforming ethyl sulfuric acid. Freshly precipitated cobalt hydroxide was added to this acid until it failed to dissolve any more. The cobalt-ethyl sulfate was crystallized by evaporation. The crystals were collected and washed in the usual manner.

### SOLUBILITIES OF COBALT AND NICKEL SALTS

The relative solubilities of cobalt sulfate and nickel sulfate, and of cobalt-ammonium sulfate and nickel-ammonium sulfate are important in considering the greater conductivities of the cobalt solutions as compared with the corresponding ones of nickel. These solubilities are considered later when discussing the greater speed of cobalt plating, and as well in considering the saturation concentration of some of the baths employed, so that a brief table of solubilities at room temperature is given herewith.

| Grams of salts dissolved by one liter of water | ° C. | Comey(*a*) | Kraut(*b*) | This Lab. |
|---|---|---|---|---|
| $CoSO_4$... ... ..... anhydrous | 23 | 362 | 380 | 362.2 |
| $NiSO_4$..... anhydrous | 23 | 405 | 379 | 363 |
| $Co(NH_4)_2(SO_4)_2$..... anhydrous | 23 | 171 | 171 | 164 |
| $Ni(NH_4)_2(SO_4)_2$..... anhydrous | 23 | 66 | 66 | 72.8 |

(*a*) A. M. Comey, "A Dictionary of Chemical Solubilities," MacMillan and Co., **1896.**
(*b*) Gmelin, Kraut's "Handbuch der anorganischen Chemie," **1909,** Vol. V, Sect. 1.

The salts actually used in making up the solutions were $CoSO_4.7H_2O$, $NiSO_4.7H_2O$, $CoSO_4.(NH_4)_2SO_4.6H_2O$ and $NiSO_4.(NH_4)_2SO_4.6H_2O$.

From the above table it is apparent that the solubilities of cobalt and nickel sulfates are not very different. These, however, do not lend themselves to satisfactory plating solutions without adding various other compounds to them. On the other hand, cobalt-ammonium sulfate is approximately 2.5 times as soluble as nickel-ammonium sulfate. As will be shown in the sequel, from the experiments performed, the saturated solution of this cobalt-ammonium sulfate offers an extremely rapid and satisfactory plating bath.

### CURRENT DENSITIES

Unless specifically stated to the contrary, the current densities given in the tables to follow and throughout the text are cathode current densities; that is, they were computed by dividing the total current by the cathode area.

An approximate notion of the anode current density may be obtained from the following statement, although it is impossible to compute it with any degree of accuracy: At the beginning of each experiment, the anode was smooth and of approximately the same area as the cathode (see above), but as the experiment proceeded, the anode gradually increased in effective area, due to unequal corrosion of its surface. At the end of some of our experiments the anode area may have been more than twice that of the cathode.

In our conclusions and through the text of this paper we speak of allowable current densities with the various solutions, and we recommend certain ranges of current density which are permissible for the best plates. In every case these are cathode current densities, but are, of course, only valid with a sufficient anode area. We have conducted our experiments under conditions which might be called good standard practice for plating shops, which means, so far as anode area is concerned, that the anode area was in every case greater than, and in many cases, twice that of the cathode area.

### EFFICIENCY TESTS

Efficiency tests were made in the usual manner by carefully weighing the quantity of metal deposited in a measured time and comparing it with the theoretical amount of metal which should have been deposited in accordance with Faraday's laws. The data for these tests for each important solution are given in Table VI, page 392.

### AGING TESTS

With all the plating baths which were found to be satisfactory or promising, both aging and efficiency tests were run. The aging tests were for the purpose of ascertaining the constancy of the bath during continued use for plating over a considerably longer period than was necessary for our experiments. The solution was analyzed for cobalt content and tested for acidity and alkalinity at intervals of 15 hours during plating runs of 100 or more hours duration. This was in addition to the series of runs already made with the given bath, operating with it to produce the plates studied. The results of these aging tests are given in Table VII, page 392.

## LABORATORY EXPERIMENTS—ELECTRODEPOSITION OF COBALT

### SERIES I—COBALT-AMMONIUM SULFATE SOLUTIONS

Langbein recommends for the nickel bath of the type *IA*, with an electrode distance of 10 cm., an electromotive force of 3 volts; he states that this will give a current density of 0.3 ampere per square decimeter.[1]

We wished to compare the cobalt solution *IA* with the corresponding nickel solution as regards their relative specific electrical conductivities or with regard to the electromotive force necessary to give a specific current density through each, other conditions being the same. An experiment was tried using solution *IA*, with which was compared the following nickel-ammonium sulfate solution:

| Nickel sulfate, $NiSO_4$ | Ammonium sulfate, $(NH_4)_2SO_4$ | Water |
|---|---|---|
| 30.9 grams | 26.3 grams | 1000 cc. |

Using the proper current to obtain a current density of 0.3 amp. per sq. dm., with the cobalt solution *IA*, it was found that the potential difference between the electrodes was 0.88 volt. With the identical electrodes and with the same distance between them, namely 10 cm., using the nickel solution, the potential difference between the electrodes was 2.1 volts. Thus we have the very great difference between 0.88 volt and 2.1 volts required to give the same current density with these two solutions, other conditions being equal, which means that the cobalt solution is of very much lower specific electrical resistance than the nickel solution.

[1] Langbein, "Electro-Deposition of Metals," 6th Edition Revised, p. 252.

Thus, in the first series of experiments with cobalt-ammonium sulfate and nickel-ammonium sulfate, we found a result which ran uniformly throughout our plating experiments, *viz.*, that the conductivity of the cobalt bath was considerably higher than that of the corresponding nickel bath.

The last 90 hours plating with Solution I*A* were with a current density of 0.60 amp. per sq. dm. It was, therefore, clear that this solution was not changing rapidly, and that the anode was dissolving satisfactorily. The slight increase in concentration was accounted for by evaporation. Very similar results were obtained with iron and steel cathodes in place of the brass ones.

Bath I*A* was not thought sufficiently important to warrant a similar series of experiments being made with the corresponding nickel bath for comparison.

The last 90 hours plating with Solution I*B* were performed at a current density of 3.0 to 3.5 amp. per sq. dm. The cathode area was 34.0 sq. cm. This solution was neutral to litmus paper, but very slightly alkaline as shown by titration with $N/10$ HCl and litmus indicator. The solution remained absolutely constant and the cobalt anode dissolved satisfactorily.

A number of the plates from Solution I*B* were given a very severe bending test to study their adhesive qualities. In every case the plates stuck to the cathode after being bent backwards and forwards at an angle of nearly 180°, in a manner equal to, if not better than, that of the best nickel plates with which we are familiar, subject to a similar test. Even after the surface of the metal base had started to break, the cobalt plate still continued to cover the furrows and ridges formed.

The data of the plating experiments for Solution I*B* show this solution to be remarkable for the extremely high-current densities, at which satisfactory plates may be obtained. We find no record of nickel plating being accomplished, except under special conditions, such as with rotating cathodes, at anything like the same speed.

It is fairly well recognized that any improvement in the chemical composition of solutions for nickel plating, in order that a faster rate of deposition may be brought about, would have to be based upon a higher concentration of the nickel ion in the solution. The inventors of "Prometheus," "Persels" and other salts for concentrated nickel solutions, no doubt had this in mind. These new baths are of comparatively recent invention, and there is considerable diversity of opinion as to their merits.

The practical plater knows that he can carry in his plating bath 12 oz. of double nickel salt per gallon of water in the summer, and about 9 oz. of the same salt per gallon in the winter, without danger of frequent crystallization. Taking the higher of these figures, we have a bath equivalent to about 80 grams $(NH_4)SO_4.NiSO_4.6H_2O$ per liter. This solution contains approximately 1.5 per cent metallic nickel. On the other hand, using the Prometheus salts as bought on the market, as much as 2 lbs. may be dissolved to the gallon of water without danger of crystallization in the summer. Since this Prometheus salt contains about 28 per cent of $NiSO_4$, this bath will contain approximately 2.6 per cent of metallic nickel in solution. This tremendously increased metal content of the latter bath accounts for the greater speed at which plating is possible with it.

Comparing the cobalt solution I*B* with this, we note that it contains 200 grams of $CoSO_4.(NH_4)_2SO_4.6H_2O$ to the liter, so that its concentration in metallic cobalt is approximately 3.0 per cent. We would, therefore, expect this solution to be a very rapid plating one, faster than the other, as we find it, but the figures do not account for the great difference between the solutions. It has the advantage of being free from magnesium sulfate, boric acid and the like, which are very considerable and necessary constituents of all the concentrated fast plating nickel solutions. Moreover, we find with all solutions of this type that the cobalt bath is a much more rapid plating one than the nickel bath, taking them at the same concentration. Experiments conducted under conditions of present plating practice demonstrated that Solution I*B* was capable of plating cobalt satisfactorily at several times the speed that the Prometheus salt was capable of plating nickel (see Series I). This comparison was for the best condition for each that was known to the practical plater in charge of the plating establishment in question, and to us as a result of these experiments.

CONCLUSIONS: 1—Cobalt plates from these cobalt-ammonium sulfate solutions, on brass and iron, are firm, adherent, hard and uniform, and may be readily buffed to a satisfactorily finished surface. They take a very high polish, with a beautiful luster, which although brilliantly white, possesses a slightly bluish cast.

2—The specific electrical conductivity of these cobalt-ammonium sulfate solutions is very much higher than that of the corresponding nickel solutions.

3—All of these cobalt plates within the current density ranges described as satisfactory, are as smooth, adhesive and generally satisfactory as the best nickel plates.

4—Solution I*A* does not lend itself to extremely fast plating like I*B*, but satisfactory plates may be obtained with it at current densities up to 0.80 amp. per sq. dm.

5—Solution I*A* may be used at higher current densities than the corresponding nickel solution, for which Langbein recommends a current density of 0.30 amp. per sq. dm.

6—Solution I*A* does not change appreciably in cobalt content or in acidity when used over long periods of time at the recommended current densities.

7—Solution I*B*, which is a nearly saturated solution of $CoSO_4.(NH_4)_2SO_4$, containing 200 grams of $CoSO_4.(NH_4)_2SO_4.6H_2O$ to the liter of water, yields satisfactory cobalt deposits at all current densities up to 4 amp. per sq. dm., *i. e.*, 37.2 amp. per sq. ft. This very rapid plating was performed in a manner similar to that of common plating practice.

8—There is no nickel bath operating in the manner of the usual commercial plating procedure at anything like as high a current density as cobalt bath I*B*. More specifically, the allowable current density with which an adherent, firm, smooth, white, hard plate may be obtained with Solution I*B*, without sign of pitting or peeling, and yet which may be readily and satisfactorily finished, is four times that for which the same results may be obtained with the fastest commercial nickel solutions.

9—Both baths I*A* and I*B* may be used for plating on the usual surface, including brass, iron and steel. No preliminary coating of copper is necessary when plating with these baths on iron and steel.

10—Solutions I*A* and I*B* may both be used with a large proportion of rolled anodes without becoming acid or depleted in metal.

11—Solution I*B* does not change appreciably in cobalt content or in acidity when used over long periods of time at the high recommended current density.

12—The current efficiency of Solution I*B* is extremely high at a current density of 1 ampere per sq. dm. The mean of our measurements, which agree very well among themselves, gave a value of 98.0 per cent. The current efficiency of Solution I*B* is as high at 3 amp. per sq. dm. as is common for the best nickel solutions that are used in nickel plating practice at very much lower current densities. The average of three current efficiency measurements with Solution I*B*, at 3 amp. per sq. dm., which measurements agreed very well among themselves, was 90.5 per cent.

13—Solution I*C* is intermediate in concentration between I*A* and I*B* and its properties, as regards speed and quality of the plates to be obtained therefrom, are correspondingly inter-

mediate. It is not nearly so rapid or as satisfactory at high current densities as I*B*.

14—Solution I*B* should be run neutral, for these plates are adherent, firm, smooth, white, hard, yet easily buffed to an excellent finish. When operated slightly alkaline it yields plates which are grayish in color, which peel, pit, and show blisters. When operated acid it yields plates that, while fairly adherent, firm and smooth, are dark and freakish.

15—Solution I*B* requires very little, if any, aging to put it in condition, but yields satisfactory plates almost from the start.

16—The "throwing" power of Solution I*B* is remarkably satisfactory.

17—The anodes in Solution I*B* are remarkably free from the coating that characterizes nickel anodes.

Solution I*B* showed so many superior qualities that it seemed highly worth while to develop it further, and particularly to study it under exact commercial conditions. This work is reported later under "Commercial Tests," page 394.

### SERIES II—COBALT-AMMONIUM SULFATE SOLUTIONS WITH AN EXCESS OF AMMONIUM SULFATE

Series II was prepared with the view of increasing the conductivity of Solution I by adding a relatively larger amount of ammonium sulfate.

Solution II does not give good results above 0.90 amp. per sq. dm.

With an unboiled solution, very dark, unsatisfactory plates were obtained at current densities between 0.30 and 0.62 amp. per sq. dm.

This solution was not thought of sufficient importance to warrant making a series of tests with rolled anodes, or aging and efficiency tests.

CONCLUSIONS: 1—Cobalt plates from this cobalt sulfate and ammonium sulfate solution, with an excess of ammonium sulfate, on brass and iron, are firm, adherent, hard and uniform, and may be readily buffed to a satisfactorily finished surface, within the narrow range recommended for them. They take a very high polish, with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

2—The specific electrical conductivity of Solution II is considerably higher than that of the corresponding nickel solution.

3—Solution II is not a fast-plating solution, and can be used only at current densities up to about 0.90 amp. per sq. dm. This bath is not nearly so rapid nor so satisfactory as others described.

4—Solution II is an analog of one proposed by Langbein for nickeling, of which he says that the nickel deposit piles up, especially in the lower portion of the object; that is, the lower part of the cathode becomes dull, burned or over-nickeled. This takes place with the nickel solution at current densities about 0.35 amp. per sq. dm., and consequently the cobalt solution is a very great improvement, as regards speed, on the corresponding nickel solution.

5—Solution II requires to be boiled at the outset to yield satisfactory plates. Otherwise the plates are dark, even at low current densities.

6—Solution II, after operating a number of hours, tends to become acid. This acid may be neutralized with ammonia, and the solution re-acidified with boric acid, to yield satisfactory plates. However, on this account and for others mentioned, this solution is not nearly as satisfactory as some others described, since it is not self-sustaining.

### SERIES III—COBALT-AMMONIUM SULFATE WITH AN EXCESS OF AMMONIUM SULFATE AND CITRIC ACID

A bath which was formerly in extended use for nickel plating is prepared by boiling 34.5 grams nickel sulfate, with 50.3 grams ammonium sulfate and adding 4.2 grams citric acid to the liter of water. Analogous to this, Solution III*A* was made up, when it was found to be not very satisfactory; 1.7 grams sodium sulfite were added to the liter, making Solution III*B*. No reagent was added during the experiments with the solutions of Series III, either to neutralize them or for any other purpose.

Solution III*A* was not thought to be of sufficient importance to warrant running a series of experiments with rolled anodes.

The last 90 hours plating with Solution III*B* was at a current density of 1.0 amp. per sq. dm. The cathode area was 34.0 sq. cm. The cobalt content and alkalinity of this solution were remaining approximately constant.

For comparison with Solutions III*A* and *B*, a set of runs on the corresponding nickel bath, Solution III*C*, was made.

Solution III*D* resembled III*A*, but was considerably less concentrated in cobalt and ammonium sulfates.

Solution III*D*, after being used for plating approximately 35 hours, became somewhat alkaline. In comparison, Solution III*C*, the corresponding nickel bath, was tested after running with the same current for an identical time. It was found to be practically in the same condition as regards alkalinity as at the start. Cast anodes were used in both of these baths throughout these runs, which were made partly for the purpose of testing the relative solubility of the anodes. This result confirmed a conclusion to be generally drawn from all our experiments, that in baths of this type the cast cobalt anodes are more soluble than the cast nickel anodes.

Solution III*E* is more than twice as saturated in cobalt sulfate as III*A*, and more than three times as saturated in cobalt sulfate as III*D*. The last 45 hours of plating with Solution III*E* was at a current density of 3.0 amp. per sq. dm. The 45 hours preceding this was at a current density of 4.75 amp. per sq. dm. This solution was gradually becoming more alkaline and its cobalt content increasing. The solution was obviously changing too rapidly to be satisfactory, but with an increased number of rolled anodes replacing cast ones, it might be used.

CONCLUSIONS: 1—Cobalt plates from the solutions of Series III on brass and iron, are firm, adherent, hard and uniform and may readily be buffed to a satisfactory finish, within the current density range recommended. They take a very high polish, with a beautiful luster, which, although brilliantly white, posseses a slightly bluish cast.

2—Solutions III*A*, *B* and *D* do not lend themselves to extremely fast plating, but satisfactory plates may be obtained from them at current densities up to 0.80, 1.0 and 0.80 amp. per sq. dm., respectively.

3—Solution III*B* maintained itself substantially constant as regards cobalt content and alkalinity during 114 hours of plating. Its current efficiency is satisfactorily high.

4—Solution III*E*, which is very much more concentrated in cobalt than the other solutions of this series, yields satisfactory plates at all current densities up to 1.5 amp. per sq. dm.

5—Solution III*E*, when used with cast anodes, gradually becomes more concentrated in metallic cobalt content, and increasingly alkaline. For this reason this solution can be used only with care, and is probably not satisfactory for general commercial plating purposes.

6—The current efficiency of Solution III*E* is extraordinarily high as compared with that of the usual commercial nickel plating solutions.

7—The current efficiencies of all the solutions of Series III are high and well over 90 per cent at the recommended current densities.

8—A number of experiments with Solution III*C* and Solution III*E* were run simultaneously, with the same current density, electrode distance and electrode area. The E. M. F. across the nickel bath was from 2 to 2.5 times as great as that across

TABLE I—EXPERIMENTAL DATA OBTAINED WITH SOLUTIONS OF SERIES I AND II

SOLUTION *IA*

Co and $NH_4$ in molecular proportions

$CoSO_4$ $NH_4{}_2SO_4$ Water Bath
30 g. 26.5 g. 1000 cc. 5 liters

Somewhat more than 1/3 saturated
Analogous to nickel plating solution recommended by Dr. Langbein

SOLUTION *IB*

Co and $NH_4$ in molecular proportions

$CoSO_4 \cdot NH_4{}_2SO_4 \cdot 6H_2O$ Water
200 g. [= 145 g. $CoSO_4$ $NH_4{}_2SO_4$] 1000 cc.

Solution nearly saturated
No additions to maintain neutrality
Sp. gr. at 15° C. = 1.053

SOLUTION *IC*

Co and $NH_4$ in molecular proportions

$CoSO_4$ $(NH_4)_2SO_4$ Water Bath
40.0 g. 34.0 g. 1000 cc. 5 liters

Intermediate in concentration between *IA* and *IB*

SOLUTION II

Co and $NH_4$ not in molecular proportions

$CoSO_4$ $(NH_4)_2SO_4$ Water
16.7 g. 56.7 g. 1000 cc.

Not nearly saturated with $Co(NH_4)_2(SO_4)_2$
Neutralized with $NH_4OH$, if too acid
Boiled in preparation and prior to using

| Sol. No. | Date 1914 | Cur. Dens. Amp. per sq. dm. | E. M. F. Volts | Electr. dist. Cm. | Cathode area Sq. cm. | Plating time Hr. | Min | Character of Deposit |
|---|---|---|---|---|---|---|---|---|
| *IA*—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 6/ 8 | 0.30 | 2.45 | 46 | 27.3 | 2 | 30 | Fairly bright, hard, pitted at bottom. |
| | 8 | 0.30 | 2.75 | 45 | 27.3 | 1 | 0 | Light gray, somewhat pitted at bottom. |
| | 22 | 0.30 | 0.75 | 10 | 27.3 | 2 | 0 | Bright and smooth, not lustrous. |
| | 25 | 0.45 | 0.83 | 10 | 27.3 | 4 | 0 | Heavy metallic, lustrous, slightly spotted. |
| | 27 | 0.50 | 0.80 | 10 | 27.3 | 3 | 0 | Metallic, lustrous, streaked and spotted. |
| | 24 | 0.60 | 1.06 | 10 | 27.3 | 2 | 0 | Metallic, uniform, not lustrous. |
| | 25 | 0.80 | 1.27 | 10 | 27.3 | 3 | 0 | Uniform, metallic, lustrous. |
| | 27 | 0.90 | 2.03 | 20 | 27.3 | 1 | 30 | Bright, smooth, bottom rough but not burned |
| | 26 | 1.0 | 1.52 | 10 | 27.3 | 1 | 30 | Uniform; lower corners burned, dull color. |
| | 30 | 1.0 | 2.25 | 20 | 27.3 | 1 | 30 | Uniform, extremely bright, thoroughly satisfactory surface when polished |
| Solution boiled | | | | | | | | |
| | 7/ 3 | 1.0 | 2.48 | 20 | 27.3 | 2 | 30 | Uniform, bright; edges slightly burned. |
| | 23 | 1.25 | 2.00 | 10 | 27.3 | 1 | 15 | Dark; badly burned at edges, bright in center. |
| | 23 | 1.50 | 2.10 | 10 | 27.3 | 1 | 15 | Burning more marked than preceding. |
| ROLLED ANODES—BRASS CATHODES | | | | | | | | |
| | 16 | 0.80 | 2.0 | 10 | 37.0 | 1 | 0 | Exceptionally good; white, uniform. |
| | 17 | 1.0 | 2.0 | 17 | 37.0 | 1 | 0 | Slightly burned at upper edges. |
| | 17 | 1.0 | 2.75 | 17 | 37.1 | 1 | 0 | Clean, smooth, bright; peeled upon heating in boiling water for a few minutes. |
| ROLLED ANODES—ZINC CATHODES | | | | | | | | |
| | 17 | 0.50 | 0.83 | 10 | 30.1 | 1 | 0 | Very rough surface, unlike anything obtained on brass or steel. Under microscope metal appeared to be deposited in small irregular masses and not to be polished. |
| *IB*—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 7/17 | 0.75 | 1.0 | 17 | 37.1 | 1 | 30 | Bright, uniform, glossy; little buffing gave satisfactory surface. |
| | 17 | 1.0 | 1.5 | 19 | 37.1 | 1 | 30 | |
| | 21 | 1.0 | 1.5 | 24 | 23.7(*a*) | 1 | 0 | Good, smooth, bright plate over entire surface. |
| | 8/ 3 | 1.0 | 1.70 | 19 | 23.7 | 2 | 0 | Very satisfactory; hard, bright, easily buffed. |
| | 7/18 | 1.2 | 1.95 | 19 | 37.1 | 2 | 0 | Bright, uniform, glossy; little buffing gave satisfactory surface. |
| | 22 | 1.2 | 1.7 | 24 | 23.7(*a*) | 1 | 0 | Beautiful smooth plate over entire surface. High and low spots evenly coated. |
| | 22 | 1.5 | 2.05 | 24 | 23.7(*a*) | 2 | 0 | Very smooth and bright, beautiful finish after slight buffing. Uniform thickness on high and low spots. Plate 0.062 mm. thick. |
| | 30 | 1.5 | 1.20 | 10 | Polished steel knife | 1 | 30 | Bright, smooth, even, hard, satisfactory. |
| | 8/ 5 | 1.5 | 2.1 | 16 | 37.1 | 1 | 30 | Beautiful, bright, smooth; easily buffed to mirror surface. |
| | 7/22 | 1.7 | 2.4 | 24 | 23.7(*a*) | 1 | 15 | Very smooth and bright. Beautiful finish after slight buffing. Uniform thickness on high and low spots. |
| | 23 | 1.8 | 2.55 | 24 | 23.7(*a*) | 2 | 45 | |
| | 24 | 2.0 | 2.85 | 24 | 28.0(*a*) | 2 | 15 | Beautiful, white, hard, lustrous; no sign of burning or scaling. |
| | 28 | 2.2 | 3.35 | 24 | 27.3(*a*) | 1 | 30 | |
| | 28 | 2.5 | 3.75 | 24 | 25.0 | 2 | 45 | |
| | 28 | 2.7 | 2.25 | 23 | 22.2 | 1 | 15 | Very smooth, even, hard; white, beautiful, satisfactory finish after slight buffing. No signs of burning. |
| | 31 | 3.5 | 3.0 | 22 | 20.0(*a*) | 1 | 30 | |
| | 31 | 4.0 | 2.9 | 20 | 18.7(*a*) | 1 | 0 | |
| | 8/ 3 | 4.5 | 4.9 | 20 | 27.5 | 1 | 30 | Fairly uniform and bright, darkened at edges. Began to peel at one corner. |
| | 3 | 4.5 | 3.0 | 10 | 27.5 | 1 | 30 | Similar to last, burning slightly marked, but no peeling. |
| | 3 | 4.5 | 2.95 | 10 | 27.5 | 1 | 0 | Similar to previous, burning not quite so marked. Buffed satisfactorily; slightly pitted, due to gas bubbles. |
| ROLLED ANODES—BRASS CATHODES | | | | | | | | |
| | 9/ 1 | 0.39 | 0.44 | 10 | 26.2 | 2 | 0 | Smooth, uniform, white; readily buffed to mirror surface. |
| | 8/31 | 0.61 | 0.55 | 10 | 26.7 | 2 | 0 | |
| | 5 | 1.0 | 1.6 | 16 | 37.0 | 24 | 0 | Very bright and metallic; split at one place; easily removed from cathode. Plate 0.34 mm. thick at edge, 0.24 mm. at center. |
| | 9/ 2 | 1.0 | 0.77 | 10 | 37.0 | 1 | 0 | Smooth, uniform, white; readily buffed to mirror surface. |
| | 8/ 4 | 1.5 | 2.2 | 16 | 37 | 16 | 0 | Beautiful, bright, smooth; began to separate from cathode at one corner. |
| | 9/14 | 2.0 | 1.30 | 10 | 26.5 | 0 | 45 | Very even, smooth; good luster when polished. |
| | 15 | 3.0 | 1.32 | 10 | 20.0 | 0 | 20 | White; good luster when polished; somewhat rough on bottom, showing heavier deposit there; also small furrows from gas streaks. |
| | 14 | 4.0 | 1.35 | 10 | 11.7 | 0 | 15 | Splendid white deposit; cracked a short distance in one place. |
| | 15 | 4.0 | 1.35 | 10 | 11.7 | 0 | 25 | Good, white; rough on bottom, showing heavier deposit there; also very small furrows from gas streaks. |
| | 8/ 4 | 4.25 | 4.25 | 20 | 27 | 1 | 15 | Burned, but not so badly as 4.5 amperes current density. |
| | 4 | 4.5 | 4.60 | 18 | 27 | 1 | 0 | Burned along edges. |
| *IC*—The electromotive force across the electrodes was progressively increased so that a series of plates was obtained at current densities from 0.30 to 1.25 amp. per sq. dm. in the manner shown in the data for Solutions *IA* and *IB*. (See descriptive text.) | | | | | | | | |
| *II*—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 9/18 | 0.31 | 0.91 | 10 | 39.4 | 1 | 15 | Good, white, even, smooth; required almost no buffing to give fine luster. |
| | 18 | 0.56 | 1.18 | 10 | 33.6 | 1 | 15 | |
| | 18 | 0.60 | 1.25 | 10 | 33.6 | 0 | 45 | Good, white, uniform; fine luster when polished. |
| | 18 | 0.75 | 1.35 | 10 | 38.7 | 0 | 45 | |
| | 24 | 0.90 | 1.27 | 10 | 38.7 | 4 | 0 | Bright, evenly deposited; not lustrous. |
| | 25 | 1.0 | 1.30 | 10 | 38.7 | 3 | 0 | Smooth and bright; somewhat spotted. |
| | 27 | 1.0 | 1.55 | 10 | 38.7 | 3 | 0 | Dark; bright with buffing. |
| This run immediately followed one at current density 1.4. After the former the solution was found rather too acid and was neutralized with ammonia and slightly acidified with boric acid | | | | | | | | |
| | 29 | 1.0 | 2.10 | 20 | 38.7 | 2 | 0 | Dark; polished brightly. |
| | 6/29 | 1.0 | 2.10 | 20 | 27.3 | 2 | 0 | Dark; buffed to satisfactory brilliant surface. |
| | 7/ 2 | 1.0 | 1.4 | 10 | 27.3 | 2 | 0 | Badly burned over entire surface. |
| | 3 | 1.0 | 1.95 | 20 | 27.3 | 2 | 0 | Very black with rough, grainy surface. Burned at sides and at bottom. |
| | 13 | 1.0 | 2.05 | 15 | 39.4 | 2 | 0 | Very poor; black and polished with difficulty. |
| | 14 | 1.0 | 2.05 | 15 | | 1 | 50 | Very unsatisfactory; black and grainy. |
| Bath stirred by bubbling air through it | | | | | | | | |
| | 15 | 1.0 | 1.42 | 15 | | 1 | 30 | Not hard, burned on sides; generally unsatisfactory. |
| | 6/26 | 1.4 | 1.95 | 10 | 27.3 | 3 | 0 | Dark and badly burned. |

(*a*) When cobalt plate was dissolved off in nitric acid, grooves lost their plate first, showing thinner deposit there than on higher places.

the cobalt bath. This is evidence, as noted throughout these experiments, of the greater conductivity of the cobalt solutions.

9—Solution *IIIC* is very concentrated in nickel salt, and is more satisfactory than the corresponding cobalt solution of the same concentration. However, the corresponding cobalt solution is not nearly saturated. The comparison with an equally saturated similar cobalt solution, *IIIE*, is in favor of the cobalt solution, for it will operate at higher current densities than *IIIC*, and yields a plate which is just as satisfactory in appearance and harder.

10—These solutions operated alike plating on iron, steel and brass, for which metals only the above conclusions apply.

11—Cobalt anodes are more readily soluble than nickel anodes in the solutions of Series III, and consequently a larger

TABLE II—EXPERIMENTAL DATA OBTAINED WITH SOLUTIONS OF SERIES III AND IV

| G. per l. water | SOL. III*A* | III*B* | III*D* | III*E* | III*C* | SOLUTION IV*A* | | | | | SOLUTION IV*B* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Grams per liter water | | | | Total | Grams per liter water | | | | Total |
| $CoSO_4$ | 34.5 | 34.5 | 25.7 | 78.5 | 34.5 g. $NiSO_4$ | $CoSO_4$ | $(NH_4)_2SO_4$ | $NH_4Cl$ | bath | | $CoSO_4$ | $(NH_4)_2SO_4$ | $NH_4Cl$ | Boric acid | bath |
| $(NH_4)_2SO_4$ | 50.3 | 50.3 | 31.5 | 129.7 | 50.3 | 23.5 | 20.0 | 30.0 | 2.5 | 1. | 23.5 | 20.0 | 18.2 | 9.5 | 2.5 1. |
| Citric acid | 4.2 | 4.2 | 4.5 | 13.7 | 4.2 | No additions to solution | | | | | Slightly acid to litmus. $NH_4OH$ added, then boric acid to slight acidity | | | | |
| Addition | None | 1.7 g. $Na_2SO_3$ | None | None | None | Sp. gr. = 1.043 or 6.0° Bé | | | | | | | | | |
| Total bath (l.) | 1.0 | 3.0 | .... | .... | 3.0 | | | | | | | | | | |

| Sol. No. | Date 1914 | Cur. Dens. Amp. per sq. dm. | E. M. F. Volts | Electr. dist. Cm. | Cathode area Sq. cm. | Plating time Hr. | Min. | Character of Deposit |
|---|---|---|---|---|---|---|---|---|
| **III*A*—CAST ANODES—BRASS CATHODES** | | | | | | | | |
| | 6/10 | 0.20 | 1.5 | 10 | 27.3 | 1 | 30 | Uniform, very dark; susceptible to bright polish with buffing. |
| | 25 | 0.50 | 1.25 | 10 | 27.3 | 3 | 0 | Black, but smooth. |
| | 29 | 0.50 | 1.39 | 20 | 27.3 | 1 | 0 | Slightly dark; buffed to beautiful bright, clean surface. |
| | 30 | 0.80 | 2.13 | 20 | 27.3 | 1 | 30 | Scaly, peeling easily; not satisfactory. |
| | 25 | 1.0 | 2.35 | 10 | 27.3 | 1 | 30 | Uniformly black and unsatisfactory. |
| **III*B*—CAST ANODES—STEEL AND BRASS CATHODES** | | | | | | | | |
| | 7/20 | 0.30 | 1.06 | 10 | Steel, 60.0 | 1 | 15 | Satisfactory and adherent. |
| | 10 | 0.30 | 0.65 | 15 | Brass, 27.3 | 2 | 0 | Very smooth, hard; buffed to bright, silvery white finish. |
| | 20 | 0.40 | 1.0 | 10 | Steel, 60.0 | 1 | 15 | Satisfactory smooth, adherent. |
| | 27 | 0.40 | 1.0 | 10 | Brass, 31.5 | 2 | 30 | Smooth, uniform; slightly dark in color; peeled at edges after removal from bath. |
| | 6/30 | 0.50 | 1.25 | 20 | 27.3 | 1 | 30 | Bright, hard, good color after polishing. No signs of pitting. |
| | 7/ 3 | 0.50 | 0.86 | .. | 27.3 | 1 | 30 | Extremely bright, smooth; free from all flaws; buffed to beautiful surface. |
| | 8/ 3 | 0.80 | 0.96 | 10 | 39.3 | 2 | 0 | Very white, uniform; satisfactory except for slight scaling on one side. |
| | 7/11 | 0.80 | 1.35 | 15 | 27.3 | 1 | 30 | Very smooth, even; buffed to satisfactory surface. |
| | 13 | 1.0 | 1.65 | 15 | 27.3 | 1 | 30 | Scaled off; unsatisfactory. |
| | 2 | 1.0 | 2.07 | 20 | 27.3 | 3 | 0 | Clean, hard, uniform; buffed to beautiful surface. |
| | 6/26 | 1.36 | 1.86 | 10 | 31.5 | 3 | 0 | Smooth, uniform; dark in color. |
| | 26 | 1.7 | 2.1 | 10 | 24 | 1 | 30 | Unsatisfactory; split. |
| ROLLED ANODES—BRASS CATHODES | | | | | | | | |
| | 17 | 1.0 | 2.5 | 15 | 37 | 1 | 0 | Clean, smooth; black. |
| **III*C*—CAST ANODES—BRASS CATHODES** | | | | | | | | |
| | 7/16 | 0.30 | 1.25 | 10 | Steel, 39.3 | 1 | 30 | Scaled easily. |
| | 13 | 0.34 | 1.28 | 10 | Brass, 39.3 | 1 | 30 | White and uniform. |
| | 31 | 0.50 | 1.45 | 10 | 39.4 | 2 | 0 | Satisfactory except for pitting; easily polished.(*a*) |
| | 22 | 0.50 | 1.45 | 10 | 39.3 | 1 | 30 | Brilliant white; buffed satisfactorily. Decidedly softer than one from Co Bath III*E* same |
| | 22 | 0.50 | 1.45 | 10 | 39.3 | 1 | 30 | date, which was run and buffed simultaneously. |
| | 23 | 0.90 | 2.35 | 10 | 46.6 | 1 | 0 | Bright metallic, lustrous. Readily buffed to satisfactory mirror. Whiter and softer than Co plate Solution III*E*, run simultaneously. |
| | 14 | 1.0 | 2.15 | 10 | 39.3 | 1 | 30 | Bright, pitted. |
| | 14 | 1.0 | 2.6 | 10 | 39.3 | 1 | 30 | Bright, pitted on surface; beautiful surface after buffing. |
| | 14 | 1.0 | 2.6 | 10 | 37.1 | 1 | 30 | Satisfactory except for few small pits. |
| | 24 | 1.0 | 2.36 | 10 | 39.3 | 1 | 30 | Darkness on edges; buffed satisfactorily. |
| | 24 | 1.0 | 2.36 | 10 | 39.3 | 1 | 30 | White; difficult to polish to satisfactory mirror surface; slightly pitted. |
| | 25 | 1.07 | 2.56 | 10 | 39.3 | 1 | 30 | Scaled slightly at lower edge. |
| | 28 | 1.25 | 2.60 | 10 | 39.4 | 1 | 45 | Dull color; buffed to satisfactory mirror surface with difficulty. |
| | 29 | 1.50 | 2.75 | 10 | 27.3 | 2 | 0 | Dull and burned. |
| | 14 | 1.5 | 2.75 | 10 | 27.3 | 1 | 30 | Bright with pits and scaling at bottom. |
| ROLLED ANODES—BRASS CATHODES | | | | | | | | |
| | 31 | 0.50 | 2.85 | 10 | 39.3 | 2 | 0 | Very satisfactory; white; readily polished to mirror surface. |
| | 31 | 0.80 | 3.30 | 10 | 39.3 | 2 | 0 | |
| **III*D*—CAST ANODES—BRASS CATHODES** | | | | | | | | |
| | 7/14 | 0.30 | 1.06 | 15 | 37 | 3 | 0 | Black; buffed satisfactorily, except for small pin holes. |
| | 7 | 0.50 | 1.36 | 15 | 37 | 3 | 0 | Dark; buffed satisfactorily. |
| | 7 | 0.50 | 1.33 | 15 | 37 | 3 | 0 | |
| | 7 | 0.70 | 1.80 | 15 | 37 | 3 | 0 | Bright but slightly rough. |
| | 11 | 0.90 | 1.89 | 15 | 37 | 3 | 0 | Dull and pitted. Current density too great. |
| | 11 | 0.90 | 1.90 | 15 | 37(*b*) | 3 | 0 | |
| | 17 | 1.0 | .... | 15 | 37 | 1 | 0 | Clean, smooth; dark. |
| | 7 | 1.0 | 2.02 | 15 | 37 | 3 | 0 | Very dull; current density too high. |
| | 7 | 1.0 | 2.0 | 15 | 37 | 3 | 0 | Dull and pitted. Current density too great. |
| | 13 | 1.0 | 2.0 | 15 | 37(*b*) | 3 | 0 | |
| **III*E*—BRASS CATHODES** | | | | | | | | |
| | 7/21 | 0.50 | 0.76 | 10 | 39.3 | 2 | 0 | Very bright uniform. |
| | 22 | 0.50 | .... | 10 | 39.3 | 2 | 0 | Bright, satisfactory.(*c*) |
| | 28 | 0.62 | 0.87 | 10 | Steel, 20 | 3 | 0 | Dark gray; metallic luster; very little buffing produced mirror surface. Satisfactory in all respects. |
| | 22 | 0.70 | 0.90 | 10 | Brass, 39.3 | 2 | 0 | Plate bright and satisfactory.(*d*) |
| | 21 | 0.80 | 0.82 | 10 | 39.3 | 2 | 0 | Very smooth; somewhat dark; polished to brilliant mirror surface.(*e*) |
| | 23 | 0.80 | 0.97 | 10 | 39.3 | 2 | 0 | |
| | 23 | 0.90 | 1.0 | 10 | 46.6 | 1 | 0 | Satisfactory, readily buffed to mirror surface.(*f*) |
| | 21 | 1.0 | 1.03 | 10 | 39.3 | 2 | 0 | Very smooth, somewhat dark; polished to brilliant mirror surface. |
| | 24 | 1.0 | 1.05 | 10 | 39.3 | 2 | 0 | Scaled off when put in boiling water. |
| | 24 | 1.0 | 1.05 | 10 | 39.3 | 2 | 0 | Dark though lustrous with no sign of scaling. |
| This plate was darker than corresponding Ni plate as removed from the bath. See III*C*, July 24th, 1.0 amp., although the Ni plate required more polishing to produce a mirror surface. | | | | | | | | |
| | 25 | 1.07 | 1.19 | 10 | 39.3 | 2 | 0 | Rather dark; showed signs of burning. |
| | 28 | 1.25 | 1.31 | 10 | 39.3 | 1 | 45 | Dark gray. Very little buffing produced mirror surface. |
| | 29 | 1.5 | 1.35 | 10 | 27.3 | 2 | 0 | Somewhat dark, readily buffed to perfect mirror surface. |
| Co plate considerably harder than corresponding Ni plate when both were ground. | | | | | | | | |
| | 31 | Bath becoming alkaline, which was neutralized by small addition of citric acid. | | | | | | |
| **IV*A*—CAST ANODES—BRASS CATHODES** | | | | | | | | |
| | 9/21 | 0.50 | 0.85 | 10 | 34.6 | 2 | 0 | Good, smooth, uniform; little buffing produced mirror surface. |
| | 6/11 | 0.55 | 0.65 | 10 | 27.3 | 3 | 0 | |
| | 9/21 | 0.75 | 0.94 | 10 | 25.8 | 1 | 0 | Good, white; uniform and velvety. Readily buffed to mirror surface. |
| | 6/26 | 1.0 | 1.1 | 10 | 24.0 | 1 | 30 | |
| | 9/21 | 1.0 | 1.45 | 10 | 35.5 | 1 | 0 | Uniform, but gray. Good finish when polished; somewhat gas-pitted. |
| | 6/25 | 1.1 | 1.2 | 10 | 24.0 | 2 | 45 | Good, smooth, uniform; velvety, took brilliant silvery polish. |
| | 14 | 1.1 | 1.15 | 10 | 27.5 | 2 | 0 | Good, smooth, uniform over entire surface; velvety. |
| This run was to determine nature of deposit at twice the current density recommended for similar Ni bath. | | | | | | | | |
| | 25 | 1.65 | 1.75 | 10 | 31.5 | 1 | 30 | Even, uniform, slightly dark in center; buffed to very satisfactory surface. |
| | 26 | 1.9 | 1.92 | 10 | 31.5 | 3 | 0 | Not satisfactory, somewhat burned on edges. |
| **IV*B*—CAST ANODES—IRON CATHODES** | | | | | | | | |
| | 8/ 4 | 0.50 | 0.90 | 10 | 45.4 | 0 | 40 | Gray, very smooth and bright; readily buffed to satisfactory mirror surface. |
| CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 6/12 | 0.55 | 0.75 | 10 | 23.3 | 3 | 0 | Hard and uniform; much whiter than solution IV*A*. |
| | 9/21 | 1.0 | 1.77 | 10 | 36.0 | 1 | 0 | Good, uniform, white. Satisfactory finish with little buffing. |
| | 6/12 | 1.10 | ..... | 10 | 27.3 | 3 | 0 | Hard and uniform, much whiter than IV*A*. |
| | 9/22 | 1.25 | 1.67 | 10 | 28.1 | 1 | 0 | Good; slightly dark at edges. No burning at this current density. |
| | 6/14 | 1.5 | 2.5 | 12 | 30.0 | 1 | 0 | Bright at first; blackened along edges, showing signs of burning. |
| | 9/22 | 1.5 | 2.27 | 10 | 34.8 | 0 | 30 | Very dark and badly burned at edges. |
| | 6/27 | 1.6 | 2.22 | 20 | 31.5 | 2 | 30 | Smooth, not uniform. Brighter nearer bottom than top. |
| | 6/26 | 1.65 | 1.86 | 10 | 24.0 | 2 | 0 | Smooth, uniform; somewhat whiter than plate Series IV*A*, June 26th, N. $D._{100} = 1$. Somewhat dark at edges. |
| | 7/29 | 1.70 | 2.15 | 10 | 27.3 | 1 | 30 | Unsatisfactory, grainy and burned. Gas at cathode. |

(*a*) It is difficult to get a plate free from hydrogen pits from this bath except at very low current densities.

(*b*) In polishing this plate the extreme hardness of the Co deposit as compared with Ni was particularly noticeable. The same result was noticed to marked extent throughout these plating experiments.

(*c*) Considerably harder than Ni plate run at same time, see III*C*, July 22nd, 0.50 amp.

(*d*) Considerably harder than Ni plate run at same time, see III*C*, July 22nd, 0.70 amp.

(*e*) Same, see III*C*, July 23rd, 0.80 amp.

(*f*) Not as white when removed from bath as Ni plate run simultaneously, see III*C*, July 23rd, 0.90 amp. Co plate much harder than corresponding Ni plate.

proportion of rolled cobalt anodes may be used than is the case with nickel.

SERIES IV—COBALT-AMMONIUM SULFATE, AMMONIUM CHLORIDE SOLUTIONS

The baths of Series IV were prepared in a manner similar to that described under Series I.

It is stated in the literature[1] that baths containing chlorides or nitrates are not suitable for nickeling over iron. They are, however, well adapted to the rapid light nickeling of cheap brass articles. Bath IV is the cobalt analogue of one sometimes used in nickeling practice for work of this lighter kind.

CONCLUSIONS: 1—Solution IV*A* yields satisfactory cobalt plates on brass and iron at all current densities up to about 1.5 amp. per sq. dm.

2—The plates of Series IV*A* buffed to a brilliant surface, similar to that described under 3 below.

3—Solution IV*B* gave satisfactory plates at all current densities up to 1.25 amp. per sq. dm. on brass and iron which are firm, adherent, hard and uniform, and may be readily buffed to a satisfactorily finished surface. They take a very high polish, with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

4—Solutions IV*A* and *B* are moderately rapid plating baths, but not nearly as rapid as Solutions I*B* and XIII*B*.

5—Solution IV*B* is considerably more rapid than the corresponding nickel bath, the latter working best at a current density of about 0.55 amp. per sq. dm.[2]

6—These solutions operated alike plating on iron, steel and brass, for which metals only the above conclusions apply.

7—The cobalt content and the neutrality of Solution IV*B* do not change appreciably with prolonged usage.

8—The current efficiency of Solution IV*B* is satisfactorily high, the average value of three measurements, agreeing well among themselves, being 92.6 per cent.

9—Solution IV*B*, with boric acid, yields somewhat whiter plates than IV*A*, but IV*A* may be operated at a somewhat higher current density.

SERIES V—COBALT CHLORIDE, AMMONIUM CHLORIDE SOLUTIONS

A bath was prepared analogous to the nickel-ammonium chloride bath which has been largely favored for nickeling over zinc. This solution is also used for dark nickeling.

CONCLUSIONS: 1—Solution V was not found to be satisfactory for obtaining a bright characteristic cobalt plate at any current density up to 1.0 amp. per sq. dm., either with rolled or cast anodes, plating on brass and iron. This refers to plating in the normal manner and without agitation of the solution. This solution could be used on brass and iron if dark cobalting were required.

2—Rolled anodes are required for a satisfactory deposit with the nickel analogue of this solution. They improve the deposit in the case of cobalt, but it is by no means satisfactory, either in speed or quality of deposition, as compared with other solutions, such as I*B* and XIII*B*.

3—Solution V may be used satisfactorily to cobalt on zinc, provided there is a sufficient mechanical agitation to remove hydrogen bubbles from the surface of the cathode. With this provision the cobalt plates are firm, adherent, hard and uniform, and of a polished appearance as removed from the solution.

SERIES VI—COBALT-AMMONIUM SULFATE, BORIC ACID SOLUTIONS

Solution VI*A* is analogous to a solution recommended by Weston for nickel baths. It has, however, never found extended usage in commercial plating for the reason that the nickel solution, after working faultlessly for a comparatively short time, begins to fail, yielding a blackened deposit.

Solution VI*B* is the nickel solution corresponding to the cobalt solution VI*A*. After Solution VI*A* was found to be unsatisfactory, its metal content was increased by further addition of cobalt sulfate. This solution was called VI*C*. In addition a much more concentrated solution of the same series, VI*D*, was prepared and studied.

CONCLUSIONS: 1—Solution VI*A* does not yield a satisfactory plate at any current density, plating with cast anodes, up to 1.0 amp. per sq. dm. The plates are dark and spotted and hydrogen is evolved. At current densities in the neighborhood of one amp. per sq. dm. or higher, the plates are badly burned and pitted. With rolled anodes there is a slight improvement at moderate current densities, that is, in the neighborhood of 0.50 amp. per sq. dm.

2—Solution VI*B*, which is the nickel analogue of VI*A*, gave very bright, clean, satisfactory plates at current densities up to 0.50 amp. per sq. dm. At current densities greater than this the plates are burned.

3—This nickel solution, VI*B*, is not nearly so fast as some of the cobalt solutions elsewhere described in this paper.

4—Solution VI*C*, which is a more concentrated solution of the type of VI*A*, operated satisfactorily at a higher current density than VI*A*, that is, up to 1.0 amp. per sq. dm. This conforms to the general conclusion throughout this work that the more concentrated cobalt solutions, which are likewise those from which plates may be obtained with the greatest speed, are the most satisfactory for practical plating purposes.

5—Solution VI*D* is not to be compared in speed with I*B*, from which it differs only by the addition of the boric acid. Solution VI*D* yields a satisfactory white cobalt plate at all current densities up to 1.25 amp. per sq. dm.

6—The current efficiencies with all solutions of Series VI are high and satisfactory, the average being better than 90 per cent.

7—These solutions operate alike plating on iron, steel and brass, for which metals only the above conclusions apply.

8—The cobalt plates from Series VI, wherever they are pronounced satisfactory, are firm, adherent, hard and uniform, and may be readily buffed to a satisfactorily finished surface. They take a very high polish, with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

SERIES VII—COBALT-AMMONIUM SULFATE, COBALT CARBONATE, BORIC ACID SOLUTIONS

This solution was prepared by boiling cobalt-ammonium sulfate crystals and cobalt carbonate in water until the evolution of $CO_2$ gas ceased, and until the solution was no longer acid to blue litmus. After settling, any undissolved cobalt carbonate was removed by filtration or decantation, and the boric acid added. After further boiling for a short time, the solution was allowed to cool and was ready for plating purposes. If the solution is too acid it may be neutralized with ammonia.

Solution VII can be used with rolled anodes, or rolled anodes with a small proportion of cast ones. The proportion of cast to rolled anodes used in this bath can be established by frequent testing of the acidity of the bath. For this purpose the following should be noted: Blue litmus paper should always be reddened, indicating the presence of boric acid; congo paper should not be turned blue, for if it does, it indicates the presence of free sulfuric acid in the bath. Red litmus paper should remain red for if it turns blue the bath has become alkaline and further addition of boric acid is required.

After plates from Solution VII*A* were found to be unsatisfactory, yielding dark deposits at current densities in the neighborhood of 1 amp. per sq. dm., sodium sulfite was added to the

[1] Langbein, "Electro Deposition of Metals," 6th Edition Revised, p. 254.

[2] *Ibid.*, p. 253.

TABLE III -EXPERIMENTAL DATA OBTAINED WITH SOLUTIONS OF SERIES V, VI AND VII

SOLUTION V

| Grams per liter water | | Total |
|---|---|---|
| $CoCl_2$ | $NH_4Cl$ | bath |
| 54.8 | 54.8 | 2.5 l. |

Dissolved in lukewarm water $NH_4OH$ added to neutrality or very slight acidity. No additions afterwards.

| G. per l. Water SOL. VI.A | | VIC VI*D* (*IB* + Boric Acid) | | VI*B* |
|---|---|---|---|---|
| $CoSO_4$ | 14.8 | $Co(NH_4)_2(SO_4)_2.6H_2O$ | 14.8 g. $NiSO_4$ | |
| $(NH_4)_2SO_4$ | 12.6 | 200.0 | 12.6 | |
| Boric acid | 18.8 | 37.2 | 18.8 | |
| Total bath (l.) | 2.5 | All boric acid dissolved by continued agitation | 2.5 | |
| Additions | None | Perfectly clear after standing several days | None | |

| SOLUTION | VII*A* | VII*B* |
|---|---|---|
| | G. per l. | water |
| $Co(NH_4)_2(SO_4)_2.6H_2O$ | 63.5 | 63.5 |
| $CoCO_3$ | 5.3 | 5.3 |
| Boric acid | 31.7 | 31.7 |
| $Na_2SO_3$ | None | 1.4 |
| Total bath (l.) | 3.5 | 3.5 |
| Additions | None | None |

| Sol. No. | Date 1914 | Cur. Dens. Amp. per sq. dm. | E. M. F. Volts | Electr. dist. Cm. | Cathode area Sq. cm. | Plating time Hr. | Min. | Character of Deposit |
|---|---|---|---|---|---|---|---|---|
| V—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 6/17 | 0.30 | 0.96 | 10 | 27.3 | 2 | 20 | Dark gray. |
| | 27 | 0.30 | 0.66 | 10 | 27.3 | 2 | 30 | Dark, even; buffed satisfactorily. |
| | 18 | 0.37 | 0.55 | 10 | 27.3 | 3 | 20 | Dull gray, spotted and rough. |
| | 18 | 0.37 | 0.55 | 10 | 27.3 | 3 | 20 | |
| | 20 | 0.50 | 0.75 | 10 | 27.3 | 3 | 20 | Dark and spotted. |
| | 22 | 0.50 | 0.69 | 10 | 27.3 | 2 | 30 | Heavy black; buffed satisfactorily. |
| | 29 | 0.90 | 1.76 | 20 | 27.3 | 2 | 0 | Very dark, slightly pitted; buffed satisfactorily. |
| | 7/15 | 1.0 | 1.15 | 11 | 37 | 1 | 0 | Somewhat dull; buffed satisfactorily. |
| | ROLLED ANODES | | | | | | | |
| | 8/3 | 0.50 | 0.70 | 10 | Iron, 45.4 | 1 | 15 | Very smooth, bright, dark gray; readily buffed to mirror |
| | 7/17 | 0.8 | 1.0 | 15 | Brass, 27.3 | 1 | 0 | Smooth, bright, slightly pitted at bottom. |
| | 17 | 1.0 | 1.1 | 16.5 | 27.3 | 1 | 0 | Smooth, uniform, dark. Bright after buffing. |
| | 8/5 | 1.0 | 0.95 | 10 | Iron, 41.2 | 2 | 20 | Smooth, dull gray, somewhat pitted; no sign of burning. Polished readily to mirror |
| | CAST ANODES PLATING ON ZINC CATHODES | | | | | | | |
| | Mechanical agitation. Solution stirred mechanically to keep off hydrogen bubbles. | | | | | | | |
| | 9/25 | 0.50 | 0.75 | 10 | Cast, 26.6 | 1 | 30 | Bright, almost as if buffed when removed from solution. |
| | 24 | 0.50 | 0.76 | 10 | 26.6 | 1 | 15 | Good white, uniform. Readily buffed to mirror. |
| | 21 | 0.75 | 1.06 | 10 | 26.6 | 1 | 0 | No agitation; poor plate, crystalline. |
| | 25 | 0.75 | 0.85 | 10 | 26.6 | 1 | 15 | Smooth, uniform, looked almost as if buffed when removed from solution. |
| | 28 | 0.75 | 1.0 | 10 | Sheet, 28.8 | 1 | 0 | Very smooth on portion of cathode where agitation removed hydrogen bubbles; rough on part away from agitation where hydrogen clung. |
| | 23 | 1.0 | 0.95 | 10 | Cast, 26.6 | 1 | 0 | Kept free of gas bubbles by rubbing for 10 min. Plate satisfactory and smooth. At end of hour without further brushing off of bubbles, plate rough and crystalline. |
| | 24 | 1.0 | 0.95 | 10 | 26.6 | 1 | 0 | Solution stirred mechanically to keep off H bubbles, but in spite of this, at this current density, gas pits appeared at top and bottom. |
| | 24 | 1.0 | 0.95 | 10 | 26.6 | 1 | 0 | |
| | 22 | 2.0 | 1.48 | 10 | 26.6 | 0 | 30 | Decidedly crystalline; very poor. Gas formed and adhered to cathode. |
| VI*A*—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 6/13 | 0.30 | 0.96 | 10 | 27.3 | 2 | 20 | Lustrous, but dark; not very smooth. |
| | 15 | 0.60 | 1.70 | 10 | 27.3 | 2 | 20 | Lustrous, but spotted; hydrogen gas given off freely. |
| | 27 | 0.63 | 1.25 | 10 | 31.5 | 2 | 30 | Smooth, fairly lustrous, but dark. Split on edges. |
| | 30 | 0.90 | 3.5 | 20 | 27.3 | 2 | 0 | Unsatisfactory, pitted and burned. |
| | 30 | 1.0 | 3.27 | 20 | 27.3 | 2 | 0 | Badly burned and unsatisfactory. Current density too great. |
| | 15 | 1.0 | 3.6 | 15 | 24.0 | 1 | 30 | Badly burned at edges. |
| | ROLLED ANODES—BRASS CATHODES | | | | | | | |
| | 7/16 | 0.5 | 2.0 | 15 | 37.3 | 1 | 30 | Bright, smooth, uniform plate. |
| | 16 | 0.8 | 2.3 | 13 | 37.3 | 2 | 0 | Unsatisfactory, burned along edges, peeled. |
| | 16 | 0.8 | 2.5 | 15 | 27.1 | 1 | 0 | |
| VI*C*—CAST ANODES —BRASS CATHODES | | | | | | | | |
| | 7/20 | 0.50 | 0.94 | 10 | 27.3 | 2 | 0 | Very smooth, bright, satisfactory; required very little buffing to finish. |
| | 23 | 0.70 | 1.12 | 10 | 27.3 | 2 | 0 | Dull metallic color; buffed satisfactorily. Showed few pits near bottom. |
| | 8/4 | 1.0 | 1.95 | 10 | 39.3 | 1 | 30 | Gray, but readily buffed to satisfactory finish. |
| | 5 | 1.5 | 2.15 | 10 | 27.3 | 2 | 0 | Dull and burned in places. |
| VI*D* BRASS CATHODES | | | | | | | | |
| | 9/25 | 0.51 | 1.0 | 10 | 35.5 | 1 | 0 | Good, even, uniform, gray; good luster when buffed. |
| | 25 | 0.75 | 1.35 | 10 | 34.1 | 1 | 30 | Smooth, uniform; good luster when polished. |
| | 26 | 1.0 | 2.85 | 10 | 34.3 | 1 | 0 | |
| | 10/1 | 1.0 | 1.25 | 10 | 34.3 | 1 | 0 | Good, smooth, uniform, gray; good luster when polished. |
| | 1 | 1.25 | 1.4 | 10 | 32.6 | 1 | 0 | |
| | 1 | 1.25 | 1.38 | 10 | 34.6 | 1 | 0 | |
| | 9/28 | 1.5 | 1.35 | 10 | 35.3 | 1 | 0 | Uniform, dull white; tendency to split at bottom and edges. |
| | 28 | 1.5 | 1.92 | 10 | 37.5 | 1 | 30 | Uniform, smooth, gray; tendency to peel at edges. |
| | 29 | 1.5 | 1.87 | 10 | 33.8 | 1 | 0 | Uniform, light gray; split at edges. |
| | 10/2 | 1.5 | 1.74 | 10 | 33.8 | 1 | 0 | Uniform, rough, gray and porous; impossible to buff. |
| | 2 | 1.75 | 2.11 | 10 | 17.8 | 0 | 30 | Uniform, gray; badly gas-pitted. |
| VI*B*—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 7/15 | 0.30 | 1.55 | 10 | 27.3 | 2 | 0 | Very white, even; so glossy when removed from solution almost no buffing required. |
| | 15 | 0.50 | 2.0 | 10 | 27.3 | 2 | 0 | Very bright, even, with no trace of burning. |
| | 29 | 0.60 | 2.27 | 10 | 39.3 | 1 | 30 | Bright in center but signs of burning at edges. |
| | 29 | 0.80 | 2.36 | 10 | 39.3 | 1 | 30 | Bright in center but burned at edges and corners. |
| | 28 | 1.0 | 3.01 | 10 | 39.3 | 1 | 30 | Very dark and grainy. Marked burning over entire surface, especially at edges. |
| VII*A*—CAST ANODES -BRASS CATHODES | | | | | | | | |
| | 7/3 | 0.35 | | 20 | 27.3 | 2 | 0 | Bright, even, without flaw; buffed satisfactorily. |
| | 3 | 0.50 | 1.50 | 20 | 27.3 | 2 | 0 | Very bright, smooth plate without flaws; buffed brightly. |
| | 9 | 0.50 | 1.55 | 20 | 39.3 | 2 | 30 | Surface granular; unsatisfactory. |
| | 10 | 0.50 | 1.53 | 20 | 39.3 | 2 | 30 | Rough and unsatisfactory; did not polish readily. |
| | 4 | 0.70 | 2.7 | 20 | 27.3 | 2 | 0 | Smooth, flawless, white but not lustrous. Buffed satisfactorily. |
| | 6 | 1.0 | 2.5 | 10 | 27.3 | 2 | 0 | Burned at sides and bottom, unsatisfactory. Current density too great. |
| | 7 | 1.0 | 2.7 | 15 | 27.3 | 2 | 0 | Burned at edges, unsatisfactory. Current density too great. |
| | 7 | 1.0* | 3.30 | 15 | 39.3 | 2 | 30 | Heavy but dull and granular. Burned. |
| | 9 | 1.0 | 3.25 | 15 | 39.3 | 2 | 30 | Burned and unsatisfactory. |
| | 11 | 1.0 | 4.15 | 15 | 27.3 | 2 | 0 | Scaly and unsatisfactory. |
| | Solution rapidly becoming more alkaline with use. | | | | | | | |
| VII*B*—CAST ANODE —BRASS CATHODE | | | | | | | | |
| | 7/11 | 1.0 | 2.05 | 15 | 27.3 | 2 | 0 | White, even, somewhat burned at edges. |
| | Solution rapidly becoming more alkaline. | | | | | | | |
| | ROLLED ANODES -BRASS CATHODES | | | | | | | |
| | 17 | 0.50 | 1.21 | 10 | 27.3 | 2 | 0 | Even and satisfactory. |
| | 17 | 0.50 | 1.15 | 10 | 27.3 | 2 | 0 | Satisfactory, bright, requiring little buffing |
| | 17 | 0.80 | 1.95 | 10 | 27.3 | 2 | 0 | Satisfactory and bright. |
| | 18 | 0.90 | 2.20 | 10 | 27.3 | 2 | 0 | Black, burned. |

bath to see if the deposit would be brighter. This latter solution is Bath VII*B*.

CONCLUSIONS: 1—Solution VII*A* gives bright, satisfactory plates, at low current densities in the neighborhood of 0.35 amp. per sq. dm., as is true of the corresponding nickel solution.

2—Solution VII*A* does not lend itself for rapid plating; at current densities over 0.80 amp. per sq. dm., the plates are burned.

3—The addition of sodium sulfite to Solution VII*A*, as in Solution VII*B*, does not materially increase the current density at which satisfactory bright plates may be obtained. These solutions are not to be compared for rapid plating with some of the others described and styled satisfactory, as I*B* and XIII*B*.

4—The solutions of Series VII become alkaline so rapidly with cast anodes that rolled anodes should preferably be used with them. In general, cobalt solutions improved by addition of sodium sulfite are not sufficiently constant with prolonged use to have the self-supporting characteristic required by most plating establishments.

TABLE IV—EXPERIMENTAL DATA OBTAINED WITH SOLUTIONS OF SERIES VIII, IX, X, XI AND XII

| G. per l. water | SOL. VIIIA | VIIIB | SOLUTION | Grams per liter | | Total bath |
|---|---|---|---|---|---|---|
| $CoSO_4$ | 26.3 | 40.5 | IX | 7.58 | 66.1 | 3.5 l. |
| $NH_4Cl$ | 17.6 | 17.6 | | | | |
| Potassium citrate | 17.6 | 17.6 | X $CoSO_4$ | $NH_4SO_4$ | $MgSO_4$ | |
| Total bath (l.) | 2.5 | 1.0 | | 22.6 | 33.8 | 2.5 l. |

| SOLUTION | Grams per liter water | | Tannic acid | Total bath |
|---|---|---|---|---|
| XI | $CoSO_4$ 25.0 | $NH_4$ tartrate 41.7 | 0.28 | 3.5 l. |
| XII | $CoSO_4$ 82.7 | Tartaric acid 27.8 | KOH 6.8 | 3.5 l. |

| Sol. No. | Date 1914 | Cur. Dens. Amp. per sq. dm. | E. M. F. Volts | Electr. dist. Cm. | Cathode area Sq. cm. | Plating time Hr. | Min | CHARACTER OF DEPOSIT |
|---|---|---|---|---|---|---|---|---|
| VIIIA—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 10/1 | 0.30 | 0.67 | 10 | 34.8 | 2 | 0 | Good, uniform, bluish white, buffed readily to mirror. |
| | 1 | 0.50 | 0.97 | 10 | 33.1 | 2 | 0 | |
| | 6/30 | 0.50 | 1.95 | 20 | 27.3 | 3 | 0 | Beautiful bright, hard, smooth, after polishing. |
| | 7/15 | 0.50 | 1.15 | 13 | 37.1 | 1 | 30 | Dark, buffed satisfactorily. |
| | 10/ 2 | 0.95 | 1.50 | 10 | 40.8 | 1 | 30 | Smooth, uniform, gray, readily buffed to mirror. |
| | 2 | 1.0 | 1.36 | 10 | 34.1 | 1 | 0 | Smooth, uniform, gray, buffed satisfactorily. |
| | 15 | 1.5 | 2.4 | 10 | 35.3 | 1 | 0 | Uniform, gray, showing burning |
| | 15 | 1.75 | 2.0 | 10 | 30.6 | 0 | 45 | |
| VIIIB—CAST ZINC CATHODE | | | | | | | | |
| | 9/22 | 0.26 | 0.95 | 10 | 26.6 | 2 | 0 | Crystalline in most parts, with small patches of smooth plate. |
| BRASS CATHODES | | | | | | | | |
| | 10 2 | 0.50 | 1.07 | 10 | 39.6 | 2 | 0 | Uniform, smooth, gray, readily buffed to mirror. |
| | 9/22 | 1.0 | 1.97 | 10 | 34.7 | 1 | 0 | Good, smooth, uniform, somewhat dark, taking a good polish when buffed |
| | 10/ 1 | 1.0 | 1.4 | 10 | 34.7 | 1 | 0 | |
| | 1 | 1.25 | 1.75 | 10 | 33.4 | 1 | 0 | Uniform, smooth, white, buffing to mirror. |
| | 9/23 | 1.5 | 2.67 | 10 | 35.0 | | 30 | Good, smooth, uniform, dark gray, taking a good polish. Slightly burned at edges |
| | 10/ 1 | 1.5 | 2.15 | 10 | 34.8 | 1 | 0 | Uniform, smooth, white, slightly pitted at top and burned at edges. Not readily buffed |
| | 2 | 1.75 | 2.35 | 10 | 34.8 | 1 | 0 | Smooth, uniform, gray, slightly burned on edges and difficult to buff. |
| CAST ZINC CATHODES | | | | | | | | |
| | 5 | 0.20 | 0.80 | 10 | 26.6 | 3 | 0 | Smooth, uniform, metallic, dark gray. Buffed readily to mirror. |
| Mechanical agitation of solution near cathode. | | | | | | | | |
| | 10 | 0.50 | 1.03 | 10 | 26.6 | 2 | 0 | |
| | 6 | 0.75 | 0.95 | 10 | 25.6 | 3 | 0 | Very rough, scaly, unsatisfactory. |
| | 9/21 | 1.0 | 1.4 | 10 | 26.6 | 1 | 0 | No agitation Poor, very decidedly crystalline. |
| IX—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 7/ 3 | 0.50 | 3.30 | 10 | 27.3 | 1 | 30 | Coated with precipitate which easily washed off. Satisfactory and readily buffed. |
| | 9/29 | 0.50 | 3.03 | 10 | 33.4 | 2 | 0 | Dark streaked. Gelatinous cobalt compound precipitate on surface of cathode. |
| | 30 | 0.75 | 3.68 | 10 | 34.1 | 2 | 0 | Dark, lustrous, streaked. Gelatinous precipitate as in last. |
| | 7/ 4 | 0.80 | 3.65 | 10 | 27.3 | 2 | 0 | Bright, satisfactory except for few black spots, which buffed off easily. |
| | 6 | 1.0 | 4.80 | 10 | 27.3 | 1 | 30 | Smooth, even, covered with bluish precipitate. Satisfactorily buffed. |
| | 7 | 1.0 | 5.0 | 20 | 27.3 | 1 | 45 | Black, streaked and unsatisfactory. |
| | 9/30 | 1.0* | 4.35 | 10 | 40.0 | 1 | 30 | Dark, streaked and unsatisfactory. Gelatinous precipitate on cathode. |
| X—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 7/29 | 0.30 | 0.70 | 10 | 39.3 | 1 | 30 | White, metallic, easily buffed to mirror. |
| | 9/29 | 0.30 | 0.75 | 10 | 36.6 | 2 | 0 | |
| | 30 | 0.40 | 0.87 | 10 | 32.2 | 2 | 0 | Good, white, uniform; readily buffed to mirror. |
| | 30 | 0.50 | 1.03 | 10 | 35.2 | 1 | 30 | |
| | 7/ 6 | 0.50 | 1.54 | 15 | 48.1 | 2 | 0 | Bright, evenly coated, except few streaks in metal portion. Readily buffed to satisfactory mirror. |
| | 16 | 0.50 | 1.1 | 14 | 37.1 | 1 | 30 | Bright, uniform, over entire surface. Readily buffed to satisfactory mirror. |
| | 29 | 0.50 | 1.15 | 10 | 46.6 | 2 | 0 | White, metallic and easily buffed to mirror. |
| | 9/30 | 0.60 | 1.17 | 10 | 34.3 | 1 | 30 | Bright, uniform, over entire surface. Readily buffed to satisfactory mirror. |
| | 7/ 7 | 0.70 | 1.70 | 15 | 48.1 | 2 | 0 | Bright, evenly coated, except few streaks in middle portion. Readily buffed to satisfactory mirror. |
| | 9/30 | 0.70 | 1.34 | 10 | 34.8 | 1 | 30 | Good, uniform, white, requiring little buffing. |
| | 7/ 7 | 0.70 | 1.30 | 15 | 48.1 | 1 | 30 | Satisfactory, white, smooth and even. Readily buffed to satisfactory mirror |
| | 15 | 0.90 | 2.25 | 15 | 37.1 | 1 | 0 | Bright and smooth at center, somewhat burned at edges. |
| | 7 | 1.0 | 2.25 | 15 | 48.1 | 1 | 30 | Bright, rough and uneven on lower portion, no burning apparent. |
| | 7 | 1.0 | 2.05 | 15 | 39.3 | 15 | 0 | Very thick, rough, dark, full of small holes, but adherent. |
| | 9 | 1.0 | 2.10 | 15 | 39.3 | 3 | 0 | Pitted and somewhat burned. |
| ROLLED ANODES—BRASS CATHODES | | | | | | | | |
| | 16 | 0.5 | 1.0 | 14 | 37.1 | 2 | 0 | Bright, smooth, uniform, over entire surface. |
| | 16 | 0.8 | 1.05 | 15 | 37.1 | 1 | 0 | Bright, smooth, over entire surface. |
| | 17 | 1.0 | 2.25 | 17 | 37.1 | 1 | 0 | Fairly smooth and bright, not very uniform in appearance, some parts darker than others. |
| | 17 | 1.0 | 2.15 | 17 | 37.1 | 1 | 0 | Very smooth, bright and uniform. |
| XI—BRASS CATHODE | | | | | | | | |
| | 7/ 7 | 0.30 | 1.5 | 25 | 41.2 | 1 | 30 | Dark, absolutely unsatisfactory. |
| Solution XI continually precipitated a cobalt compound both when in use and upon standing idle. It gave the same unsatisfactory deposit as in the run shown above, at the several current densities tried. | | | | | | | | |
| XII—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 7/ 6 | 0.30 | 1.17 | 20 | 37.1 | 2 | 0 | White, uniform and velvety. Readily buffed to mirror |
| | 10/ 1 | 0.30 | 1.25 | 10 | 39.5 | 2 | 0 | |
| | 9/29 | 0.39 | 1.25 | 10 | 33.6 | 2 | 0 | Smooth, uniform, dark; buffed to satisfactory mirror. |
| | 30 | 0.50 | 1.45 | 10 | 34.6 | 2 | 0 | |
| | 10/ 1 | 0.50 | 1.40 | 10 | 34.8 | 2 | 0 | Uniform, smooth, gray; buffed to satisfactory finish. |
| | 2 | 0.50 | 1.53 | 10 | 41.2 | 2 | 0 | |
| | 9/30 | 0.75 | 2.03 | 10 | 39.1 | 1 | 30 | Uniform, smooth, gray; buffed satisfactorily. |
| | 7/13 | 1.0 | 3.6 | 15 | 37.0 | 1 | 30 | |
| | 10/ 2 | 1.0 | 2.18 | 10 | 32.6 | 1 | 0 | |
| | 2 | 1.25 | 2.55 | 10 | 32.9 | 1 | 30 | Very even, smooth, and satisfactory. |
| | 3 | 1.50 | 2.86 | 10 | 30.9 | 0 | 45 | |
| | 15 | 1.50 | 3.5 | 10 | 34.6 | 1 | 0 | |
| | 15 | 1.96 | 4.25 | 10 | 30.7 | 0 | 30 | |
| | 12 | 3.87 | 6.0 | 10 | 34.0 | 0 | 15 | |
| | 12 | 4.0 | 3.95 | 10 | 14.2 | 0 | 30 | |
| | 15 | 5.0 | | 10 | 13.0 | 0 | 20 | Good, smooth, white, nearly polished as removed from solution. |
| | 16 | 6.0 | | 10 | 13.0 | 0 | 15 | |
| | 16 | 7.0 | 6.0 | 10 | 9.9 | 0 | 10 | |
| | 17 | 8.0 | 4.9 | 10 | 10.1 | 0 | 8 | |
| | 17 | 10.0 | 6.0 | 10 | 10.6 | 0 | 7 | |
| | 17 | 12.0 | 5.5 | 10 | 11.5 | 0 | 5 | Burned at edges. |
| | 17 | 15.6 | 5.8 | 10 | 9.3 | 0 | 8 | Badly burned at edges—splitting. |
| ROLLED ANODES—BRASS CATHODES | | | | | | | | |
| | 7/16 | 1.0 | 3.0 | 14 | 37.0 | 1 | 30 | Smooth and uniform, but dark. Solution from which this plate was taken had been operated for 48 hours |

5—The solutions of Series VII operated alike plating on iron, steel and brass, for which metals only the above conclusions apply.

6—The cobalt plates from Series VII, wherever they are pronounced satisfactory, are firm, adherent, hard and uniform, and may be readily buffed to a satisfactory finished surface. They take a very high polish, with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

SERIES VIII—COBALT SULFATE, POTASSIUM CITRATE, AMMONIUM CHLORIDE SOLUTIONS

This bath is analogous to one recommended by Langbein,[1] C. H. Proctor,[2] and W. Pfanhauser,[3] and which is reported to be particularly satisfactory for plating on copper and zinc.

[1] Langbein "Electro-Deposition of Metals" 6th Edition Revised

[2] *Metal Industry*, **1911**, p. 353

[3] W. Pfanhauser, "Elektroplattiring," **1900**.

TABLE V—EXPERIMENTAL DATA OBTAINED WITH SOLUTIONS OF SERIES XIII, XIV, XV AND XVI

| G. per l. water | Sol. XIII*A* | XIII*B* | XIII*C* |
|---|---|---|---|
| $CoSO_4$ | 181.2 | 312.5 | 312.5 g. $NiSO_4$ |
| NaCl | 11.35 | 19.6 | 19.6 |
| Boric acid | .. | 37.8 | Nearly to saturation |
| Total bath (l.) | 4.0 | 1.5 | .... |
| Sp. gr. 15° C | .... | 1.25 | .... |
| Saturated with Co | No | Yes | .... |

| SOL. XIV | Grams per liter of water | | | | | Total bath |
|---|---|---|---|---|---|---|
| | $CoSO_4$ | $(NH_4)_2SO_4$ | $MgSO_4$ | $H_3BO_3$ | | |
| | 37.5 | 21.7 | 3.3 | 12.1 | | 3.5 l. |
| XV | $Co(C_2H_3O_2)_2$ | $SO_4)_2$ | $Na_2SO_4$ | $NH_4Cl$ | | |
| | 100.0 | | 10.0 | 5.0 | 2.0 l. | |

| G. per l. water | SOL. XVI*A* | XVI*B* | XVI*C* |
|---|---|---|---|
| $CoSO_4$ | 90.7 | 90.7 ($NiSO_4$) | 150.0 |
| $(NH_4)_2SO_4$ | 27.6 | 27.6 | 150.0 |
| $NH_4Cl$ | 15.0 | 15.0 | $CoSO_4$ |
| Boric acid | 5.2 | 5.2 | 11.3 g. |
| Addition | $NH_4OH$ to neutrality (see text) | | |

| Sol. No. | Date 1914 | Cur Dens. Amp. per sq. dm | E. M. F. Volts | Electr. dist. Cm. | Cathode area Sq. cm. | Plating time Hr. | Min. | Character of Deposit |
|---|---|---|---|---|---|---|---|---|
| XIII*A*—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 7/10 | 0.70 | 1.56 | 23 | 37.1 | 1 | 30 | Rather dark; little buffing required to finish satisfactorily; greatly resembled Ni in color. |
| | 10 | 0.70 | 1.56 | 23 | 37.1 | 1 | 30 | |
| | 10 | 0.97 | 2.0 | 15 | 37.1 | 2 | 0 | Fairly smooth and uniform, but dark. |
| | 11 | 1.0 | 1.8 | 16 | 37.1 | 2 | 0 | |
| | 11 | 1.0 | 1.87 | 15 | 37.1 | 1 | 0 | Good, smooth, uniform, bright, somewhat streaked on upper half of plate. |
| | 14 | 1.0 | 1.45 | 10 | 37.1 | 1 | 30 | Very smooth and uniform on lower half; badly streaked in upper portion. |
| | 14 | 1.0 | 1.85 | 15 | 37.1 | 1 | 0 | |
| | 14 | 1.0 | 1.7 | 13 | 37.1 | 1 | 0 | Solution stirred continuously by bubbling air through near cathode. Plate brighter and more metallic looking than last runs, but badly split and peeled. |
| | 15 | 1.0 | 1.9 | 12 | 37.1 | 0 | 45 | Very poor, dark streaked and peeling. |
| XIII*B* BRASS CATHODES | | | | | | | | |
| | 10/2 | 0.50 | 1.02 | 10 | 33.6 | 3 | 0 | Uniform, rough, dark. Impossible to polish without grinding |
| | 2 | 0.75 | 1.23 | 10 | 32.6 | 1 | 30 | Smooth, uniform, gray, buffed to satisfactory finish with difficulty. |
| | 3 | 1.0 | 1.53 | 10 | 34.0 | 1 | 0 | Uniform, dark gray, difficult to buff. |
| | 5 | 1.25 | 1.75 | 10 | 34.0 | 1 | 0 | |
| | 6 | 1.50 | 1.25 | 10 | 32.0 | 1 | 0 | Uniform, smooth gray, buffed more readily than preceding plates with this solution. |
| | 6 | 5.46 | 5.5 | 10 | 34.8 | 0 | 30 | Good, smooth, white, buffed readily to mirror. |
| | 9 | 6.0 | .... | 10 | 32.7 | 0 | 10 | |
| | 10 | 6.15 | 6.0 | 10 | 32.7 | 0 | 15 | Good, smooth, white, buffed readily to mirror. |
| | After severe aging test described below | | | | | | | |
| | 8 | 8.0 | 4.83 | 10 | 17.6 | 0 | 12 | |
| | 9 | 8.0 | 6.0 | 10 | Iron, 20.0 | 0 | 10 | Good, smooth, white, buffed readily to mirror. This plate was given a severe bending test, being doubled on itself backwards and forwards to an angle of 180 degrees. The metal furrowed and split on surface and end, but plate clung absolutely. |
| | 9 | 8.0 | 6.0 | 10 | Iron, 20.0 | 0 | 10 | |
| | 8 | 8.8 | 6.5 | 10 | Iron, 22.5 | 0 | 12 | Good, smooth, white, buffed readily to mirror. |
| | 10 | 8.88 | 5.90 | 10 | Brass, 20.0 | 0 | 15 | |
| | After severe aging test. | | | | | | | |
| | 8 | 9.77 | 6.5 | 10 | Iron, 22.5 | 0 | 12 | |
| | 15 | 10.7 | 6.3 | 10 | 1.5.1 | 0 | 20 | Good, smooth, white, buffed readily to mirror. |
| | 8 | 10.0 | .... | 10 | Brass, 17.6 | 0 | 5 | |
| | 8 | 14.6 | 6.5 | 10 | 14.7 | 0 | 5 | |
| | Best obtained with this solution to date, although all plates at current densities from 6 amperes up were good. | | | | | | | |
| | 13 | 16.5 | 5.7 | 10 | 10 | 0 | 5 | Good, smooth, white, readily buffed to mirror Excellent plate. |
| | 6 | 17.5 | 6.85 | 10 | 10.6 | 0 | 5 | |
| | BRASS CATHODES—HEAVY PLATE | | | | | | | |
| | 6–7 | 5.35 | 6.0 | 10 | 32.8 | 15 | 15 | Firm, adherent, massive, showing no tendency to split or curl. Smooth in center, with nodules at edges. Weight approximately 37 grams, thickness approximately 1 mm. |
| | The area of the effective cathode increased from 32.8 sq. cm. at the start, to approximately 40.0 sq. cm. at the end of the run. This latter figure is not sufficiently accurate to admit of exact computation, but the figures show in a general way that the current efficiency was very high. | | | | | | | |
| | 7 | 16.5 | 5.5 | 10 | 10.0 | 17 | 30 | Firm, adherent, massive, showing no tendency to split or curl. Weight, about 30 grams. |
| | 13 | 5.26 | 6.0 | 10 | Circular, 18.9 | 67 | 0 | Firm, adherent, massive, showing no tendency to split or curl; about 5 mm. thick. |
| | *Plate on brass cathodes with grooves, depth 1.62 mm. to 7.0 mm to study "throwing" property of this solution.* | | | | | | | |
| | 7 | 9.0 | 5.5 | 10 | 18.3 | | 5 | |
| | 7 | 3.77 | 5.5 | 10 | Block 60.1 total surface | | 10 20 | Good, smooth, uniform, white. All grooves satisfactorily covered, and satisfactorily buffed to mirror finish. |
| | 7 | 3.83 | 5.5 | 10 | | | | |
| | In last two, grooves faced toward anode, but entire block, back as well as grooves, satisfactorily covered to admit of severe and satisfactory buffing after only 10 minutes' plating. | | | | | | | |
| XIII*C*—BRASS CATHODES | | | | | | | | |
| | 10/15 | 3.95 | 5.3 | 10 | 33.8 | 0 | 20 | Good, smooth, uniform, nearly polished as removed from solution. |
| | 15 | 5.9 | 3.7 | 10 | 13.5 | 0 | 15 | Smooth, white, but splitting at edges. |
| | 15 | 7.76 | .... | 10 | 12.5 | 0 | 10 | |
| XIV—CAST ANODES—BRASS CATHODES | | | | | | | | |
| | 10/1 | 0.50 | 1.05 | 10 | 32.4 | 2 | 0 | |
| | 1 | 1.25 | 1.92 | 10 | 35.3 | 1 | 0 | |
| | 2 | 1.50 | 2.20 | 10 | 35.3 | 1 | 0 | |
| | 2 | 1.75 | 1.68 | 10 | 18.5 | 0 | 45 | Uniform, smooth, white, readily buffed to mirror. |
| | 2 | 2.0 | 1.55 | 10 | 11.1 | 1 | 30 | |
| | 2 | 2.5 | 1.77 | 10 | 11.3 | 0 | 30 | |
| | 3 | 3.0 | 2.47 | 10 | 17.2 | 0 | 30 | |
| | 5 | 3.0 | 3.32 | 10 | 19.6 | 0 | 20 | Uniform, smooth, white, slightly burned on edges. |
| | 3 | 3.51 | 2.88 | 10 | 16.8 | 0 | 30 | Uniform, smooth, white, readily buffed to mirror. |
| | 5 | 4.0 | 2.98 | 10 | 13.3 | 0 | 20 | Uniform, smooth, white, slightly burned on edges. |

XV A number of cobalt depositions were made with Solution XV at various current densities, both with and without mechanical agitation and for varying lengths of time. Mechanical agitation caused the plates to crack. One of the depositions was continued for a period of eight 24-hour days; a uniform, dense, hard, satisfactory plate was found. This deposit was made on a plate approximately half a millimeter thick at a current density of 0.30 amp. per sq. dm. It was, of course, not as hard a deposit as some of the heavy plates deposited from Bath XIII*B* at very much higher current densities

XVI*A* and XVI*B*—Solution XVI*A* and its nickel analogue XVI*B*, in an extended series of experiments were found to give satisfactory plates at low current densities, but to fail by splitting and burning when current densities of 1.0 amp. per sq. dm. or more were reached.

Solution XVI*C* was found to precipitate a red compound on the anode.

A very much greater hardness of the cobalt plate than the nickel plate was particularly noticeable throughout.

Langbein specifies for the nickel solution on copper and copper alloys a current density of 0.45 amp. per sq. dm., and on zinc a current density of 0.8 to 1 amp. per sq. dm.

CONCLUSIONS: 1—Cobalt plates from the solutions of Series VIII, on brass and iron, are firm, adherent, hard and uniform, and may be readily buffed to a satisfactorily finished surface. They take a very high polish, with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

2—Neither Solution VIII*A* nor *B* lends itself to fast cobalt plating like Solutions I*B* and XIII*B*. Solution VIII*A* yields satisfactory deposits at all current densities up to 1.0 amp. per sq. dm., while VIII*B*, which is more concentrated in cobalt sulfate, yields satisfactory plates at all concentrations up to 1.25 amp. per sq. dm. These figures are for plating on brass and iron.

3—Solution VIII*B* may be used for plating on zinc at low current densities up to 0.50 amp. per sq. dm., particularly if the solution near the cathode is agitated.

### SERIES IX—COBALT PHOSPHATE, SODIUM PYROPHOSPHATE SOLUTIONS

Langbein[1] recommends a solution containing nickel phosphate 15.8 grams, sodium pyrophosphate 66.1 grams, and water 1000 cc. for dark nickeling upon iron, brass and copper. This is supposed to be particularly serviceable where darker tones of nickel are required for decorative purposes. It was found in trying to prepare the analogous cobalt phosphate solution that the solubility of the cobalt phosphate was lower than that of nickel phosphate.

[1] Langbein, "Electro-Deposition of Metals," 6th Edition Revised, p. 258.

Solution IX is saturated in cobalt phosphate. The cobalt phosphate prepared for this bath was made by mixing two solutions, one containing 30.0 grams $CoSO_4.7H_2O$ in 3.4 liters of warm water, and the other containing 24.9 grams sodium phosphate in 3.4 liters of warm water. These two solutions were mixed, with constant stirring, and the precipitated cobalt phosphate filtered off. These quantities yielded 15.8 grams

TABLE VI—CURRENT EFFICIENCY TESTS—ALL CATHODES BRASS

| Series | Number of Solution | Run | Run lasted Min. | Current density Amp per sq. dm. | Cathode area Sq. cm. | Average amperes through bath | Grams Cobalt Deposited Theory | Grams Cobalt Deposited Actual | Current efficiency Per cent |
|---|---|---|---|---|---|---|---|---|---|
| I | *B* | 1(*a*) | 60 | 1.0 | 29.2 | 0.300 | 0.331 | 0.325 | 97.7 |
| | | 2 | 60 | 1.0 | 47.4 | 0.475 | 0.523 | 0.5133 | 98.2 |
| | | 3 | 60 | 3.0 | 29.5 | 0.907 | 0.996 | 0.911 | 91.5 |
| | | 4 | 60 | 3.0 | 20.0 | 0.599 | 0.659 | 0.5952 | 90.3 |
| | | 5 | 60 | 3.0 | 20.0 | 0.598 | 0.659 | 0.5906 | 89.7 |
| III | *B* | 1(*a*) | 30 | 1.0 | 20.5 | 0.250 | 0.138 | 0.1340 | 97.3 |
| | | 2 | 60 | 1.0 | 32.6 | 0.328 | 0.361 | 0.3563 | 98.6 |
| | *C* | 1 | 60 | 1.0 | 24.2 | 0.242 | 0.266 | 0.2473 | 92.8 |
| | | 2 | 60 | 1.0 | 40.0 | 0.400 | 0.440 | 0.4063 | 92.2 |
| | *E* | 1 | 45 | 0.80 | 40.0 | 0.321 | 0.265 | 0.2619 | 98.8 |
| | | 2 | 60 | 0.80 | 40.0 | 0.321 | 0.353 | 0.3514 | 99.4 |
| IV | *B* | 1(*a*) | 60 | 1.0 | 36.8 | 0.368 | 0.405 | 0.3736 | 92.3 |
| | | 2 | 60 | 0.42 | 43.4 | 0.182 | 0.200 | 0.1895 | 95.0 |
| | | 3 | 60 | 1.0 | 51.0 | 0.512 | 0.563 | 0.5144 | 91.2 |
| VI | *B* | 1 | 45 | 0.50 | 40.0 | 0.200 | 0.165 | 0.1397 | 84.8 |
| | | 2 | 60 | 0.50 | 40.0 | 0.201 | 0.221 | 0.2133 | 96.4 |
| | | 3 | 63 | 0.50 | 63.5 | 0.365 | 0.420 | 0.3702 | 87.8 |
| | | 4 | 63 | 0.50 | 68.6 | 0.344 | 0.378 | 0.3512 | 98.0 |
| | *C* | 1 | 60 | 0.50 | 72.0 | 0.357 | 0.395 | 0.3723 | 94.6 |
| | | 2 | 60 | 0.50 | 72.0 | 0.361 | 0.397 | 0.3717 | 93.7 |
| | | 3 | 60 | 1.0 | 39.2 | 0.394 | 0.433 | 0.4097 | 94.6 |
| | | 4 | 60 | 1.0 | 40.0 | 0.402 | 0.442 | 0.4184 | 94.6 |
| XIII | *B* | 1 | 60 | 1.2 | 35.0 | 0.435 | 0.478 | 0.4812 | 100.0 |
| | | 2 | 60 | 1.0 | 43.4 | 0.324 | 0.356 | 0.3563 | 100.0 |
| | | 3 | 60 | 5.0 | 68.2 | 0.922 | 1.012 | 1.009 | 99.6 |
| XIV | | 1 | 60 | 1.0 | 51.0 | 0.513 | 0.564 | 0.5484 | 97.2 |
| | | 2 | 60 | 1.0 | 40.0 | 0.402 | 0.442 | 0.4255 | 96.3 |

(*a*) Asphaltum on back of cathode, all others polished on both sides.

cobalt phosphate. The final bath was prepared by dissolving the sodium pyrophosphate in warm water, and adding the cobalt phosphate, which dissolved up to the quantity indicated in Bath IX as determined by analysis but not up to the quantity recommended by Langbein for nickel.

CONCLUSIONS: 1—Solution IX is more satisfactory than the corresponding nickel phosphate solution for the purpose of dark cobalting for decorative purposes. The voltage required for moderate current densities is extremely high as compared with that required for other cobalt solutions described as satisfactory.

2—Cobalt phosphate, in the presence of sodium pyrophosphate, as indicated in Solution IX, is less soluble than the corresponding nickel salt. This is the only case among those studied in which the cobalt bath could not be made more concentrated in metallic cobalt than the corresponding nickel bath, with consequent greater electrical conductivity and correspondingly higher permissible current density for plating.

SERIES X—COBALT AMMONIUM SULFATE, MAGNESIUM SOLUTIONS

CONCLUSIONS: 1—Cobalt plates from Solution X on brass and iron are firm, adherent, hard and uniform, and may be readily buffed to satisfactory mirror surface. They take a very high polish with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

2—The soft yellowish tinge which is observed when plating with the nickel analogue of Solution X was not found with the cobalt solution. On the contrary, the plates are beautifully white and hard.

3—The specific electrical conductivity of Solution X is very much higher than that of the corresponding nickel solution.

4—All of the cobalt plates deposited at current densities between 0.25 and 0.75 are as smooth, adhesive and generally satisfactory as the best nickel plates.

5—Solution X does not lend itself to extremely fast plating as do Solutions *IB* and XIII*B*, but satisfactory plates may be obtained with it at current densities up to 0.75 amp. per sq. dm. Solution X may be used at very higher current densities than the corresponding nickel solution, for which a current density of 0.20 amp. per sq. dm. is recommended.

SERIES XI—COBALT SULFATE, AMMONIUM TARTRATE, TANNIC ACID SOLUTIONS

Neutral ammonium-tartrate is obtained by saturating a solution of tartaric acid with ammonia. The cobalt salt should also be neutral. The solution was prepared by dissolving the ingredients in water, boiling for about fifteen minutes, adding water to make desired quantity and filtering.

CONCLUSION: Solution XI is not satisfactory for cobalt plating under the usual conditions of plating practice.

SERIES XII—COBALT SULFATE, POTASSIUM TARTRATE, TARTARIC ACID SOLUTIONS

The cobalt sulfate, tartaric acid and caustic potash were dissolved in water and then mixed, adding sufficient water to make the bath.

CONCLUSIONS: 1—Cobalt plates from Solution XII, which is simple cobalt sulfate in the presence of potassium tartrate with an excess of tartaric acid, on brass and iron, are firm, adherent, hard and uniform and may be readily buffed to a satisfactorily finished surface. They take a very high polish with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

2—All of the cobalt plates from this solution within the current density ranges described as satisfactory, are as smooth, adhesive and generally satisfactory as the best nickel plates.

3—Solution XII is an extremely fast-plating solution when compared with the fastest nickel solutions. It yields satisfactory plates at all current densities up to 11.0 amp. per sq. dm.

4—Solution XII may be used for plating on brass, iron and steel, for which cathodes alone these conclusions apply.

5—There is no nickel bath, of which we are aware, operating in the manner of the usual plating practice at anything like as high a current density as the cobalt solution XII.

SERIES XIII—COBALT SULFATE, COBALT CHLORIDE, BORIC ACID SOLUTIONS

Solution XIII*A* is analogous to one suggested to us by Mr. W. S. Barrows, foreman of the plating department, Russell Motor Car Company, Toronto, Ontario, as being satisfactory and rapid for nickel plating.

TABLE VII—AGING TESTS OF BEST PLATING SOLUTIONS—DATA (EXCEPT XIII*B*) BEGUN ON AUG. 26TH AFTER RUNS RECORDED IN TABLES I TO V

| SOLUTION I*A* After plating Hrs. | SOLUTION I*A* G. Co. per 100 cc. | SOLUTION I*B* After plating Hrs. | SOLUTION I*B* G. Co. per 100 cc. | SOLUTION III*B* After plating Hrs. | SOLUTION III*B* G. Co. per 100 cc. | SOLUTION III*E* After plating Hrs. | SOLUTION III*E* G. Co. per 100 cc. | SOLUTION IV*B* Acidity of solution | SOLUTION IV*B* After plating Hrs. | SOLUTION IV*B* G. Co. per 100 cc. | SOLUTION XIII*B* Date October | SOLUTION XIII*B* Hrs additional run | SOLUTION XIII*B* Grams cobalt deposited | SOLUTION XIII*B* At cur dens. Amp. per sq. dm. | SOLUTION XIII*B* G.Co per 100 cc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 31 | 0.94 | 80 | 2.54 | 24 | 1.11 | 26 | 1.72 | Neutral | 16 | 0.76 | 6 | 2 | | | 8.55 |
| 46 | 0.94 | 95 | 2.58 | 39 | 1.10 | 41 | 1.81 | Very sl. alk | 31 | 0.80 | 7 | 15½ | 37 | 8.35 | 8.40 |
| 61 | 0.95 | 110 | 2.52 | 54 | 1.14 | 56 | 1.95 | Sl. alk. | 46 | 0.74 | 8 | 17.5 | 30 | 16.5 | 8.20 |
| 76 | 0.94 | 125 | 2.55 | 69 | 1.10 | 71 | 2.12 | Neutral | | | 8 | 5 min. | | 15.4 | *b* |
| Diluted to original volume | | | | | 1.11 | 86 | 1.95 | Sl. alk. | 61 | 0.75 | 9 | 13 | 40 | 11.0 | 8.30 |
| 87 | 0.96 | 140 | 2.58 | 84 | 1.12 | 101 | 1.99 | > Alk. | 77 | 0.96 | 10 | 16 | | 5.0 | 7.95 |
| 102 | 0.97 | 155 | 2.60 | 99 | 1.13 | 116 | 2.11 | > Alk. | | | 13 | 67 | | 5.26 | 7.59 |
| 117 | 0.99 | 170 | 2.62 | 114 | 1.14 | 131 | 2.17 | > Alk. | | | 13 | 5 min. | | 16.25 | *b* |
| Neutral solutions throughout tests | | | | Very slightly alkaline throughout | | | | Neutral throughout (*a*) | | | Strongly acid to litmus throughout tests | | | | |

(*a*) Solution IV*B* was neutral to litmus paper and slightly alkaline by titration with $N/10$ HCl and litmus indicator.
(*b*) Good, smooth, white plate obtained; buffed readily to a mirror surface. (Note severe anode current densities and good behavior of solution.)

CONCLUSIONS: 1—The extreme importance of proper concentration of cobalt sulfate solutions is shown by the results of this series. Solution XIII*A* is unsatisfactory for plating purposes at all current densities tried. Solution XIII*B*, which is a more concentrated solution of the same type, is the most completely satisfactory solution, for a great variety of purposes, which we have found. We know of no solution, plating with nickel, which begins to compare with Solution XIII*B* for the range of work which it will do, and for the extreme high current densities at which it will operate. It is possible to get a plate in three minutes or less with Solution XIII*B*, which will stand all the usual physical commercial tests, and which will buff as satisfactorily as a plate which has taken one hour in the usual nickel-plating baths.

2—Cobalt plates from this simple cobalt sulfate solution in the presence of sodium chloride and boric acid, Bath XIII*B*, on brass and iron, are firm, adherent, hard and uniform, and may be readily buffed to a satisfactorily finished surface. They take a very high polish, with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

3—The specific electrical conductivity of Solution XIII*B* is much higher than that of the corresponding nickel solution.

4—Solution XIII*B* does not yield the best cobalt plates at low current densities, that is, in the neighborhood of 0.50 to 1.0 amp. per sq. dm., which is a common range for nickel-plating work. Solution XIII*B* begins to plate most satisfactorily at a current density in the neighborhood of 3.5 amp. per sq. dm., and continues to give satisfactory plates at all current densities up to 26.4 amp. per sq. dm. This is equivalent to a current density of over 240 amp. per sq. ft., and even at this speed, the limit of the solution has not yet been reached.

5—All of these cobalt plates within the wide current density range described as satisfactory for Solution XIII*B*, are as smooth, adhesive and generally satisfactory as the best nickel plates.

6—Solution XIII*B* does not change appreciably in cobalt content nor in acidity when used over long periods of time at current densities as high as 1 amp. per sq. dm. It showed only a very gradual diminution in cobalt content under the most severe conditions of the aging test described in Table VII. We know of no other cobalt solution and of no nickel solution which would stand up under the conditions of this aging test.

7—There is no nickel bath of which we are aware operating in the manner of the usual commercial plating procedure at anything like as high current density as Bath XIII*B*.

8—Solution XIII*B* may be used for plating on brass, iron and steel, for which cathodes the above conclusions apply.

9—Solution XIII*B* may be used to deposit a heavy cobalt plate. These plates may apparently be deposited to any desired thickness, and they are firm, adherent, massive, of extreme hardness and show no tendency to curl or split.

10—Heavy plates may be obtained from Solution XIII*B* to much better advantage than from Solution XV, which has been particularly patented for the purpose with nickel; that is, heavy deposits may be obtained from Solution XIII*B* at current densities of 5 or 6 amp. per sq. dm., whereas Solution XV must be operated at low current densities in the neighborhood of 0.30 amp. per sq. dm. If a current density of above 6 amp. per sq. dm. is used with Solution XIII*B* for heavy deposits, under the conditions in dimension of our baths, it was found that trees were formed on the cathode.

11—Our experiments show that Solution XIII*B* "throws" very satisfactorily.

12—Among the satisfactory properties of this remarkable solution should be mentioned an extremely high current efficiency, which we found at 1.0 and 5.0 amp. per sq. dm. to be almost 100 per cent.

13—Solution XIII*C*, which is the nickel analogue of Solution XIII*B*, yielded satisfactory plates to about 5 amp. per sq. dm., but showed splitting at current densities greater than that. Nickel solution XIII*C* does not possess the remarkable qualities of its cobalt analogue XIII*B*, although in many respects it is an improvement on standard nickel solutions.

14—Solution XIII*B* requires very little aging; it operates satisfactorily almost from the start.

15—Solution XIII*B* is so remarkable in its properties that it was thought highly worth while to develop it further under commercial conditions. See COMMERCIAL TESTS, p. 394, *et seq.*

### SERIES XIV—COBALT SULFATE, AMMONIUM SULFATE, MAGNESIUM SULFATE, BORIC ACID SOLUTIONS

CONCLUSIONS: 1—Cobalt plates from Solution XIV, on brass and iron, are firm, adherent, hard and uniform, and may be readily buffed to a satisfactory mirror surface. They take a very high polish with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

2—Solution XIV yields satisfactory plates at all current densities up to about 3 amp. per sq. dm.

3—The current efficiency of Solution XIV is satisfactorily high, being in the neighborhood of 96 to 97 per cent under the conditions of our experiments.

4—All of the cobalt plates from Solution XIV within the current density range described as satisfactory are as smooth, adhesive and generally satisfactory as the best nickel plates.

### SERIES XV—COBALT ETHYLSULFATE, SODIUM SULFATE, AMMONIUM CHLORIDE SOLUTIONS

This solution is the cobalt analogue of a nickel solution patented by Dr. G. Langbein & Co., Leipzig, Germany.[1] The inventor claims for this solution that very dense, hard, uniform, deposits of nickel may be obtained from it, and particularly "deposits of any desired thickness can be produced if the bath be constantly agitated by mechanical means or by the introduction hydrogen." It, of course, is not permissible to agitate this bath with air, as that would cause oxidation.

CONCLUSIONS: 1—Dense, hard, uniform deposits of cobalt may be obtained from a cobalt-ethylsulfate solution made up like Solution XV, without mechanical agitation, provided that the current density be low, not exceeding 0.30 amp. per sq. dm.

2—For heavy depositions of cobalt, where density, hardness and speed of deposition are important, Solution XV is not nearly as satisfactory as Solution XIII*B*. However, the cobalt-ethylsulfate solution deposits cobalt more satisfactorily than the corresponding nickel-ethylsulfate solution deposits nickel.

### SERIES XVI—COBALT SULFATE, AMMONIUM SULFATE, AMMONIUM CHLORIDE, BORIC ACID SOLUTIONS

In making this solution it was reasoned, as in many instances already reported, that a greater current density might be used if the metal content were increased. This solution, contrary to a number of others reported, would not, however, admit of very great increase in cobalt content without giving disturbing effects of crystallization in the bath.

Current efficiency runs were made with these solutions, which show them to be in the neighborhood of 90 per cent, but they were not thought of sufficient importance to warrant a careful study.

CONCLUSIONS: 1—Plates from Solution XVI*A* and the corresponding nickel solution are both satisfactory at current densities below 1 amp. per sq. dm. At higher current densities both solutions fail.

2—A solution of the type of Series XVI cannot be prepared in much greater concentration than XVI*A*, without obtaining troublesome crystallization. Therefore, Series XVI does not offer a highly concentrated rapid plating cobalt solution.

3—Cobalt plates from Solution XVI*A*, on brass and iron, are firm, adherent, hard and uniform, and may be readily buffed

[1] Kaiserliches Patenamt, *Patentschrift* No. 134,736 Kl 48*a*, Sept. 18, 1902.

TABLE VIII—COMMERCIAL EXPERIMENTS WITH COBALT SOLUTION *IB* AT THE RUSSELL MOTOR CAR CO. PLANT

SOLUTION IB—Cobalt-ammonium sulfate, 5 lbs. Water, 6 gals. Acidity, neutral. Specific gravity, 1.050

| Date 1914 | Cur. Dens Amp. per sq. dm. | E. M. F Volts | Elec. dist In. | CATHODE Material | Area Sq. in. | Plating time Hr. | Min | Anode area Sq. in | CHARACTER OF DEPOSIT |
|---|---|---|---|---|---|---|---|---|---|
| 9/10 | 8.6 | 3.75 | 5 | Steel | 15 | 0 | [illegible] | 28 | Blackened in 30 sec. |
| | 3.4 | 3.25 | 5 | | 45 | 0 | 30 | 56 | Poor; buffed easily; blisters appeared, long and narrow in form; small pinholes on some portion. Slightly burned on lower ends. |
| 11 | 2.3 | 1.25 | 5 | Brass hub cap | 15 | 0 | [illegible] | 28 | Slow, spotted, streaked, very dark |
| 11 | 4.3 | 2.0 | 5 | | 15 | 0 | 5 | 90 | Deposition rapid. Plate spotted, not uniform. Cathode not covered at end |
| 12 | 3.9 | 2.5 | 5 | | 15 | 0 | 5 | 90 | of run. |
| 12 | 3.3 | 3 | 5 | Steel | 10 | 0 | 30 | 28 | Good, firm adherent; very hard and smooth. Color similar to nickel before buffing. Colored easily and to good finish of slightly bluish tone. |
| 12 | 3.3 | 2.75 | 5 | | 36 | 0 | 15 | 90 | Did not cover; streaked, very hard, brittle. |
| 12 | 3.3 | 3 | 5 | Brass | 15 | 0 | 50 | 28 | Good color. Porous spots in casting, refused to cover at edges. Indented portions of cathode not coated. Spot beneath slinging wire bare. |
| 14 | 3.0 | 2.5 | 5 | | 15 | 1 | 0 | 28 | Struck the piece with nickel for 30 seconds. Cobalt deposit began readily and uniformly. Color darkened quickly, imperfect in spots, rough and streaked. |
| | 3.0 | 2.5 | 5 | Steel | 12 | 0 | 15 | 28 | Deeper portions of piece not covered. |
| | 2.3 | 2 | 5 | | 4 | 0 | 5 | 14 | Plate scaled, chipped. Deeper portions not covered. |
| Solution rendered slightly alkaline | | | | | | | | | |
| | 3.0 | 2.5 | 5 | | 12 | 0 | 15 | 28 | Plate peeled badly. Several tests were made with similar results. |
| Solution rendered slightly acid | | | | | | | | | |
| 15 | 1.6 | 1.5 | 5 | | 40 | 1 | 15 | 42 | Color very dark, otherwise a good plate; buffed easily; did not cut through. |
| 15 | 1.0 | 1.5 | 5 | | 40 | 0 | 5 | 42 | Color very dark, buffed to good finish. |
| 15 | 1.5 | 1.5 | 5 | | 86 | 1 | 0 | 42 | Surface covered instantly and in good condition. Gas liberated more freely than heretofore, but no indication of pinholes or streaks. Color very dark, resembling burnt nickel deposit. When dried it had a velvety appearance. Soft to the touch, buffed easily on soft wheel. |
| 15 | 3.0 | 2 | 5 | Brass | 45 | 0 | 30 | 56 | Very dark. Surface covered with minute blisters or pits, which disappeared when buffed. Surface covered quickly and completely. Color satisfactory after buffing. |
| 15 | 3.0 | 2 | 5 | Steel | 40 | 0 | 30 | 56 | Very dark, buffed easily and to good finish. Very hard plate, superior to 1-hour nickel from Prometheus solution |
| 16 | Tests made during the following ten days resulted in similar plates; 6 lbs. cobalt salts were then added to the bath. Sp. gr. 12° Bé. No further additions were made acidity, very slightly acid. After aging treatment the solution was practically neutral. | | | | | | | | |
| 28 | 2.1 | 1.75 | 5 | | 36 | 0 | 25 | 42 | Surface covered well, gas not as free as formerly, deposit marred by circular mark entire length and breadth of cathode. Color darker than nickel, hard and fine grained. |
| 29 | 3.9 | 2 | 8 | Brass | 12 | 0 | 5 | 28 | Surface covered splendidly and color very good; withstood very hard buffing, but required only light treatment to finish. Very satisfactory results. |
| Electrolyzed solution for 32 consecutive hours with an average current of 10 amp. at 2 volts—90 sq. in. anode surface. Added 24 drops liquid ammonia. Temperature 70° F., sp. gr. 1.085. Anode coated with brownish red film when at rest. Salts creep to hooks and remain moist. Solution neutral. Slight sediment at bottom of tank. | | | | | | | | | |
| 10-3 | 2.8 | 2 | 5 | Steel | 28 | 24 | 0 | 90 | Smooth, hard, adherent; No evidence of cracks or burning. Thickness approximately $\frac{1}{32}$ in. |
| 3 | 3.7 | 2.25 | 5 | Steel tube | 18 | 2 | 0 | 56 | Smooth, white, hard plate. Drew the tube from 1 in. diameter to $\frac{9}{16}$ in. with no damage to deposit. |
| 3 | 4.0 | 2.25 | 5 | Brass | 24 | 0 | 10 | 56 | Equal portions were nickel- and cobaltplated for 1 hour. The two coatings were then buffed with same stroke. Repeated trials cut the nickel through before the cobalt. In no case did the cobalt expose the brass. *Very convincing test.* |
| 8 | 3.7 | 2 | 5 | | 12 | 0 | 15 | 28 | Good color, buffed easily to splendid finish; bending, hammering, twisting did not crack nor loosen plate. |
| 8 | 4.2 | 3.5 | 8 | Sheet steel | 72 | 1 | 0 | 90 | The cathode consisted of six pieces steel hooked to wire frame. Plate good color, smooth, hard; did not crack when bent or twisted. Buffed to good finish. |
| 14 | 4.5 | 4 | 8 | Steel | 72 | 1 | 0 | 90 | Deposit began with current density of 30 amp. per sq. ft. and gradually increased to 42. After a 10-minute run with this current density, plate began to show signs of darkening. This, however, was not considered serious until expiration of 20 minutes. Entire surface finished easily on soft buff. While the plate was not a good specimen from a commercial viewpoint, the remarkable efficiency of the bath was clearly demonstrated. |
| 15 | 5.2 | 4.5 | 8 | | 72 | 1 | 0 | 90 | Same cathode as last test, arranged differently in frame. Plate gray but not burned; adherent, hard, smooth; did not break when bent; buffed easily to good finish. |
| 16 | 5.2 | 4.5 | 8 | Cast iron | 12 | 1 | 0 | 14 | This cathode was a piece of stove casting. Plate on one side only, and of splendid color over entire surface, the backgrounds being equally as white as average nickel plate. When buffed the piece could not be detected from nickelplated piece except by our acquaintance with the fact. |

31 Current densities as high as 6.3 amp. per sq. dm. were employed in several tests, but the results were not such as to merit recording. The solution at this date was proving very efficient in every detail.

NOTE.—To transform amperes per square decimeter to amperes per square foot, multiply by 9.3.

to a satisfactory surface, within current density range recommended. They take a very high polish, with a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

4—The cobalt plates from Solution XVI*A* are very much harder than the nickel plates from its analogue, XVI*B*. This is noticeable throughout all our plating experiments, but is particularly striking in this case where the plates were obtained in series and simultaneously.

5—The specific electrical conductivity of Solution XVI*A* is very much higher than that of the corresponding nickel solution XVI*B*.

6—The current efficiencies of both nickel and cobalt solutions of the type XVI*A* are in the neighborhood of 90 per cent under the conditions of our experiments.

ACKNOWLEDGMENT

The numerous analyses in connection with these experiments were made by Mr. Russell C. Wilcox, and during the summer of 1914 a number of plating experiments were run by Mr. C. S. Allin. The authors acknowledge with thanks their indebtedness to these gentlemen.

COMMERCIAL TESTS WITH SOLUTIONS *IB* AND XIII*B*

The results with Solutions *IB* and XIII*B* were thought by the authors to be so unusual and of sufficient importance to warrant verification and further development under standard commercial conditions. We therefore arranged with the Russell Motor Car Company of Toronto, Ontario, and particularly with Mr. W. S. Barrows, *Foreman Electro-Plater* with the same company, to have a plating tank operated under standard commercial conditions at their plant, using Solutions *IB* and later Solution XIII*B*.

Mr. Barrows has had twenty years' experience with all sorts of electro-plating work, to which he has particularly devoted himself. He has considered these two cobalt solutions entirely from the point of view of commercial practicability and value.

COMMERCIAL REPORT ON SOLUTION *IB*

Salts identical with those used in this laboratory were sent by the authors to Mr. Barrows, with instructions for making up Solution *IB* identical with that used by us and described on page 384.

ANODES—Cobalt anodes were cast at this laboratory of the size (7 in. × 2½ in.) required by Mr. Barrows for his tank, and sent him for use in these experiments. The anodes used in a bath had a surface of approximately 1 sq. ft. area. They analyzed as follows:

| Co | Ni | Fe | As | P | S | C |
|---|---|---|---|---|---|---|
| 98.75 | None | 1.35 | None | 0.0067 | 0.052 | 0.061 |

Mr. Barrows, in collaboration with the authors, tested Solution I*B* for plating purposes, during the months of August and September, 1914. The plating was accomplished under standard commercial conditions on copper, brass, iron, steel, tin, German silver, lead and Britannia metal. Various articles, such as brass castings, sheet brass, steel stampings, skates, automobile hubs, etc.—articles of very different shapes and sizes—were plated under exactly the same general conditions as for nickel plating practice at the Russell Motor Car Company.

The tests were made in a still solution, *i. e.*, without agitation of any kind, and the resulting plates were subjected to the most severe practical tests. This work was regarded by Mr. Barrows purely from the commercial viewpoint, and with this in mind, he particularly tested and studied the following points: the color of the plate, the uniformity and freedom from defects of the plates, the allowable speed of plating without pitting or burning (*i. e.*, the maximum allowable current density), the solubility of the anodes, the required voltage, the "throwing" properties of the bath (*i. e.*, its ability to cover the deeper parts of the object in a satisfactory manner), the solubility of the salts, the hardness of the plates, the ease of "coloring" the plate on a buff, the efficiency of the plating solution, the time required for aging of the bath, the adhesiveness of the plate to the cathode under bending and hammering tests, the general cleanliness of the bath, the corrosion of the plate, and many other special features.

In a letter to one of the authors, dated November 2nd, Mr. Barrows gives a very complete report of his commercial tests of Solution I*B*. This letter follows in full as received, and serves admirably to cover this portion of the work.

To DR. HERBERT T. KALMUS:

After preparing a cobalt plating solution according to your formula for Bath I*B*, and having used this bath daily during the past eight weeks, plating a great variety of copper, brass, iron, steel, tin, German silver, lead and Britannia metal articles of different shapes and sizes under exactly the same conditions as met with in general nickel plating at the factory of the Russell Motor Car Company, West Toronto, and after regarding the characteristics of this particular solution absolutely from a commercial viewpoint, I can heartily confirm any statement you have made to me regarding this remarkable solution. This bath was equipped with cobalt anodes, 98.75 per cent cobalt, which were sent to me from your laboratory.

The runs made have varied from 5 minutes to 24 hours, and in each case the bath has proved wonderfully efficient.

The cobalt plates obtained were smooth, white and fine grained, very adherent and uniform. In fact, the surfaces of these deposits, after several hours' run, were so very smooth and uniform that a 4 inch cotton buff colored them to a mirror finish quite easily. We use 14 inch and 16 inch buffs to color 3-hour deposits of nickel.

To test the hardness of the cobalt as compared with nickel, with reference to either buffing or polishing with emery, we plated strips of brass, one-half the surface with cobalt and one-half with nickel, always giving the nickeled portion the thickest plate. Then buffing or polishing across the two deposits, we found invariably that the nickel was removed from the brass before the cobalt, and in some cases in one-half the time.

Though so hard and firm, these plates color beautifully with little effort, and require the use of much less buffing composition than comparatively thin plates of nickel. Automobile parts of irregular shape were plated from 10 to 20 minutes, and finished on a 6-inch buff operated at 3,000 R. P. M. without the slightest evidence of a defect in the plating. To accomplish this with our fastest nickel baths would require at least 60 minutes of plating.

As a protective coating for iron or steel surfaces, I am convinced that a comparatively thin plate of cobalt will prove equally as effective as a thick plate of nickel from an ordinary double sulfate nickel bath, and the time and power required for the production of such plates is decidedly in favor of the cobalt.

The deposits are also very adherent, no difficulty having been experienced in this respect, although tests were made repeatedly by bending, hammering and burnishing.

One of the weak points of several so-called rapid nickel plating solutions, which we have tried commercially, is their poor "throwing" powers, *i. e.*, they do not deposit the nickel readily in the indentations or cavities of the cathode. The cobalt solution I*B* meets this requirement in a most efficient manner; the deposits on the distant portions of the cathode withstand the tests imposed in every case.

Another most important feature of this solution, which should commend itself to every practical plater and manufacturer of plated wares, is the extremely high current density at which this solution may be employed without danger of pitting the plated surface. I have plated with this cobalt solution, I*B*, satisfactorily and under commercial conditions, at a current density of 42 amp. per sq. ft. This is 4⅕ times the speed of our fastest commercial nickel solutions.

As a further test, we plated steel tubes of 1 in. diameter for two hours, with a current density of 27 amp. per sq. ft., and then drew the tubes down to ⅝ in. diameter without injuring the deposit. Though extremely hard, the ductility of the deposited metal proved remarkable.

All of our tests have been made in a still solution, without agitation of any kind, and the plates were subjected to the most severe treatment considered practical for high-grade metallic coatings on the various metals heretofore mentioned.

We are also of the opinion that the anodes in the cobalt bath I*B* will remain free from coatings, such as characterize average anodes used in nickel baths, and that the cost of maintenance will be practically nothing compared to double sulfate nickel solutions.

I can assure you that my experience thus far with these cobalt solutions has been intensely interesting, and I sincerely believe that their use commercially would revolutionize the art of electro-plating such wares as are now nickelplated.

The simplicity of its composition, its self-sustaining qualities, the remarkable speed of deposition, together with the several points mentioned previously, should appeal to the commercial requirements of this progressive age.

WALTER S. BARROWS

November 2, 1914

COMMERCIAL REPORT ON SOLUTION XIII*B*

After the completion of the test on Solution I*B* by Mr. Barrows, salts identical with those used by the authors were sent to him, with instructions for preparing Bath XIII*B*, identical with that described on page 393.

TABLE IX—COMMERCIAL EXPERIMENTS WITH COBALT SOLUTION XIII*B* AT THE RUSSELL MOTOR CAR CO. PLANT

SOLUTION XIII*B*—Cobalt sulfate crystals, 26 lbs. 10 [illegible] oz. Salt NaCl [illegible] oz. Water 4 [illegible] gal. Boric acid 3 lbs. Sp. gr. [illegible] Bé. Temperature, 64° F. Acidity [illegible] acid

| Date 1914 | Cur. Dens. Amp. per sq. dm. | E. M. F. Volts | Elec. dist In. | Cathode Material | Cathode Area Sq. in. | Plating time Hr. | Plating time Min. | Character of Deposit |
|---|---|---|---|---|---|---|---|---|
| 11/2 | 6.5 | 4.5 | 5.0 | Brass | 12 | 0 | 5 | Smooth, hard, firm, very adherent; stood bending test and twisting. Buffed on 12 in. cotton buff wheel at 3600 R. P. M. with pressure approximately same as for heavy nickel plate. No evidence of cutting through; splendid results. |
| | 4.4 | 3.5 | 5.0 | Steel | 28 | 1 | 0 | Mottled, burnt, impossible to buff or polish to a satisfactory surface. Solution full of floating particles of boric acid. |
| | 8.2 | 3.5 | 5 | Brass | 42.5 | 1 | 0 | Mottled, cloudy plate at edges, center quite brilliant, but difficult to color. Poor plate. |
| | | (Filtered solution) | | | | | | |
| 5 | 3.5 | 5 | 5 | Brass hub cap | 70 | | 30 | Very heavy, dirty gray; flaked on sides; burnt at edges; rough and impossible to color. Inside well covered ($2^1/_2$ in. deep). |
| 6 | 9.0 | 4 | 5 | Brass | 12 | | 5 | Gray, streaked. |
| | 12.0 | 6 | 5 | | 12 | | 5 | Whiter, better than last test. |
| | 13.1 | 4.5 | 2.5 | | 4 | | 2 | White, tough at center, edges badly burnt. |
| | 21.4 | 6 | 5 | Copper | 4 | | 2 | Excellent. Good thickness, corners cracked only slightly. Deposit could be felt with finger nail; buffed to good color. Did not crack when bent double. |
| 6 | 20.0 | 6.5 | 5 | | 4 | 0 | 2 | |
| 9 | 6.9 | 4.5 | 5 | | 9 | 0 | 15 | Smooth, hard, white, adherent. Buffed to good finish. |
| 11 | 8.3 | 4 | 5 | Corrugated steel | 9.5 | 0 | 10 | Best plate thus far. Buffed to mirror finish over entire surface. Deepest grooves in good condition. |
| 11 | 4.2 | 3.5 | 5 | Thick steel | 28 | 0 | 30 | Appeared satisfactory when removed from bath, but scaled at center when dipped in hot water. |
| 12 | 8.6 | 9 | 5 | Brass | 16.5 | 0 | 1 | Smooth, uniform, white plate, withstood hard buffing. Colored easily to mirror finish |
| 12 | 8.6 | 8 | 5 | Brass hub cap | 45 | 0 | 1 | Smooth, white plate, buffed to excellent finish. No evidence of a defect. |
| 12 | 19.4 | 8 | 5 | Perforated brass | 8 | 0 | 2 | Beautiful results; high and low spots perfect. |
| 12 | 19.4 | 8 | 5 | Same piece | | 0 | 1 | Cleaned the piece just plated and plated on the first deposit without stripping. No indication of trouble from this source. |
| 12 | 9.7 | 6 | 5 | Same piece | | 0 | 5 | Splendid plate, colored by rubbing with flannel cloth, afterwards stood severe buffing test. |
| 12 | 10.7 | 3 | 5 | Same piece | | 0 | 15 | Dull, muddy color when removed from bath, buffed readily to good luster. Background not as white as when higher voltage was used |
| 17 | 16.8 | 6 | 5 | Cast iron | 18 | 0 | 1 | Burnished the piece with 400 lbs. steel balls for 15 minutes; good finish. No evidence of wearing through deposit. Placed the casting in acidulated water (15 to 1) for 36 hours, wiped dry. No evidence of defective coating; casting remained in good condition. |
| 17 | 17.1 | 6.5 | 5 | Embossed brass | 12 | 0 | 1 | Buffed on 10 in. wheel at 3600 R. P. M., excellent finish. Did not cut through letters or raised parts. |
| 17 | 19.4 | | 5 | 6 of same | 72 | 0 | 1 | Excellent plate. |
| 17 | 26.4 | | 5 | Brass | 2.5 | 0 | 1 | Splendid plate; hard, yet pliable. Plated 200 of these pieces in same manner, in 1 doz. lots. |
| 17 | 16.9 | | 5 | Polished lead | 12 | 0 | 5 | Adherent plate, hard, smooth and good color, buffed readily. Did not break when bent. Cut lead in pieces without scaling deposit. |
| 18 | 16.8 | | 5 | Britannia metal | 30 | 0 | 5 | Very satisfactory plate, adherent and white. |
| 18 | 16.8 | | 5 | Steel skate blade | 33.3 | 0 | 5 | Not as white as desired, but otherwise very good plate. |
| 19 | 17.0 | 6 | 5 | German silver | 10 | 0 | 2 | Excellent plate. |
| 19 | 16.8 | 6.5 | 5 | Tin | 15 | 0 | 5 | This deposit stood every conceivable abuse, and was easily colored on small buff. |
| 20 | 16.3 | | 5 | Brass hub cap | 45 | 0 | 3 | Buffed to a beautiful finish. Required very severe buffing on wheel revolving at 1500 R. P. M. to cut through; apparently equal to a 1 hour nickel deposit. |
| 20 | 17.0 | | 5 | Brass | 10 | 0 | 1 | Plated 100 pieces, and buffed them ready for stock in 1 hour. |
| 20 | 17.0 | | 5 | | 60 | 0 | 1 | |
| 23 | 16.8 | 6 | 5 | Steel tube | 18 | 0 | 15 | Drew tube from 1 to $^3/_4$ in., buffed same and found perfect, then drew tube to $^5/_8$ in., buffed again and still perfect. |
| 23 | 11.6 | 6 | 5 | Cathodes—Oxidized silver-faced Britannia metal 14 sq. in. anode surface | 12 | 15 | 15 | The die was merely washed with alcohol, rinsed in water and placed in cobalt bath. A current of 15 amp. was passed through the bath for 10 minutes, while the cathode was kept constantly moving. Current then reduced to 9 amp. and cathode closely watched during the following hour. Bath switched to battery circuit and allowed to remain undisturbed during the night. Resulting deposit was quite smooth at center, edges rough but solid; face of die in fine condition. The finest lines perfect. The deposit did not curl nor lift from the master die during run. Deposit about $^3/_{32}$ in. Extraordinary results for die work. |
| 24 | 21.1 | 6.5 | 5 | [illegible] in. brass | 4 | 0 | 5 | Splendid plate, beautiful color after buffing. |
| 24 | 16.8 | 6.5 | 2.5 | Brass | 12 | 0 | 5 | Firm, tough, adherent plate, white in color, began to darken at edges, oiled off edges with emery, then buffed entire surface to splendid finish. |
| 25 | 20.0 | 6.5 | 5 | Brass | 4 | 0 | 10 | Adherent, white, smooth plate, buffed very easily to good finish. |

NOTE—To transform amperes per square decimeter to amperes per square foot, multiply by 9.3.

ANODES—Cobalt anodes, identical with those used for Solution I*B* (p. 395), were furnished from this laboratory.

Tests were made of this solution in the manner and from the same point of view as those for Solution I*B*.

In a letter to one of the authors, dated December 1st, Mr. Barrows gives a complete report of his commercial tests of Solution XIII*B*. This letter follows in full as received:

TO DR. HERBERT T. KALMUS:

After thoroughly testing Cobalt Plating Bath XIII*B*, made according to your formula, I take pleasure in submitting the following report:

I found the bath very simple to prepare and at once began to operate the solution with high current densities. The results obtained were exceedingly gratifying. Evidently Bath XIII*B* will require no prolonged aging treatment, as splendid, white, hard, perfect deposits were obtained with extremely high current densities within 3 hours after bath was prepared.

The experiments have been varied and the tests of plates severe and deliberate; the results have invariably been such as to cause me to regard Cobalt Bath XIII*B* the greatest achievement in modern electro-plating improvements.

The operation of the bath is positively fascinating: the limit of speed for commercial plating is astonishing, while the excellence of the plates produced is superior to those of nickel for many reasons.

The efficiency of the freshly prepared solution, together with the self-sustaining qualities of the bath, are without a parallel in any plating solution of any kind I have ever used.

Thin embossed brass stampings were plated in Bath XIII*B* for only one minute, then given to a buffer who did not know the bath existed and who was accustomed to buffing $1^1/_4$ hour nickel deposits on these same stampings. This man buffed the cobalt plates upon a 10-in. cotton buff wheel revolving at 3000 R. P. M. The finish was perfect with no edges exposed. These stampings have been plated in two dozen lots for one minute, and from a total of 500 stampings we have found but three stampings imperfect after buffing. Each stamping is formed to a spiral after finishing without injury to the deposit. Grey iron castings with raised designs upon the surface were plated 1 minute in Cobalt Bath XIII*B*, then burnished with 400 lbs. of $^1/_8$ in. steel balls for $^1/_4$ hour without the slightest injury to the cobalt coating, as was proven by a 36-hour immersion in 15 oz. of water acidulated with 1 oz. of sulfuric acid.

While attempting to reach the limit of current densities which would be practical with this bath, XIII*B*, I have plated brass automobile trimmings with a current density of 244

amp. per sq. ft. These pieces were plated in lots of 6, and a total of 100 were plated, buffed and ready for stock in 1 hour's time. No unusual preparation was made for the run and the work was performed by one man. The size of piece plated was $1^1/_2$ in. $\times$ 5 in.

Automobile hub caps were plated 3 minutes in Cobalt Bath XIII*B* and buffed to a beautiful luster of deep rich bluish tone by use of a 7-in. cotton buff revolving at 1200 R. P. M. The deposits were ample for severe treatment usually received by such articles. Comparative tests of these deposits were made as follows: Same style castings plated in double sulfate nickel solution one hour were suspended as anodes in a solution of equal parts muriatic acid and water; sheet lead cathodes were used and a current of 200 amperes at 10 volts passed through the bath. The nickel was removed from the castings in 30 seconds, while 45 seconds time was required to remove the cobalt plates.

The above-mentioned plating tests were made with still solution, no form of agitation being employed. By aid of mechanical agitators these current densities could be greatly exceeded with highly satisfactory results.

These cobalt plates were very hard, white and adherent and colored easily with slight effort.

Several plates were produced upon sharp steel surgical instruments; these instruments finished perfectly and, owing to the hardness of the cobalt plate, only a thin deposit was required to equal the best nickel deposits which we received as samples. Cobalt deposits should prove especially valuable for electroplating surgical instruments, since non-adherent thick deposits are very dangerous for this class of work.

Owing to the unusual mild weather in this locality during the past month, I have not concluded the test with cobalt plates on highly tempered nickel steel skate blades, but judging from appearances and various severe indoor tests we do not hesitate to report success in this direction. A 3-minute deposit from Bath XIII*B* resists corrosion equally as long as a one-hour nickel deposit; the finish is even superior to nickel, while every test employed during the process of manufacturing the nickel-plated article has proved equally ineffective with cobalt plates; therefore by reason of the effectiveness of thin cobalt deposits we believe cobalt plates should prove wonderfully efficient on skates or any keen-edged tool requiring a protective metallic coating.

The runs made with Bath XIII*B* have varied from one minute to $15^1/_2$ hours, and in each case the results were remarkable. Electrotypes were reproduced $^1/_{10}$ in. thick. Electro-dies were faced with cobalt $^1/_8$ in. thick, the electrotypes being graphite covered wax and lead moulds, while the dies were made on oxidized silver-faced Britannia metal.

The deposits from Cobalt Bath XIII*B* were very adherent and pliable; by proper regulation of the current, beautiful white, hard, tough plates may be produced quickly on any conducting surface.

The "throwing" powers of Cobalt Bath XIII*B* make possible its employment for plating deeply indented or grooved articles such as reflectors, channel bars or articles with projecting portions.

We also obtained the best plates with extremely high current densities, although plates finished with 75 amp. per sq. ft. were of good color and easily buffed. The production of excellent plates with a current density of 150 amp. proved particularly easy, and densities in this neighborhood were employed for the greater portion of our tests.

Cobalt Bath XIII*B* will produce excellent, hard, white, tough plates absolutely free from pits or blemish at a current density of 150 amp. per sq. ft. and under ordinary commercial conditions. This is 15 times the speed of our fastest commercial nickel solution.

Furthermore, the anode tops and hooks remain free from creeping salts. The solution retains its original clean appearance and the anodes dissolve satisfactorily with no slime nor coating formed; brushing or cleaning anodes therefore will be unnecessary. The anodes used with this bath were 98.75 per cent cobalt which were sent me from your laboratory. The bath at the commencement of our tests was strongly acid to litmus, and has remained unchanged throughout our experiments. The specific gravity of the solution when freshly prepared was 1.24 and is the same today.

The rich, deep, bluish white tone of the cobalt plates upon polished brass surfaces is particularly noteworthy; this feature should assist greatly in making cobalt deposits very popular for brass fixtures, trimmings and plumbers' supplies.

My experience with Cobalt Bath XIII*B* is by no means at an end. I intend to continue its use until present supplies are exhausted and then equip a larger bath if supplies are obtainable. As a commercial proposition I am satisfied it is wonderfully efficient and economical.

Taking into account the difference in cost of cobalt as compared with nickel, I am satisfied the metal costs for plating a given quantity of work with cobalt would be considerably less than for nickel plating a like quantity.

Furthermore, the use of Cobalt Bath XIII*B* equipped with automatic apparatus for conveying parts through the bath would reduce the labor cost 75 per cent, and such apparatus would be practical for a greater variety of wares than is now the case with nickel.

We cannot speak too highly of Cobalt Bath XIII*B*, and confidently believe its future history will surpass the history of any electro-plating bath now in general use.

In conclusion, please accept my warmest congratulations upon your successes with cobalt solutions. Heartily appreciating the opportunity of testing these solutions, I desire to sincerely thank you, kind sir, for the benefits derived therefrom.

WALTER S. BARROWS

December 1, 1914

## GENERAL CONCLUSIONS FROM COMMERCIAL TESTS ON COBALT PLATING SOLUTIONS

1—Several cobalt solutions were found to be suitable for electro-plating with cobalt under the conditions of commercial practice. Best among these are the following:

SOLUTION I*B*

Cobalt-ammonium sulfate, $CoSO_4.(NH_4)_2SO_4.6H_2O$, 200 grams to the liter of water, which is equivalent of 145 grams of anhydrous cobalt-ammonium sulfate, $CoSO_4.(NH_4)_2SO_4$, to the liter of water. Sp. gr. = 1.053 at 15° C.

SOLUTION XIII*B*

| | |
|---|---|
| Cobalt sulfate, $CoSO_4$ | 312 grams |
| Sodium chloride, NaCl | 19.6 grams |
| Boric acid | Nearly to saturation |
| Water | 1000 cc. |

Sp. gr. = 1.25 at 15° C.

2—Cobalt plates from these solutions, on brass, iron, steel, copper, tin, German silver, lead and Britannia metal articles, of different shapes and sizes, deposited under conditions identical with those met with in general nickel plating practice, are firm, adherent, hard and uniform. They may be readily buffed to a satisfactorily finished surface, having a beautiful luster, which, although brilliantly white, possesses a slightly bluish cast.

3—The electrical conductivity of these solutions is considerably higher than that of the standard commercial nickel solutions, so that, other things being equal, they may be operated at a lower voltage for a given speed of plating.

4 Solution I*B* is capable of cobalt plating on the

various sizes and shapes of objects met with in commercial practice at a speed at least 4 times that of the fastest satisfactory nickel solutions.

5—Solution XIII*B* is capable of cobalt plating on the various sizes and shapes of objects met with in commercial practice at a speed at least 15 times as great as that of the fastest satisfactory nickel solutions.

6—Plates from both of these solutions on various stock pieces satisfactorily withstood the various bending, hammering and burnishing tests to which commercial nickel work is ordinarily submitted.

7—These two very rapid cobalt solutions are remarkable for their satisfactory throwing power; *i. e.*, they readily and satisfactorily deposit the cobalt in the indentations of the work.

8—These two rapid solutions operate at these high speeds in a perfectly still solution without agitation of any kind.

9—These solutions are both cleaner, *i. e.*, freer from creeping salts and precipitated matter, than the standard commercial nickel baths.

10—The cobalt deposited at this rapid speed is very much harder than the nickel deposited in any commercial nickel bath. Consequently a lesser weight of this hard cobalt deposit will offer the same protective coat as a greater weight of the softer nickel deposit. Considering Solution XIII*B*, operating at 150 amp. per sq. ft., on automobile parts, brass stampings, etc., a sufficient weight of cobalt to stand the usual commercial tests, including buffing and finishing, is deposited in 1 minute. With the best nickel baths it takes 1 hour at about 10 amp. per sq. ft. to deposit a plate equally satisfactory. Therefore, the actual weight of metal on the cobalt plate must be approximately one-quarter that of the nickel.

11—For many purposes, under the condition of these rapid plating solutions, one-quarter the weight of cobalt, as compared with nickel, is required to do the same protective work. Consequently, if nickel is worth 50 cents per lb., in the anode form, cobalt could be worth nearly $2.00 per lb., in the same form, to be on the same basis, weight for weight, of metal. In addition there are other advantages of cobalt in saving of labor, time, overhead, etc.

12—A smaller plating room would handle a given amount of work per day with cobalt than with nickel.

13—With these very rapid plating solutions, by the use of mechanical devices to handle the work, the time required for plating, as well as the labor costs, may be tremendously reduced. Solution I*B*, and, particularly, Solution XIII*B*, are so rapid as to be revolutionary in this respect.

14—Obviously, the cost of supplies, repairs, etc., would be less with cobalt plating than with nickel plating, as the size of the plant for a required amount of work is less.

15—The voltage required for extremely rapid cobalt plating is greater than that for most nickel plating baths; it is not so great but that the machines at present in use may in general be operated. For the same speed of plating, the cobalt solution requires much the lower voltage.

16—For a given amount of work the power consumption for this rapid cobalt work is less than that for nickel. This is obvious, because the total amount of metal deposited in the case of cobalt is very much less, whereas the voltage at which it is deposited is not correspondingly greater.

17—Ornamental work on brass, copper, tin or German silver would require only a 1-minute deposit. Even wares exposed to severe atmospheric influences, or friction, could be admirably coated with cobalt in Bath XIII*B* in 15 minutes. The tremendous possibilities of this solution are not to be completely realized unless mechanical devices are applied to reduce hand labor to a considerable extent.

18—Thick deposits from these solutions are vastly superior to any that we have seen produced from nickel solutions. The tendency to distort thin cathodes is less pronounced, while electrotypes and electro-dies have been given a superior thick deposit in a most satisfactory manner. The lines were hard, sharp and tough and the surface smooth. Nickel does not equal cobalt for excellence of massive plates.

19—Many of these tests were passed upon by uninterested skilled mechanics at the plant of the Russell Motor Car Company, who invariably reported in favor of the cobalt as above.

20—Both Baths I*B* and XIII*B* are substantially self-sustaining, once they are put into operating condition, and the amount of aging required to do this is very much less for them than that for the present commercial nickel baths.

A number of automobile parts, and a large number of skates, cobaltplated, were turned out at the plant of the Russell Motor Car Company under Mr. Barrows' direction, and many of the skates have now (February 6, 1915) been under observation in actual use for several months. On this date Mr. Barrows reported that skates plated from Solution XIII*B*, many of which had had extremely hard usage in the hands of boys, etc., were showing up with surprising satisfaction. There is absolutely no stripping of the plate along the edge of the skate, either before or after use, which, unfortunately, is not uncommon with nickelplated skates. Furthermore, the cobaltplated skates seem to be decidedly superior to the nickelplated skates as regards their resistance to corrosion. Another very noticeable feature about the cobaltplated skates is that they are very free from scratches after rough usage as compared with nickel; that is to say, the cobalt plate is decidedly harder than the nickel plate. Most of the skates in question were plated in 3 minutes at 90 to 100 amp. per sq. ft. Nickel plates at the same plant are plated in 1 hour at about 4 amp. per sq. ft. There is apparently considerably more cobalt metal plate on these skates than need be to make them equivalent to nickelplated skates.

The authors take great pleasure in expressing their thanks to the Russell Motor Car Company for their collaboration, and particularly to Mr. W. S. Bar-

rows for the careful, vigorous and painstaking manner in which he has subjected the solutions and plates to the various tests that were required to establish their commercial importance and value.

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## THE FUSIBILITY OF COAL ASH IN VARIOUS ATMOSPHERES[1]

By A. C. FIELDNER AND A. E. HALL

Received April 1, 1915

### INTRODUCTION

In connection with a general study of the fusibility of coal ash under various fuel-bed conditions, at the Pittsburgh Experiment Station of the Bureau of Mines, considerable experimental data have been obtained concerning some of the factors affecting the softening temperature of ash when molded in the form of Seger cones. It was realized that the so-called "fusing temperature" tests made by this method were likely to give exceedingly variable results in different laboratories, as numerous investigators have shown in the case of Seger pyrometric cones, which are of much simpler composition than coal ash. Indeed, L. S. Marks[2] has recently called attention to differences as great as 390° C. which were obtained on the same sample of ash by two different commercial laboratories. It, therefore, seems advisable to present in some detail the results that have been obtained in our investigation in order that fuel chemists may fully appreciate the empirical nature of the test.

### RELATION OF SOFTENING TEMPERATURE OF ASH TO MELTING TEMPERATURE OF EUTECTIC

A complex mixture of oxides and silicates like coal ash has no single, definite melting point. On slowly heating a sample of ash it successively shrinks, sinters and then gradually softens into a more or less viscous slag. From the viewpoint of clinker formation, we wish to know the temperature at which the ash may form a slag of sufficient fluidity to flow or agglomerate in the fuel bed. Since this temperature is probably below the temperature of complete melting of the ash, *i. e.*, the lowest temperature at which the melt on sudden cooling is all converted to glass, the "softening" or "flowing" temperature of the ash when made in the form of a cone seems a more likely indicator of clinkering tendencies.

The deformation of a cone is also a rough measure of viscosity, which undoubtedly is a very important factor. It must, however, be kept in mind that the deformation of the cone does not afford a melting point or any other fixed transformation based on any change of state. As pointed out by Day and Shepard,[3] a cone made of silicate mixtures, which are capable of forming eutectics, begins to weaken as soon as the eutectic begins to melt; its further progress is then governed entirely by the relative quantity of eutectic present and its viscosity after melting. If the constituents of the ash are such as to form a relatively large proportion of thinly fluid eutectic, the deformation point of the cone will lie close to the melting point of the eutectic; on the other hand, if there is a large excess of some refractory component, such as silica or aluminum silicate, or if the eutectic is viscous, the excess component will form a rigid skeleton which is not pulled down by the flowing eutectic. In the latter case the deformation point will approach more nearly the melting point of the rigid component.

### FACTORS INFLUENCING THE SOFTENING POINT

The rate of deformation is also influenced by the rate of heating. Reactions between different constituents take place before their melting points are reached. Some of these reactions are slower than others. Also some constituents have a slow time-rate of melting, as, for example, silica and feldspar. These substances can be heated above their melting points and yet remain in a crystalline form for some time. It is obvious, then, that the deformation temperature of an ash cone must be affected by (1) rate of heating; (2) size, shape and inclination of cone; (3) fineness of ash; and (4) nature of atmosphere in which the cone is heated.

### INFLUENCE OF IRON OXIDES

On account of the presence of iron oxide in considerable quantities in many ashes, the nature of the atmosphere in which the ash cone is heated has a marked influence on the softening point. Under suitable conditions iron may exist as metallic iron, pure or alloyed with carbon, as ferrous oxide (FeO), magnetite ($Fe_3O_4$), or ferric oxide ($Fe_2O_3$). On complete combustion at low temperatures, the pyrite in coal is converted to $Fe_2O_3$. According to Walden,[1] ferric oxide ($Fe_2O_3$) dissociates at 1350° C., when heated in air at atmospheric pressure, into magnetite ($Fe_3O_4$) and oxygen. Therefore, in determining the softening temperature of an ash cone in an atmosphere of air (no reducing gases present), we are dealing with the formation of slags in which the iron component enters the reaction as ferric oxide or magnetite. Peters[2] states that "ferric oxide forms compounds with silica which require a high temperature for their fusion, and is consequently an unwelcome base for slags; although this substance is an almost invariable constituent of oxidized ores, it seldom makes any trouble in the blast furnace, for the reason that it is easily reduced by the fuel gases to ferrous oxide (FeO).....

"In the more neutral atmospheres of the reverberating smelter, however, it is likely to cause delay by combining with silica, making it more difficult to melt the slag."

On the other hand, if the ash cone is heated in a slightly reducing atmosphere of hydrogen or carbon monoxide, the ferric oxide is reduced to ferrous oxide

[1] Published by permission of the Director U. S. Bureau of Mines.

[2] L. S. Marks, "The Clinkering of Coal," *Power*, **40** (1914), 932–4.

[3] A. L. Day and E. S. Shepard, "The Lime-Silica Series of Minerals," *Am. J. Sci.*, [4] **22** (1906), 267. Also a full discussion of the theory of Seger cones, see "The Physical Chemistry of Seger Cones," by R. B. Sosman, *Trans. Am. Ceram. Soc.*, **15** (1913), 482–498.

[1] P. T. Walden, "On the Dissociation Pressure of Ferric Oxide," *J. Am. Chem. Soc.*, **30**, 1350.

[2] Edward Dyer Peters, "Principles of Copper Smelting," Hill Pub. Co., New York, **1907**, pp. 399–400.

which is a strong fluxing agent. Steffe[1] found the following formation temperatures for various ferrous silicates:

| Formation temperature | ° C. |
|---|---|
| $4FeO.SiO_2$ | 1158–1174 |
| $2FeO.SiO_2$ | 1162–1183 |
| $4FeO.3SiO_2$ | 1162–1181 |
| $FeO.SiO_2$ | 1158–1171 |
| $2FeO.3SiO_2$ | 1321–1334 |

The viscosity of ferrous-silicate slags is lower than when the iron component enters the reaction in the ferric form, as shown by Greiner;[2] so the conclusion seems logical that in general lower softening temperatures may be expected if the atmosphere surrounding the cone is able to reduce all the iron to the ferrous state before fusion begins, but not to metallic iron, for in the latter event one of the most active fluxing constituents is removed from the system. Most ashes have already an excess of high-melting constituents like silica and alumina, so that any considerable reduction of iron oxide to metallic iron would tend to increase the refractory effect of the silica and alumina. Hence, lower softening temperatures may be expected in tests made in gas furnaces where some reducing gases come in contact with the ash, while higher results should be found both in furnaces where air only surrounds the cone and in carbon or graphite electric furnaces where strongly reducing atmospheres reduce the iron oxides to metallic iron.

## EXPERIMENTAL

In the following experiments the authors have studied the effect of various factors in the softening temperature of ash, by making tests on a considerable number of different ashes in different types of furnaces such as are in more or less common use for the purpose. Before giving the results obtained in each furnace, the coals tested and general method of operation will be described.

The description and origin of the coal samples are given in Table I, and the analyses of the ashes and partial analyses of the coals in Table II. As may be

TABLE I—DESCRIPTION AND ORIGIN OF SAMPLES

| Sample No. | Lab. No. | Description | Bed | Location of Mine: Nearest Town | County | State |
|---|---|---|---|---|---|---|
| 1 | 15840 | Bituminous | Coal Creek | Fraterville | Anderson | Tenn. |
| 2 | 15841 | Bituminous | American | Parrish | Walker | Ala. |
| 3 | 15842 | Bituminous | Sterling | Manring | Claiborne | Tenn. |
| 4 | 15843 | Bituminous | Jellico | Jellico | Campbell | Tenn. |
| 5 | 15844 | Bituminous | Mingo | Fork Ridge | Claiborne | Tenn. |
| 6 | 15845 | Bituminous | Coal Creek | Oliver | Morgan | Tenn. |
| 7 | 15846 | Bituminous | Mary Lee | Red Star | Walker | Ala. |
| 8 | 15847 | Bituminous | Nickel plate | Jefferson | Jefferson | Ala. |
| 9 | 15848 | Bituminous | Thompson | Marvel | Bibb | Ala. |
| 10 | 16018 | Bituminous | Red stone | Lemely Jct. | Barbour | W. Va. |
| 11 | 16019 | Bituminous | Pittsburgh | Morgantown | Monongalia | W. Va. |
| 12 | 16243 | Bituminous | No. 5 | Booneville | Warrick | Ind. |
| 13 | 16583 | Semi-bituminous | Pocahontas No. 3 | Simmons | Mercer | W. Va. |
| 14 | 16584 | Semi-bituminous | Pocahontas No. 3 | Bramwell | Mercer | W. Va. |
| 15 | 16585 | Semi-bituminous | Pocahontas No. 3 | Elk Ridge | McDowell | W. Va. |
| 16 | 16586 | Semi-bituminous | Pocahontas No. 3 | Big Four | McDowell | W. Va. |
| 17 | 16587 | Semi-bituminous | Pocahontas No. 3 | Jenkin Jones | McDowell | W. Va. |
| 18 | 16589 | Semi-bituminous | Pocahontas No. 3 | Boissevain | Tazewell | Va. |
| 19 | 17081 | Anthracite (buckwheat) | | | | Pa. |
| 20 | 17189 | Anthracite (buckwheat) | | Shenandoah | Schuylkill | Pa. |
| 21 | 17534 | Anthracite (buckwheat) | | | Luzerne | Pa. |
| 22 | 17590 | Anthracite (buckwheat) | | Shamokin | Northumberland | Pa. |
| 23 | 18248 | Anthracite (buckwheat) | | | | Pa |
| 24 | 14762 | Anthracite (buckwheat) | | | | Pa |
| 25 | 17563 | Semi-bituminous | Georges Creek | Lonaconing | Allegheny | Md. |
| 26 | 7244(*a*) | Semi-bituminous(*c*) | Pocahontas No. 3 | Pocahontas | Tazewell | Va. |
| 27 | 7305(*a*) | Semi-bituminous(*c*) | Pocahontas No. 3 | Pocahontas | Tazewell | Va. |
| 28 | 7308 | Semi-bituminous(*c*) | Pocahontas No. 3 | Pocahontas | Tazewell | Va. |
| 29 | 7309(*b*) | Semi-bituminous(*c*) | Pocahontas No. 3 | Pocahontas | Tazewell | Va. |
| 30 | 18193 | Semi-bituminous | Pocahontas No. 3 | Pocahontas | Tazewell | Va |
| 31 | 18198 | Semi-bituminous | Pocahontas No. 3 | Pocahontas | Tazewell | Va. |
| 32 | 18203 | Semi-bituminous | Pocahontas No. 3 | Pocahontas | Tazewell | Va |
| 33 | 18349 | Semi-bituminous | Pocahontas No. 3 | Pocahontas | Tazewell | Va. |
| 34 | 18350 | Semi-bituminous | Pocahontas No. 3 | Pocahontas | Tazewell | Va. |
| 35 | 18208 | Semi-bituminous | Lower Kittanning | Ebenburg | Cambria | Pa. |
| 36 | 18296 | Semi-bituminous | | Bering River Field | | Alaska |
| 37 | 18297 | Semi-bituminous | | Bering River Field | | Alaska |
| 38 | 18298 | Semi-bituminous | | Bering River Field | | Alaska |
| 39 | 18302 | Semi-bituminous | | Bering River Field | | Alaska |
| 40 | 18308 | Semi-bituminous | | Bering River Field | | Alaska |
| 41 | 18310 | Semi-bituminous | | Bering River Field | | Alaska |
| 42 | 18312 | Semi-bituminous | | Bering River Field | | Alaska |
| 43 | 18300 | Semi-bituminous | | Bering River Field | | Alaska |
| 44 | 18303 | Semi-bituminous | | Bering River Field | | Alaska |
| 45 | 18306 | Semi-bituminous | | Bering River Field | | Alaska |
| 46 | 18348 | Semi-bituminous | | Bering River Field | | Alaska |
| 47 | 18347 | Semi-bituminous | | Bering River Field | | Alaska |
| 48 | 18350 | Semi-bituminous | | Bering River Field | | Alaska |
| 49 | 12690 | Bituminous | Pittsburgh | Greensburg | Westmoreland | Pa. |
| 50 | 12691(*b*) | Bituminous | Pittsburgh | Greensburg | Westmoreland | Pa. |
| 51 | 7228(*a*) | Bituminous | Pittsburgh | Marianna | Washington | Pa |
| 52 | 7230 | Bituminous | Pittsburgh | Marianna | Washington | Pa |
| 53 | 7141(*a*) | Bituminous | Pittsburgh | Marianna | Washington | Pa. |
| 54 | 7458(*b*) | Bituminous | Pittsburgh | Carnegie | Allegheny | Pa. |
| 55 | 13316 | Sub-bituminous | | Batan | | Philippine Island |
| 56 | 7548(*b*) | Lignite | | Rockdale | Milan | Texas |
| 57 | 7381(*a*) | Lignite | | Rockdale | Milan | Texas |
| 58 | 7490(*a*) | Lignite | | Lytle | Medina | Texas |
| 59 | 7494(*a*) | Lignite | | Lytle | Medina | Texas |
| 60 | 7522(*b*) | Lignite | | Calvert | Robertson | Texas |
| 61 | 7534 | Lignite | | Calvert | Robertson | Texas |
| 62 | 7536(*a*) | Lignite | | Calvert | Robertson | Texas |
| 63 | 7459(*a*) | Peat briquettes | | Elizabeth City | Pasquotauk | N. C. |

(*a*) Clinker from gas producer. (*b*) Clinker from boiler furnace. (*c*) Bone coal.

[1] Herman Steffe, "On the Formation Temperature of a Few Ferro Calcic Slags and of a Few Ferrous Slags Free from Calcium, the Knowledge of which is Significant for the Smelting of Lead Ores," Dissertation, Berlin, 1908.

[2] E. Greiner, "Ueber die Abhängigkeit der Viscosität in Silikat schmelzen von ihrer Zusammensetzung," Inaugural Diss., Jena, 1907, p. 55.

seen from an inspection of these tables, the series of fuels tested include anthracite, bituminous, semi-bituminous, sub-bituminous, lignite and peat; the compositions of the ashes cover a fairly wide range, silica varying from 12.3 to 76.0 per cent; alumina from 8.6 to 34.7; ferric oxide from 3.8 to 69.7; lime from 0.6 to 18.6; and magnesia from 0.2 to 10.0 per cent.

The coal samples were ground to 60 mesh with crusher, rolls and ball mill as described in our Technical Paper 8.[1] The 60 mesh material was spread out on shallow, 6-inch, fireclay roasting dishes, and completely ashed with occasional stirring in a muffle furnace at a temperature not exceeding 750° C. All

TABLE II—PERCENTAGE ANALYSES OF ASH AND DRY COAL

| Sample No. | Analyses of Ash | | | | | | | | | Dry Coal | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | $Na_2O$ | $K_2O$ | $SO_3$ | S | Ash |
| 1 | 35.7 | 23.5 | 32.9 | 1.2 | 3.2 | 1.1 | 0.3 | 1.1 | 0.5 | 3.1 | 10.8 |
| 2 | 47.3 | 34.6 | 9.8 | 1.8 | 1.3 | 0.4 | 2.1 | 2.5 | 0.1 | 1.7 | 17.4 |
| 3 | 55.8 | 33.5 | 5.0 | 0.9 | 1.5 | 0.7 | 0.5 | 2.2 | 0.1 | 0.8 | 15.6 |
| 4 | 43.3 | 31.4 | 13.6 | 1.6 | 4.2 | 1.4 | 0.6 | 2.9 | 1.4 | 1.5 | 8.6 |
| 5 | 42.2 | 30.6 | 19.0 | 1.2 | 1.3 | 1.0 | 1.3 | 2.9 | 0.2 | 1.4 | 7.5 |
| 6 | 12.3 | 12.2 | 69.7 | 0.4 | 3.9 | 0.7 | 0.3 | 0.6 | 0.2 | 5.8 | 8.2 |
| 7 | 54.1 | 34.7 | 4.5 | 1.5 | 1.2 | 0.9 | 0.6 | 2.5 | 0.2 | 0.7 | 17.7 |
| 8 | 46.8 | 28.7 | 18.0 | 1.4 | 0.6 | 0.9 | 1.6 | 2.4 | 0.3 | 2.3 | 12.7 |
| 9 | 54.8 | 27.0 | 7.0 | 1.3 | 4.3 | 1.7 | 0.3 | 3.1 | 1.4 | 0.6 | 17.5 |
| 10 | 38.4 | 24.2 | 22.4 | 1.1 | 7.7 | 0.9 | 0.3 | 1.9 | 3.8 | 2.1 | 7.9 |
| 11 | 50.4 | 24.0 | 20.4 | 1.4 | 1.7 | 0.2 | 1.0 | 1.0 | 0.3 | 2.7 | 10.9 |
| 12 | 37.1 | 17.6 | 35.9 | 0.7 | 3.2 | 0.9 | 0.4 | 1.8 | 2.3 | 5.8 | 11.5 |
| 13 | 54.8 | 27.0 | 7.8 | 1.6 | 1.6 | 1.5 | 2.2 | 1.9 | 0.5 | 0.7 | 8.0 |
| 14 | 54.8 | 29.2 | 5.9 | 1.8 | 1.4 | 0.6 | 1.9 | 2.1 | 1.0 | 0.7 | 7.5 |
| 15 | 54.1 | 24.8 | 9.4 | 2.3 | 4.0 | 1.4 | 1.0 | 0.8 | 2.8 | 0.6 | 7.1 |
| 16 | 37.2 | 25.5 | 11.8 | 1.5 | 12.6 | 1.9 | 1.4 | 0.4 | 5.6 | 0.6 | 5.9 |
| 17 | 51.1 | 25.2 | 10.1 | 1.8 | 5.1 | 1.6 | 0.8 | 0.9 | 3.1 | 0.6 | 6.8 |
| 18 | 51.8 | 25.0 | 9.0 | 2.0 | 4.0 | 1.5 | 1.3 | 0.8 | 4.3 | 0.7 | 5.6 |
| 19 | 56.1 | 31.4 | 5.0 | 1.9 | 1.0 | 1.0 | 0.7 | 3.1 | 0.5 | 0.7 | 21.5 |
| 26 | 68.9 | 21.4 | 4.5 | 2.6 | 2.0 | 0.7 | 0.6 | 0.5 | ... | 0.6 | 17.2 |
| 27 | 69.4 | 21.5 | 4.8 | 2.0 | 1.6 | 0.8 | 0.5 | 1.4 | ... | 0.7 | 14.8 |
| 28 | 64.7 | 24.2 | 4.7 | 2.6 | 1.2 | 0.8 | 0.3 | 0.5 | 1.5 | 0.7 | 14.8 |
| 29 | 69.6 | 19.7 | 5.2 | 2.2 | 2.0 | 0.4 | 0.4 | 0.5 | ... | 0.7 | 14.1 |
| 49 | 54.7 | 32.9 | 8.9 | ... | 1.6 | 0.9 | 0.6 | 0.2 | ... | 0.9 | 11.1 |
| 51 | 54.5 | 27.0 | 12.1 | 1.8 | 1.5 | 0.4 | 0.5 | 1.9 | ... | 1.7 | 11.4 |
| 52 | 53.2 | 26.0 | 15.8 | 1.4 | 1.0 | 0.7 | 0.3 | 1.6 | 0.4 | 1.7 | 11.4 |
| 53 | 54.6 | 25.7 | 12.4 | 1.4 | 4.3 | 0.6 | 0.6 | 1.3 | ... | 1.4 | 12.5 |
| 54 | 56.8 | 28.2 | 11.3 | 1.2 | 1.0 | 0.8 | 0.6 | 1.6 | ... | 1.8 | 12.3 |
| 55 | 15.2 | 8.6 | 13.3 | ... | 18.1 | 10.0 | 5.3 | 1.8 | 26.9 | ... | 8.2 |
| 56 | 47.9 | 23.7 | 5.5 | 2.0 | 18.6 | 3.3 | 0.4 | 0.2 | ... | 1.5 | 16.6 |
| 57 | 46.2 | 24.3 | 6.2 | 1.8 | 18.5 | 3.0 | 0.6 | 0.5 | ... | 1.5 | 15.5 |
| 58 | 43.2 | 16.9 | 7.1 | 1.6 | 12.2 | 1.7 | 0.2 | 0.3 | 16.0 | 2.2 | 19.1 |
| 59 | 52.5 | 21.5 | 8.8 | 1.6 | 14.4 | 2.4 | 0.5 | 0.2 | ... | 2.2 | 19.1 |
| 60 | 47.5 | 29.1 | 5.3 | 2.0 | 14.0 | 2.2 | 0.4 | 0.3 | ... | 1.4 | 18.6 |
| 61 | 39.3 | 24.8 | 3.8 | 1.9 | 14.9 | 1.7 | 0.2 | 0.4 | 12.5 | 1.4 | 16.6 |
| 62 | 46.5 | 28.4 | 5.2 | 2.0 | 16.1 | 2.3 | 0.7 | 0.2 | ... | 1.4 | 16.6 |
| 63 | 76.0 | 11.7 | 4.5 | 1.0 | 2.8 | 3.1 | 1.0 | 0.9 | ... | 1.4 | 32.3 |

of the ash was finally put through a 100 mesh screen and thoroughly mixed.

### PREPARATION OF CONES

Sufficient ash to make the desired number of cones was transferred to an agate mortar, moistened with 10 per cent dextrin solution and worked into a plastic mass with a spatula or pestle. After moistening the brass mold (Fig. 1) with kerosene to prevent sticking, the plastic material was firmly pressed into it with a knife spatula, and the surface struck off smooth to make a neat solid triangular pyramid. The cone was then pushed out of the mold by applying a small knife blade at the base. With a little practice and proper lubrication of the mold this can be done at once after molding without waiting for the cone to dry.

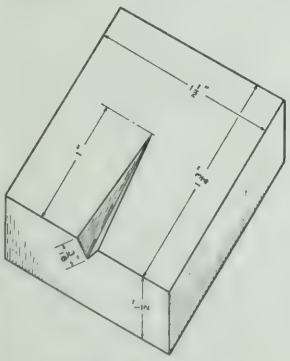



FIG. 1—BRASS CONE MOLD

After drying, the cones were mounted in a refractory base made up of a mixture of two parts of kaolin to one part of alumina ($Al_2O_3$). This mixture was moistened with water to make it workable and enough taken for the base to be made and spread upon a sheet-iron plate. A small hole was made into which the cone was set and the base material worked around the bottom of the cone so that it would be firmly set at the desired inclination in the base. The iron plate was then put on a hot-plate and the mounted cones dried slowly until all water was driven off. The dextrin was then burned out by igniting the mounted cones in a muffle, after which they were ready for use. In the earlier experiments the cones were made directly from the 100 mesh ash; later it was found that grinding the ash to an impalpable powder (or at least to pass 200 mesh) made a more substantial and more easily molded cone than 100 mesh material. Four different sizes of cones were used:

No. 1, side of base 1/4 inch, height 1 inch
No. 2, side of base 1/4 inch, height 1 1/2 inches
No. 3, side of base 3/16 inch, height 1 inch
No. 4, side of base 1/2 inch, height 2 1/2 inches

### GENERAL METHOD OF HEATING

The general procedure in making a softening temperature determination was the same with all the furnaces used, though necessarily the details varied in the different furnaces. The test piece was put into the cold, or nearly cold, furnace and the furnace was heated at the rate of 10 to 15° per minute up to a point not less than 200° C. below the probable softening point, at which point the rate (usually 2 or 5° per minute) which had been adopted for that particular determination was begun. Temperature readings were taken every 5 minutes, and more frequently when approaching the softening temperature. Observations of the appearance of the cone were made at least as often as temperature readings were taken, special care being taken to note any deformation or warping due to shrinking before actual softening began. The point of initial softening or deformation was taken as the temperature where the first noticeable bending, rounding at the top, or swelling of the cone took place. Warping of the cone due to shrinkage was not considered as the beginning of fusion.

The softening point, deformation point, or "fusion point" so-called, was taken as the temperature where the apex of the cone had bent over to touch the base, or, failing to bend, had fused down to a lump or ball. Sketches (Fig. 2) were made of the appearance of the cone at the initial and final deformation points and at several intermediate points of deformation, with the corresponding temperatures. Immediately after reading the temperature corresponding to complete deformation, the current or other source of heat was reduced so that the appearance of the cone could be verified by examination after removal from the furnace.

[1] F. M. Stanton and A. C. Fieldner, "Methods of Analyzing Coal and Coke," *Technical Paper* 8, Bureau of Mines (1913), pp. 7–9.

TEMPERATURE MEASUREMENTS

The temperature measurements were made in two ways: (1) by means of a Heraeus Pt-PtRh thermocouple with Siemens and Halske high-resistance millivoltmeter, in the platinum-resistance, Meker and muffle No. 2 furnaces, and the down-draft ceramic kiln; (2) by means of a Wanner optical pyrometer in the molybdenum, carbon-resistance, and Northrup furnaces. The thermocouple and millivoltmeter were

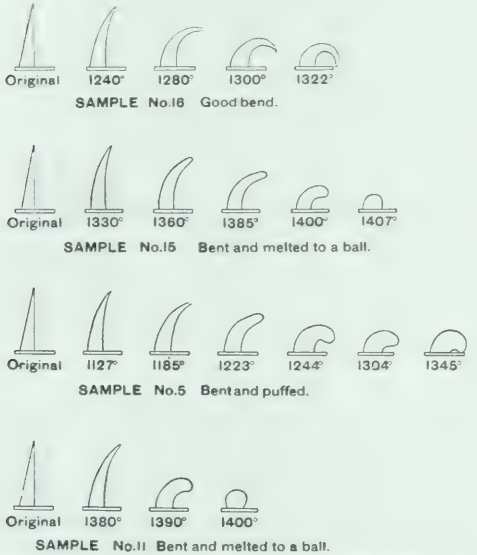



FIG. 2—APPEARANCE OF ASH CONES AT VARIOUS STAGES OF SOFTENING

standardized from time to time in the physical laboratory of the Bureau under the direction of Dr. J. K. Clement by comparison with a standard thermocouple. The cold junction was kept at the temperature of melting ice during standardization and during use in measuring temperatures. Further checks on the system of furnace and pyrometer were obtained by placing crystals of pure diopside[1] in the positions occupied by the ash cones and noting the temperature of melting; usually the crystal melted between 1381 and 1395° C. (corrected temperature readings). The melting point of diopside is 1391° C.[2]

The Wanner pyrometer, which was originally standardized by the Reichsanstalt, was rechecked by the Bureau of Standards after most of the work described in this paper was completed and found to conform to the original standardization. It was checked daily against the amyl acetate flame. As this pyrometer was used only with those furnaces which had strongly reducing atmospheres, it was possible to check the accuracy of the pyrometer readings and the blackbody conditions of the furnace by placing thin strips of Kahlbaum's pure copper or Kahlbaum's pure nickel in place of the cones and noting the apparent melting temperature. This was done at least once a week, and at the beginning and the end of each series of tests. The results obtained in these checks will be given in the discussion pertaining to each furnace.

[1] Obtained through the kindness of Dr. Arthur L. Day, Director of the Geophysical Laboratory.

[2] Arthur L. Day and R. B. Sosman, "The Melting Points of Minerals in the Light of Recent Investigations on the Gas Thermometer," *Am. J. Sci.*, [4] 31 (1911), 340.

RESULTS OBTAINED IN DIFFERENT FURNACES

A—MEKER MUFFLE FURNACE NO. 29

This furnace (Fig. 3) is a simple gas muffle furnace. It consists of a sheet-iron shell, with a refractory fireclay lining. The muffle *a* is of magnesite and rests on the front of the furnace and on two points at the rear. Except that at the front it is entirely surrounded by the combustion space over the Meker burner *b*, which is supplied with two inlets, one for gas and one for air under pressure, the gas burns under and around the muffle and the products of combustion pass out of the chimney. In order to attain the higher temperatures it was necessary to adjust the gas and air so that a slight flame issued from the chimney.

In operation, the cones *c*, generally four in number, were set in one base and the base raised about $^3/_{16}$ inch from the bottom of the muffle by small supports at each end. The front was closed by an asbestos board door, *d*, with a slit in it just large enough to admit the thermocouple *e*, which could be moved so that the couple could be placed very close to each cone as it went down. The thermocouple was protected from reducing gases by a glazed Marquardt tube 6 mm. in diameter and closed at one end. The maximum variation in temperature in moving the couple along

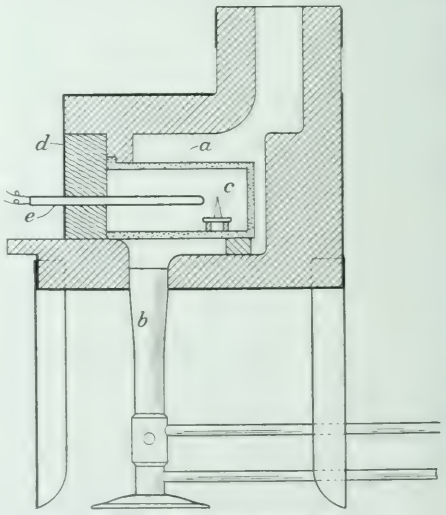



FIG. 3—MEKER MUFFLE FURNACE NO. 29

the line of cones from one side of the muffle to the other was from 10 to 15° C. Inasmuch as four different cones were heated simultaneously it was not possible to begin the 2°-per-minute rate of heating at 200°

below the approximate softening point of each cone. Usually the furnace was heated up to about 1000° C. in 1 hour. The rate was then decreased to 2° per minute until the last cone had fallen, provided it would soften in the possible range of the furnace: 1437° C. was the highest temperature that was reached, and in many cases, owing to fluctuating gas pressure, 1375° was the upper limit. Naturally the rate of heating at the higher temperatures was unavoidably reduced to 1 and even $^1/_5$° per minute. Natural gas and air at a pressure of about 15 pounds per square inch were available. No attempt was made to remove reducing gases from the muffle by circulating air, hence, variable quantities of reducing gases undoubtedly penetrated the magnesite muffle.

All the results obtained, using two different sizes of cones, are given in Table III.

TABLE III—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MEKER MUFFLE FURNACE, USING TWO SIZES OF CONES

Rate of heating, 2° per minute; 100 mesh ash; cones inclined 35° from the vertical

| Sample No. | Softening point Cone 1 $^1/_4$ in. × $1^1/_2$ in. ° C. | Softening point Cone 2 $^1/_4$ in. × 1 in. ° C. | Difference in duplicates of Cone 1 | Difference in duplicates of Cone 2 | Difference in average values of Cones 1 & 2 | Average softening interval Cone 1 ° C. | Average softening interval Cone 2 ° C. |
|---|---|---|---|---|---|---|---|
| 10 | 1235 | .... | ... | .. | .... | 115 | .. |
| 11 | 1239 | .... | ... | .. | .... | .. | ... |
| | 1323 | .... | ... | .. | .... | ... | ... |
| | 1281 | .... | 12 | .. | .... | 157 | ... |
| 12 | 1275 | .... | ... | .. | .... | 197 | ... |
| 13 | 1406 | 1298 | ... | .. | .... | ... | ... |
| | .... | 1248 | ... | .. | .... | ... | ... |
| | .... | 1273 | ... | 50 | 133 | 48 | 49 |
| 14 | .... | 1403 | ... | .. | .... | ... | ... |
| | .... | 1431 | ... | .. | .... | ... | ... |
| | .... | 1417 | ... | 28 | .... | ... | ... |
| 15 | .... | 1200 | ... | .. | .... | ... | ... |
| | .... | 1171 | ... | .. | .... | ... | ... |
| | 1307 | 1186 | ... | 29 | 121 | 54 | 68 |
| 16 | 1233 | 1213 | ... | .. | .... | ... | ... |
| | 1216 | 1211 | ... | .. | .... | ... | ... |
| | 1225 | 1212 | 17 | 2 | 13 | 44 | 34 |
| 17 | 1278 | 1190 | ... | .. | .... | ... | ... |
| | 1206 | 1174 | ... | .. | .... | ... | ... |
| | 1242 | 1182 | 72 | 16 | 60 | 74 | 24 |
| 18 | 1271 | 1223 | ... | .. | .... | ... | ... |
| | 1306 | 1185 | 35 | 38 | +85 | 57 | 38 |
| | 1289 | 1204 | ... | .. | .... | ... | ... |
| 1 | 1164 | .... | ... | .. | .... | ... | ... |
| | 1303 | .... | 139 | .. | .... | 96 | ... |
| | 1234 | .... | ... | .. | .... | ... | |
| 4 | 1265 | 1300 | ... | 10 | —40 | ... | 13 |
| | .... | 1310 | ... | .. | .... | ... | |
| | .... | 1305 | ... | .. | .... | ... | |
| 5 | 1388 | 1376(*a*) | ... | .. | +12 | 8 | 45 |
| 6 | 1437 | .... | ... | .. | .... | 220 | ... |
| 8 | 1357 | 1350 | ... | .. | .... | ... | ... |
| | .... | 1336 | ... | 14 | +14 | ... | 46 |
| | .... | 1343 | ... | .. | .... | ... | |
| 9 | 1335 | 1309 | ... | 18 | +17 | 35 | 220 |
| | .... | 1327 | ... | .. | .... | ... | .. |
| | | 1318 | ... | .. | .... | ... | .. |
| Average..... | | | 55 | 23 | +46 | 92 | 60 |

The $^1/_4$ inch by $1^1/_2$ inch cone gave more definite indications of softening than the $^1/_4$ inch by 1 inch cone as shown by the smaller softening interval (temperature range from initial to final deformation) and smaller differences in duplicate determinations. The softening points of the taller cone average 46° less, as would be expected on account of the greater bending moment.

### B—MUFFLE FURNACE NO. 2

This furnace was a fireclay assay muffle set in a chamber made of firebrick and heated by a Buffalo Dental Company burner, using natural gas and compressed air.

The operation of this furnace was similar to that of the Meker muffle furnace, the front being closed by a door of asbestos board with a slit in it for the thermocouple. The essential difference between this furnace and the Meker furnace was in the size and texture of the muffle, it being larger: 8 inches long, 4 inches wide, and 3 inches high. Also the fireclay, being quite porous, permitted easier penetration of the furnace gases than the dense magnesite muffle of the Meker furnace.

TABLE IV—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MUFFLE FURNACE NO. 2, USING TWO SIZES OF CONES

Rate of heating, 2° per minute; 100 mesh ash; cones inclined 35° from the vertical

| Sample No. | Softening Point Cone 1 $^1/_4$ in. × 1 in. ° C. | Softening Point Cone 2 $^1/_4$ in × $1^1/_2$ in. ° C. | Difference in duplicates of Cone 2 | Difference in average values | Average softening interval Cone 2 ° C. |
|---|---|---|---|---|---|
| 1 | .... | 1195 | .. | .... | .. |
| | .... | 1189 | .. | .... | .. |
| | .... | 1192 | 6 | .... | 38 |
| 4 | 1276 | 1226 | .. | +50 | 19 |
| 5 | .... | 1320 | .. | .... | 73 |
| 6 | .... | 1320 | .. | .... | ... |
| | .... | 1316 | .. | .... | ... |
| | .... | 1318 | 4 | .... | 153 |
| 8 | .... | 1251 | .. | .... | 94 |
| 9 | .... | 1242 | .. | .... | ... |
| | .... | 1325 | .. | .... | ... |
| | .... | 1284 | 83 | .... | 85 |
| 10 | 1237 | 1212 | .. | .... | ... |
| | .... | 1186 | .. | .... | ... |
| | .... | 1199 | 26 | +38 | 38 |
| 11 | 1268 | 1212 | .. | .... | ... |
| | .... | 1215 | .. | .... | ... |
| | .... | 1214 | 3 | +52 | 34 |
| 12 | .... | 1195 | .. | .... | ... |
| | .... | 1168 | .. | .... | ... |
| | .... | 1182 | 27 | .... | 135 |
| Average..... | | | 25 | +47 | 74 |

As shown in Table IV the average softening intervals, differences in average values of Cones 1 and 2, and differences in duplicates, are practically the same as those obtained in the Meker furnace. However, a striking difference is shown on comparing the softening points of those samples which were run in both furnaces, under apparently the same conditions; with

TABLE V—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MEKER FURNACE AND MUFFLE FURNACE NO. 2

Rate of heating, 2° per minute; 100 mesh ash; cones inclined 35° from the vertical

| Sample No. | Size of cone Inches | Softening Point Muffle furnace No. 2 ° C. | Softening Point Meker furnace ° C. | Difference |
|---|---|---|---|---|
| 4 | $^1/_4 \times 1^1/_2$ | 1226 | 1310 | —84 |
| 5 | $^1/_4 \times 1^1/_2$ | 1320 | 1376 | —56 |
| 8 | $^1/_4 \times 1^1/_2$ | 1251 | 1343(*a*) | 92 |
| 9 | $^1/_4 \times 1^1/_2$ | 1284(*a*) | 1318(*a*) | 34 |
| 10 | $^1/_4 \times 1$ | 1237 | 1235 | + 2 |
| 11 | $^1/_4 \times 1$ | 1268 | 1281(*a*) | —13 |
| | | | Average, | —46 |

(*a*) Average of two determinations.

but one exception the results of the muffle furnace No. 2 are from 13 to 92° lower than those of the Meker furnace, the average difference as given in Table V being 46°. (This difference is believed to be due to a greater reduction to ferrous iron due to the greater penetration of reducing-furnace gases through the walls of the porous fireclay muffle than through the denser magnesite muffle of the Meker furnace.) Both furnaces were usually operated with some flame appearing at the chimney, since it was only by this method of adjusting gas and air that the higher tempera-

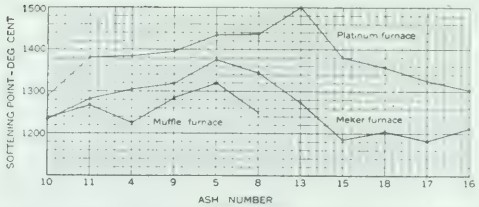
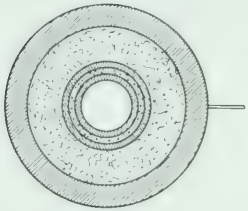



FIG. 4—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MEKER FURNACE AND MUFFLE FURNACE NO 2

tures could be attained at the desired rate of heating. As a matter of fact, the gray appearance of the base material, in which the cone was mounted, in many of the tests was in itself an evidence of reduction, since when heated under strictly oxidizing conditions it took on a slight reddish tint. The marked lowering of softening temperature by partial reduction is shown graphically in Fig. 4, where the muffle and Meker furnace results are compared with those obtained on the same ashes in a platinum-resistance furnace. Obviously no reduction could take place in the electric furnace. Differences of over 200° C. were found in some cones.



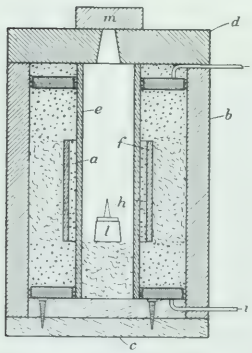



FIG. 5—Carbon resistance furnace: *b*, fireclay cylinder, 8 inches external diameter, 10 inches high, 1-inch wall; *d*, fireclay cover plate, 2 inches thick; *m*, fireclay plate covering peep-hole; *f*, alundum tube, 3-inch bore, 4 inches long, 5/16-inch wall; *e*, alundum tube, 2-inch bore, 9 inches long, 1/4-inch wall; *a*, granular carbon resistor consisting of electrode carbon crushed to pass a 6-mesh and remain on a 12-mesh screen; *i*, *i*, wrought-iron electrodes; *o*, granular carbon; *p*, magnesia insulating material; *l*, inverted alundum crucible; *h*, ash cone.

### C—CARBON RESISTANCE FURNACE

On account of ease of construction and ability to attain high temperatures, various forms of granular carbon, graphite, or kryptol resistance furnaces are often used for determining the softening temperatures of refractory materials.[1] A furnace of this type was built as shown in Fig. 5. The resistor or heating element was the 1/4 inch thick annular ring of granular carbon, *a*, between the two concentric alundum tubes *e* and *f*. This heating zone was 1 inches high. The current of 20 to 30 amperes was regulated with a water rheostat, the temperature being measured with a Wanner optical pyrometer. A uniform heating zone was obtained by carefully packing the carbon between the exactly centered alundum tubes. After 10 or 15 runs, heating became irregular, due to oxidation of the resistor, which then necessitated repacking the resistor and sometimes renewal of the alundum tubes. In view of these difficulties, the interior of the furnace deviated somewhat from black-body conditions, which introduced an error in the absolute values of the temperature measurements. Observations of the melting points of copper and nickel indicated that this error was usually less than 30° at the copper point, and less than 50° C. at the nickel point.

All the softening temperatures determined in the carbon resistance furnace are given in Table VI. The rate of heating, fineness of ash, size and inclination of cone were the same as in the preceding series. The essential difference was a reducing atmosphere of carbon monoxide which reduced the ferric oxide of the ash more or less completely to metallic iron. Consequently, the softening points obtained bear little relation to those obtained subsequently in air as shown by comparison with the platinum-furnace series in Fig. 8; with but one or two exceptions the results are considerably lower (15° to 250° C.). A closer relation is shown between the carbon-furnace series and the two muffle-furnace series as plotted in Fig. 6.

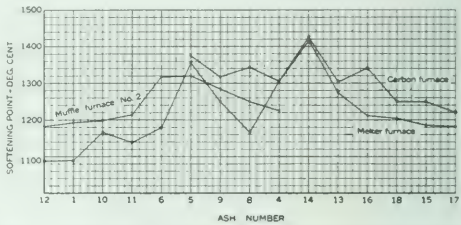



FIG. 6—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN THE CARBON RESISTANCE FURNACE, MEKER FURNACE AND MUFFLE FURNACE NO. 2

TABLE VI—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN THE CARBON RESISTANCE FURNACE, USING TWO SIZES OF CONES

Rate of heating, 2° per minute, 100 mesh ash; cones inclined 35° from vertical

| Ash No | Softening Point in °C. | | | | | | | | Maximum difference of determinations | | Difference in average values of Cones 1 and 2 | Average softening interval Cone 2, 5° C. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cone 1 1/4 in. × 1 in. | | | | Cone 2 1/4 in. × 1 1/2 in. | | | | | | | |
| | Individual determinations | | | Average | Individual determinations | | | Average | Cone 1 | Cone 2 | | |
| 1 | 1100 | | | 1100 | 1076 | 1104 | | 1090 | | | −10 | 8 |
| 2 | 1675 | 1587 | .... | 1631 | 1587 | 1562 | 1630 | 1593 | 88 | 68 | −38 | 53 |
| 3 | 1570 | 1545 | .... | 1558 | 1562 | .... | .... | 1562 | 25 | | −4 | |
| 4 | 1335 | 1241 | 1494 | 1357 | 1182 | 1213 | 1210 | .... | 253 | | | |
| | .... | .... | .... | .... | 1210 | 1480 | 1540 | 1306 | .. | 358 | −51 | 70 |
| 5 | 1331 | 1371 | 1500 | 1401 | 1259 | 1263 | 1402 | .... | | | | |
| | .... | .... | .... | .... | 1502 | .... | .... | 1356 | 169 | 243 | −45 | 121 |
| 6 | 1260 | 1161 | 1199 | 1207 | 1179 | | | 1179 | 99 | | +28 | 18 |
| 7 | 1630 | 1695 | | 1663 | 1645 | 1630 | | 1638 | 65 | 15 | +25 | 70 |
| 8 | 1185 | 1199 | .... | 1192 | 1164 | 1167 | .... | 1166 | 14 | 3 | +26 | 56 |
| 9 | 1365 | 1271 | 1345 | 1327 | 1245 | 1251 | 1230 | 1249 | 94 | 41 | +78 | 51 |
| 10 | 1185 | 1188 | | 1187 | 1161 | 1173 | .... | 1167 | 3 | 12 | +20 | 31 |
| 11 | 1173 | 1206 | | 1190 | 1124 | 1185 | | 1139 | 33 | 32 | +51 | 24 |
| 12 | 1084 | 1092 | | 1088 | 1088 | 1088 | .... | 1088 | 8 | 0 | 0 | 30 |
| 13 | 1380 | 1400 | | 1390 | 1322 | 1331 | 1313 | 1322 | 20 | 18 | +68 | 129 |
| 14 | 1520 | 1520 | | 1520 | 1420 | 1427 | .... | 1424 | 0 | 7 | +96 | 136 |
| 15 | 1322 | 1300 | | 1311 | 1274 | 1241 | 1234 | 1250 | 22 | 40 | +61 | 85 |
| 16 | 1402 | 1385 | | 1394 | 1350 | 1331 | | 1341 | 17 | 19 | +53 | 94 |
| 17 | 1267 | 1234 | | 1251 | 1241 | 1210 | 1210 | 1220 | 33 | 31 | +31 | 39 |
| 18 | 1331 | 1300 | | 1316 | 1241 | 1255 | 1255 | 1250 | 31 | 14 | +66 | 83 |
| Average | | | | | | | | | +57 | +58 | +41 | 64 |
| Average, excluding 4 and 5 | | | | | | | | | +37 | +23 | | |

As in the muffle- and Meker-furnace tests, the 1/4 inch by 1 1/2 inch cone softened at from 10 to 90° lower in temperature than the 1/4 inch by 1 inch cone, the average difference being 41° and the former

[1] A. V. Bleininger and G. H. Brown, "The Testing of Clay Refractories, etc.," Technologic Paper No. 7, Bureau of Standards, **1911**, p. 14; Zay Jeffries "Notes on the Gran-Annular Electric Furnace," *Met. and Chem. Eng.*, **12** (1914), 154–157.

cone giving better duplication. The average softening intervals and the average differences in duplicates of Cone 2 were practically the same as in the gas furnaces.

D—NORTHRUP FURNACE

The Northrup high-temperature electric furnace[1] has a cylindrical heater unit of Acheson graphite which is surrounded by a refractory cylinder and non-conducting material. The whole is enclosed in an air-tight monel-metal jacket. Carbon monoxide is formed by the oxidation of a thin-walled graphite cylinder which fits snugly within the heater unit; this reducing atmosphere protects the resistor from rapid oxidation. Fig. 7 is a vertical section through the heater unit with the ash cone in position for testing.

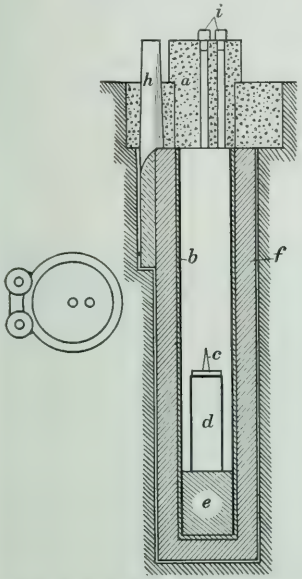



FIG. 7—Arrangement for softening-temperature test in Northrup furnace: *f*, graphite heater unit; *b*, graphite tube for protecting heater from oxidation, 1-5/8" internal diameter, 12¾ inches long; *c*, solid graphite cylinder, 2 inches high; *d* inverted alundum extraction capsule, 3 inches high; *a*, a refractory plug; *i*, *i*, observation holes, ¼ inch diameter

Temperature measurements were made with a Wanner optical pyrometer which was sighted directly on the cone and its base through the peep-hole *i* in the center of the cover plug *a*. The degree of accuracy of the temperature measurements is shown by the following melting points of copper and nickel obtained under test conditions:

| Kahlbaum's pure copper M. p. = 1083° C.(*a*) | Apparent melting point | Kahlbaum's pure nickel M. p. = 1450° C.(*a*) | Apparent melting point |
|---|---|---|---|
| July 10, 1914 | 1088 | July 11, 1914 | 1448 |
| July 14, 1914 | 1088 | July 22, 1914 | 1455 |
| July 27, 1914 | 1096 | July 27, 1914 | 1447 |
| Aug. 13, 1914 | 1088 | | |

(*a*) Provisional temperature scale used by Bureau of Standards

A change of procedure was made in the Northrup-furnace series, in that the ash was ground to an impalpable powder and molded into a $^3/_{16}$ inch by 1 inch cone which was mounted vertically. It will be shown hereinafter in the discussion of the tests made in the molybdenum and platinum furnaces that the difference in softening points due to changing these factors is small, usually less than 30°, and, therefore, not sufficient to materially affect the comparison of the Northrup-furnace series with the other furnace series, to show the influence of different atmospheres.

[1] E. F. Northrup, "A New High-Temperature Electric Furnace," *Met. and Chem. Eng.*, **12**, 31.

Since both the Northrup and granular-carbon resistance furnace produced atmospheres of carbon monoxide, similar softening temperatures were expected in the two series; that such did not prove to be the case is shown in Table VII and Fig. 8. In 16 of 18 samples tested, the softening points in the Northrup furnace were higher than in the carbon furnace; the maximum was 396° and the average difference for the series was 134°. The check made on materials of known melting points, at various times during the course of these experiments, effectually rule out the possibility of attributing these large differences to errors of temperature measurement. The only explanation we have to offer is that in the carbon furnace the reduction of ferric oxide to metallic iron did not proceed as rapidly or as completely as in the Northrup furnace; in the latter furnace the ash cone is heated in a closed tube of graphite which excludes practically all air circulation so that only nitrogen, CO, and a fractional per

TABLE VII—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN NORTHRUP GRAPHITE RESISTANCE FURNACE WITH THOSE OBTAINED IN CARBON RESISTANCE FURNACE

Reducing atmosphere of carbon monoxide; rate of heating, 2° per minute

| Ash No. | Softening point in ° C. Northrup(*a*) furnace | Carbon(*b*) furnace | Difference | Softening interval, in ° C. Northrup furnace | Carbon furnace |
|---|---|---|---|---|---|
| 1 | 1131 | 1090 | + 41 | 67 | 8 |
| 2 | 1645+ | 1593 | + 52 | 167 | 53 |
| 3 | 1502 | 1562 | — 60 | 100 | ... |
| 4 | 1360 | 1306 | + 54 | 181 | 70 |
| 5 | 1645 | 1356 | +289 | 30 | 121 |
| 6 | 1455 | 1179 | +276 | 355 | 18 |
| 7 | 1645 | 1638 | + 7 | 75 | 70 |
| 8 | 1562 | 1166 | +396 | 392 | 56 |
| 9 | 1440 | 1249 | +191 | 70 | 51 |
| 10 | 1385 | 1167 | +218 | 72 | 31 |
| 11 | 1185 | 1139 | + 46 | 85 | 24 |
| 12 | 1080 | 1088 | — 8 | 16 | 30 |
| 13 | 1520 | 1322 | +198 | 18 | 129 |
| 14 | 1551 | 1424 | + 27 | 124 | 136 |
| 15 | 1427 | 1250 | +177 | 140 | 83 |
| 16 | 1470 | 1341 | +129 | 48 | 94 |
| 17 | 1390 | 1220 | +170 | 95 | 39 |
| 18 | 1455 | 1250 | +205 | 124 | 83 |
| | | Average, | +134 | 120 | 64 |

(*a*) Ash ground to an impalpable powder; $^3/_{16}$ inch by 1 inch cones in vertical position. Single determinations only.
(*b*) 100 mesh ash; ¼ inch by 1¼ inch cones inclined 35° from vertical; average of two or more determinations in most cases.

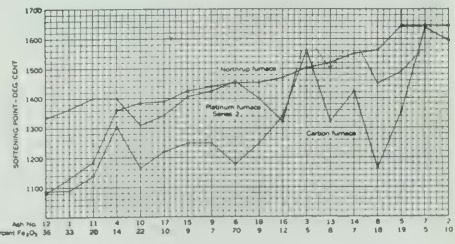



FIG. 8—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN NORTHRUP CARBON RESISTANCE AND PLATINUM FURNACES

cent of $CO_2$ would surround the ash at temperatures above 1100°. Such an atmosphere would reduce the ferric oxide to metallic iron and thus prevent the formation of a low melting ferrous silicate eutectic. On the other hand, the carbon furnace permitted air to leak into the heating space as shown by the appearance of carbon monoxide flames at the peep-hole and around the cover-plate. Sufficient carbon dioxide may, therefore, have been present to retard the reduction to metallic iron, thus leaving enough of the strongly fluxing ferrous oxide in the ash to form a low-melting fluid

eutectic which caused the cone to collapse at a comparatively low temperature. Examination of polished sections of fused cones from both furnaces disclosed more metallic iron in those from the Northrup furnace.

*(To be concluded in June issue)*

BUREAU OF MINES, PITTSBURGH, PA.

## PRACTICAL METHODS FOR THE DETERMINATION OF RADIUM[1]

### I—INTERCHANGEABLE ELECTROSCOPE AND ITS USE

By S. C. LIND

Received January 4, 1915

The interest in radium-bearing ores and other radioactive products intermediate between ores and high-grade radium salts has become so general that the quantitative determination of radium has ceased to be a problem exclusively of the physicist or the radioactivitist. The time appears to have come when any good analyst or assayer should be prepared to make radium determinations, and it is the object of this paper to describe a modified form of electroscope as well as some methods which it is hoped may prove useful in this direction.

The "emanation-method," which will be fully described in Part II of this paper, is recognized as the most accurate method for determining radium in small quantities. The two difficulties against its general employment are at present the time required and the expense of the necessary apparatus. To obtain the highest degree of accuracy with present methods, accumulation of emanation in a closed volume for a month is required in many instances to insure that the quantity of emanation is proportional to the radium content. This delay of one month in obtaining the results is for practical purposes almost prohibitive.[2] Furthermore, only one determination per day can be conveniently carried out with one electroscope, so that in a laboratory where a number of daily determinations are to be made the initial expense for electroscopes becomes excessive.

To overcome this latter difficulty an electroscope of simple construction has been devised. All of its parts except the telescope can be made by any mechanic. Its chief advantage lies, however, in the fact that it is constructed in two easily detachable parts; the upper part, consisting of the telescope and leaf system, may be transferred to any number of separate discharge chambers. The latter are inexpensive and hence the interchangeable top permits one to employ any desired number of instruments with little additional expense.

Methods of shortening the time required for an analysis to a few days without sacrificing accuracy can also be attained and will be described with examples in a second paper.

The classes of substances which one has to analyze for radium, are, in America, chiefly the uranium ores, carnotite and pitchblende, and the crude radium-barium sulfates or chlorides of varying degrees of concentration of radium. The practice up to the present with respect to ores has been to estimate the radium from the uranium content, while buying and selling exclusively on the latter. Whatever uncertainty may have been involved, due to the supposed variability of the Ra/U ratio in carnotites appears to have been removed by the recent establishment of its constancy at normal value.[1] This would appear to justify more than ever the existing practice, but, on the other hand, it is incontestable that the accurate determination of uranium is difficult and time-consuming. It is the author's opinion that radium can be determined directly with more accuracy than uranium, and hence it is recommended to replace the uranium determination by a direct electroscopic measurement of radium by the emanation method.

Of course in dealing with any ore in which uranium has been removed or added, or the Ra/U ratio in any

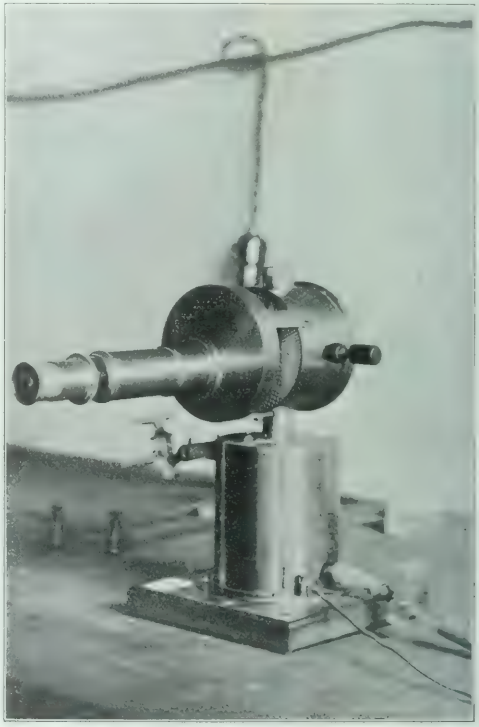


FIG. 1

way disturbed, it becomes essential to determine radium directly. This applies also to crude sulfate or chloride, or any kind of mill products, and to any ore suspected of addition of uranium, or to one from which radium has been wholly or partly removed, or to any sample of ore to which a spurious addition of radium has been made.

It may also be mentioned that the failure of many attempts to extract radium profitably on a commercial scale may be attributed in most cases to the neg-

[1] Published with permission of the Director of the Bureau of Mines.

[2] For further discussion see paper to follow.

[1] Lind and Whittemore, *J. Am. Chem. Soc.*, **36** (1914), 2066.

lect or the inability of the operator to make an accurate quantitative determination of radium in the various products obtained at each step of the process. Consequently the radium has often been lost or the whole operation conducted blindly without hope of success. Photographic methods, for example, are wholly unsuitable for this or any quantitative measurement; and even radiation methods using the $\alpha$-ray electroscope for solids, though presenting great convenience of operation, must be subject always to control by the emanation method.

CONSTRUCTION OF THE ELECTROSCOPE

The detachable electroscope is shown in Figs. 1 and 3, and the detached emanation chamber in Fig. 2. The latter is a gas-tight brass cylinder 4 in. in height and $3^1/_2$ in. in diameter with a volume of about one-half a liter. The brass wall of the cylinder is about $^1/_{16}$ in. thick, except the bottom plate, which is about $^1/_8$ in. thick. The bottom plate projects $^1/_2$ in. outside the cylinder and is screwed to a wooden base $6 \times 6$ in. This projection also carries a binding post for grounding the instrument. The vertical cylinder projects into the base into which it is carefully soldered so as to make a gas-tight joint.

On account of the difficulty of obtaining gas-tight brass stop-cocks, glass ones have been used and are connected to the plain brass outlet tubes *o* (Fig. 3) from the cylinder by means of heavy rubber tubing wired on and with the ends covered with piscein glue. These outlet tubes are $^1/_4$ in. internal diameter and placed $^1/_2$ in. from the top and bottom on opposite sides of the cylinder.

The electrode (*e*) is a brass cylinder $^1/_2$ in. in diameter, projecting downward in the vertical axis of the cylinder to within $^1/_2$ in. of the bottom and clearing the top by the same distance. The electrode is suspended by a small brass rod $^1/_8$ in. in diameter which screws into the top of the electrode, passes upward through the insulating material (*d*) and terminates in a small conical cap (*c*) serving to make metallic contact with the leaf system above.

The best insulating material for an instrument of this type has been found to be a high-grade sealing wax, such as "bankers' specie." It has the advantage over sulfur of furnishing at the same time a gas-tight connection and a good electrical insulation, and is, of course, much less expensive than amber. The sealing wax insulation is bridged across the bottom of a cylindrical neck $^3/_8$ in. internal diameter and 1 in. high above the top of the cylinder. It is desirable to have the minimum layer of wax which will give the necessary strength. A layer $^1/_4$ in. deep should be ample. The additional height of the neck merely furnishes a friction support for the upper part of the instrument. The electrode and insulation can be removed by unscrewing the whole collar, which is threaded into the upper brass plate of the cylinder $^3/_{16}$ in. thick. The collar screws down on a thin lead or rubber washer to insure gas-tightness. The removal of the collar and electrode enables one to melt the wax into place with great ease and also to place the electrode in position without disturbing the soldered joint at the bottom of the emanation chamber.

A friction cap (see Fig. 2) fitting snugly down over the neck and the projecting electrode stem protects the insulation from contamination when detached from the upper part of the instrument.

The leaf system and telescope are carried by the upper part of the instrument (Fig. 1) and have the advantage over some instruments of being fixed in a perfectly rigid position with respect to each other.

The horizontal cylinder *b* (Fig. 3) containing the leaf system is $1^1/_4$ in. deep and $3^1/_4$ in. in diameter; the ends are closed by sheet mica held in place by steel wire rings which fit in grooves in the edge of the cylinder in the same way that an automobile tire is held in place. This system has proved most convenient and far preferable to the use of screws. Inside the mica plates and in close contact with them, fine iron wire gauze serves to conduct off any stray electrical charge. Circular openings in the gauze $1^1/_2$ in. in diameter furnish a clear field of vision opposite the leaf system.

The leaf system (*f*) is supported from the top of the cylinder where it is held in place by the sealing wax insulation set in a milled-head cap (*g*) which screws into a vertical collar on the cylinder $^1/_4$ in. in height. The cap is hollowed out inside to contain the insulating wax from which a flat brass rod (*f*) $^1/_4$ in. broad, about $^1/_{16}$ in. thick, and $2^1/_4$ in. long projects downward, terminating below in a light brass spring (*s*) to make a

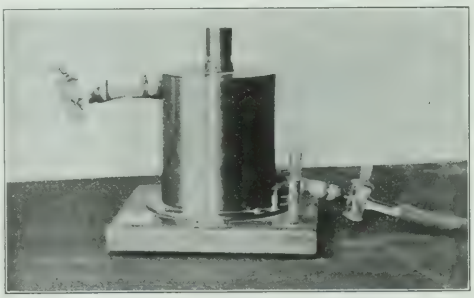


FIG. 2

slight contact with the conical top of the electrode of the ionization chamber.

This spring should touch the electrode lightly or it will throw the leaf system out of position. The aluminum leaf itself, about 2 in. in length, is attached to a small offset at the top of the brass rod by a moisture contact. The whole leaf system may be removed by unscrewing the cap without disturbing the rest of the instrument. In case the cap does not screw down tightly into the desired position, it may be advisable to put a drop of solder across the joint between screw head and collar to prevent accidental displacement of the leaf.

The charging device (*k*) consists of a brass rod threaded horizontally through the side of the case in a hard rubber insulation (*n*), sloping first upward inside the case at an angle of 45° and then horizontally, so as to make contact with the brass rod of the leaf system while charging, or by turning to be grounded against the wire grating of the outer case.

A collar $^3/_4$ in. long below the bottom of the cylinder makes a fairly snug contact fit over the collar on top

of the discharge chamber and serves as support. It is also desirable to have some kind of wooden frame to hold the upper half of the instrument when detached from the base.

Opposite the aluminum leaf is a vertical brass plate (not shown in diagram) parallel to the leaf which may be pushed in almost to touch the latter and thus protect it from mechanical disturbance during transportation. Whenever the instrument is in use this protector should be withdrawn against the outer case, turning it crosswise, if necessary, to remove it as far as possible from the leaf.

Instead of supporting the telescope on an upright fixed to the same wooden base as the rest of the electroscope, it appeared preferable to fasten it firmly to the case carrying the leaf system. Three arms such as the one shown in Fig. 1, carrying a solid brass vertical plate, are firmly screwed on to the case of the leaf system. The telescope fits tightly into a heavy horizontal collar which is screwed into the front plate thickened by one or two plates fastened to the brass front plate to increase the depth of the screw thread. The telescope may be fit very firmly into place and soldered after focusing, or the collar may be split and carry a tightening screw for readjustment.

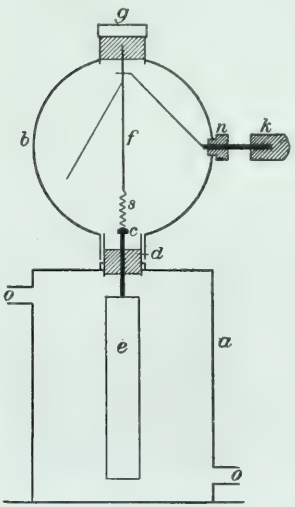



FIG. 3—CROSS SECTION OF ELECTROSCOPE WITH DETACHABLE IONIZATION CHAMBER

The telescope used is a Bausch and Lomb type with a 32 mm. objective and a No. 5 eyepiece, carrying a micrometer scale serving to measure the rate of discharge of the leaf. The eyepiece fits very firmly into its case so as to rotate with difficulty after the micrometer scale has been set parallel to the leaf.

Whenever possible it is desirable to have a charging battery by means of which a charge can be maintained for some time on the instrument. Otherwise one can charge with amber or hard rubber (with an ordinary rubber comb for example).

The glass tube (see Figs. 1 and 2) fixed into the wooden base of the instrument about $1^1/_2$ in. from the cylinder, serves to hold a small sealed tube of radium salt used in controlling the calibration of the instrument. A suitable quantity of radium (about 1 mg. of element, in a sealed tube) furnishes a constant source of penetrating radiation which may be conveniently employed to control the calibration by measuring the rate of discharge when this tube is placed in the glass tube fixed into the base, and by making comparison with the discharge obtained in the same way at the time the calibration with emanation was originally made. Such a measurement can be made in a few minutes and saves a great deal of time in avoiding the repetition of the calibration with emanation, in case no marked change is found to have taken place in the rate of discharge, which is usually the case.

USE OF THE ELECTROSCOPE IN THE EMANATION METHOD

The principle underlying the use of the emanation electroscope is that, in a given discharge chamber containing at two different times different quantities of radium emanation, the ionization and consequent rate of discharge will in each case be proportional to the quantity of emanation present. If in one case this quantity is known, the unknown quantity can be determined by a direct comparison of the two rates of discharge. The principle seems very simple and with the observation of a few essential precautions is really so in application.

Owing to the rapid decomposition of radium emanation into the series of elements, Radium A, B, and C, which deposit as a solid "active layer" on the walls of the chamber, and contribute very materially to the activity, it is necessary to wait three hours after the introduction of the emanation for the active deposit to have rached a *maximum*. This maximum is maintained with little change between the third and fourth hours and hence the measurement of the rate of discharge may be made during this period.

It is also to be noted, however, that these active decomposition products of radium emanation carry a positive electrical charge when formed and hence the position at which they are deposited in the chamber will be somewhat dependent upon the electrical field to which they are exposed during deposition, and in turn the ionization and rate of discharge will be influenced. It would seem simple to allow the deposition of the active layer always to take place with no electrical field, but the difficulty here is, that as soon as the field is made for measuring the rate of discharge, a shift in the position of newly formed RaA takes place so rapidly that even in the few minutes necessary for measurement, the rate of discharge may change considerably, either increasing or decreasing according to whether as the new position of RaA is more or less favorable to ionization. To overcome this difficulty one practice is to keep the electroscope charged during the entire three hours of activation, but this may be quite inconvenient if different instruments are being used on the same charging line, and it has been found more satisfactory in this laboratory to charge *for fifteen minutes* before the measurement. This allows any shift of RaA to be practically completed and that of RaC (through RaB, an $\alpha$-rayless product), not to have proceeded to any considerable degree.

The measurement itself consists in determining with a stop-watch the time elapsing during the passage of the leaf over a certain part of the scale, always reading between the same scale divisions. Two or three closely

agreeing measurements suffice, but if the deviations are greater than 1 per cent, an average of ten measurements should be taken. The discharge is then reckoned in terms of scale divisions per second, from which is subtracted the "natural leak" of the instrument which should be determined before the introduction of emanation. Even with a double contact of wax insulation, the natural leak should maintain a low value of about 0.003–0.005 divisions per second.

Another source of error, which seems especially pronounced in using sealing wax as insulation, is found in the so-called "electrical soak" of the insulator, meaning that a certain time is necessary for the insulator to become fully charged. Unless sufficient time is allowed (not less than 15 minutes) for this process to complete itself, the rate of discharge will be erratic.

The procedure in the use of the electroscope is then as follows:

1—Set up electroscope as shown in Fig. 1, and charge for 15 minutes from a battery with just sufficient voltage to hold the leaf on the part of the scale to be used later.

2—Observe the natural leak during 15 minutes.

3—Carry out the calibration control by means of penetrating rays if radium is available for this purpose.

4—Detach the top and evacuate the lower chamber to the desired vacuum.

5—Pass the emanation-air mixture through a sulfuric acid drying tube into the evacuated chamber and restore normal pressure.

6—Allow the emanation to stand in the discharge chamber for three hours.

7—Charge for fifteen minutes as before.

8—Take three readings if agreements are good, or ten if deviations are greater than one per cent.

9—Clean out the emanation chamber by drawing dry, dust-free air through it for some time (over night if convenient).

10—Calculate the discharge and subtract the natural leak, expressing both in divisions per second.

11—The corrected discharge is compared with the calibration of the instrument to determine the quantity of radium under measurement.

### CALIBRATION OF THE ELECTROSCOPE

The calibration of the electroscope is carried out in exactly the same way as in ordinary measurement, except that a known quantity of emanation is introduced. This known quantity may be obtained in two ways:

(1) From a standard solution of some radium salt by passing air through it until its emanation is all transformed into the electroscope. This practice has two disadvantages, the necessity of having and taking care of such a standard solution and the uncertainty attaching to the quantity of radium emanation removed from it, owing to the great tendency of radium in such small quantity to be precipitated out in part or be occluded in the walls of the vessel during prolonged standing. In short, the practice of employing standard radium solutions, though quite general, is not to be recommended, and has been pronounced unsatisfactory at the Radium Institute[1] in Vienna. (2) The preferable practice is to use high-grade analyzed pitchblende, dissolving a suitable quantity for each standardization, and calculating the quantity of radium from the uranium analysis. The quantity of radium emanation obtained on dissolving will not correspond exactly to the radium content because a small fraction (2 to 5 per cent) of the gas diffuses from the ore; this fraction, termed the "emanating power," must be determined by sealing a quantity of the ore in a tube for a month or more, and drawing off the emanation into an electroscope by the passage of air. The emanating power thus determined in the standard sample is used as a subtractive correction. Quantities of radium emanation are convenient which will produce a discharge of the order of 1 to 2 scale divisions per second.

### EXAMPLE

Given a standard pitchblende containing 60 per cent uranium metal and having an emanating power of 3 per cent. If the Ra/U ratio is $3.33 \times 10^{-7}$, one milligram of pitchblende contains $2 \times 10^{-10}$ g. of radium, but since only 97 per cent of this radium can give off emanation, one milligram of pitchblende on dissolving will furnish emanation equivalent to $1.94 \times 10^{-10}$ g. of radium. For the electroscope herein described use 20 to 40 mg. of high-grade pitchblende.

Contamination of the discharge chamber may come about through the gradual accumulation of active deposit on the inner walls, which results in the increase of the natural leak of the instrument. For this reason more emanation than necessary for a measurement should never be introduced. The removal of emanation from the chamber should take place at once after the completion of the measurement, and to avoid the introduction of any emanation that may be present in the laboratory air, it is better to draw air from the outside, passing it through a train of cotton batting to remove dust and through sulfuric acid to remove moisture. Should the discharge chamber become contaminated in spite of all precautions, the chamber should be opened and the walls thoroughly washed with dilute (1 to 3) nitric acid, and then with distilled water and finally dried. Repeat this operation until the natural leak is sufficiently reduced. Contamination of the insulation itself usually necessitates its complete removal.

In measurements of great accuracy it is desirable to calibrate each discharge chamber separately, but by taking greater precaution in the construction and position of the electrode each chamber could be made to have the same electrical capacity and hence one calibration would serve for all. It seems quite practicable to reproduce chambers which shall have the same calibration value within two per cent.

The convertible electroscope may also be used with other forms of discharge chamber than that used for emanation. For example, it may be used in water analysis by attaching to a water chamber of the fontacto-

[1] 48th Communication, p. 5, by Stefan Meyer, *Sitzb. Vienna Acad.*, **122**, *IIa*, June, 1913

meter type, or may be attached to an open $\alpha$-ray chamber such as is used for the cursory examination of ores, or to any other desired form of discharge chamber.

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## HEAT TRANSMISSION CAPACITY OF A SILICA DISH

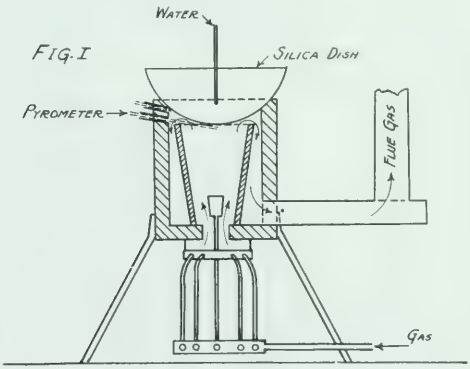
By W. K. LEWIS

Received January 20, 1915

In coöperation with the Thermal Syndicate Company, an investigation[1] has been carried on in this laboratory into the heat transmission capacity of fused silica dishes as used in the concentration of corrosive liquids, such as sulfuric and phosphoric acids, zinc chloride, etc. The only source of energy employed was the cooling of hot combustion gases, formed by burning Boston City gas in an ordinary gas crucible furnace, arranged for this work as shown in Fig. I. It is here desired to make a report of the results to date.

The temperature under the dish was controlled by regulation of the gas and air supply, the flame being

FIG. I




at all times non-luminous. This temperature was measured at various points under the dish by movable thermo-couples as indicated in the diagram. The setting of the dish was such that the surface exposed was 66 sq. in. Solutions of different concentrations were evaporated, the boiling points ranging from 100° C. for water up to 240° C. for strong zinc chloride. Each solution was kept constant in amount and boiling point by running in water at exactly the rate at which it was evaporated; the measurement of this rate of feed of make-up water gave the heat absorption of the solution, the heat consumption per unit weight of water evaporated being equal to the total heat of the steam at the temperature and pressure evolved, less the heat of the liquid fed in. These quantities were taken from the steam tables. Each run was continued a sufficient length of time to eliminate any appreciable error due to uncertainty as to the constancy of the amount of boiling liquid in the dish.

The heat supply coming from the cooling of hot gases, there must evidently be a drop in the temperature of the gases under the dish. Measurements made as stated, with the thermo-couple, proved this to be approximately a straight line function from the center out as far as the dish was exposed to the gases. This is shown for a typical run in Fig. II. The total drop in temperature from the center to the exposed edge increased as the temperature under the center was raised, as is depicted in Fig. III. The total heat absorbed by the boiling liquid in the case of water itself is shown as a function of the average temperature[1] under the dish in Fig. IV.

Mere inspection of this last plot shows that the heat transfer rises much more rapidly than the first power of the temperature difference, and that in consequence the phenomena must involve more than simple conduction. To appreciate the significance of this curve in any way an analysis of the factors involved is essential. A hot body can give up heat to a cold one in only three ways—by conduction, by convection, and by radiation. The hot gas, which is the source of energy in this case, is incapable of radiating energy in appreciable amounts, and must therefore give up its heat by conduction and convection only. The work of Langmuir[2] makes it probable that the transfer of heat from a hot gas to a solid is essentially a matter of conduction through a thin stationary film of gas on the surface of the solid, convection currents in the body of the gas outside this film being sufficient to transport the energy up to the outside surface of the stationary gas as rapidly as it is conducted through this film to the solid. Under the experimental conditions of this investigation it is probable, therefore, that the heat given up by the gas is proportional to the difference in temperature between the gas and the solid with which it is in contact, and furthermore that the proportionality factor, namely, the coefficient of heat transfer, may be considered as constant through the relatively narrow temperature range employed in this work.

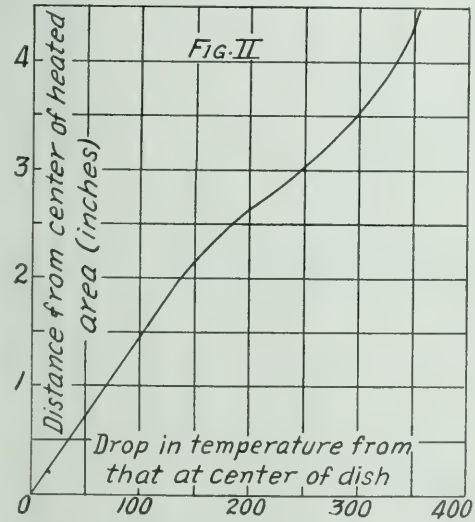
On the other hand, the hot gases in this furnace were in contact not only with the surface of the dish which it was desired to heat, but with the surface of the furnace walls as well. These walls are therefore heated to a temperature approximating that of the gas itself, but at this high temperature they also lose heat rapidly. Even neglecting heat conducted away through these walls to the outside air, which on account of their thickness and low heat conductivity will be small, large amounts of heat will be given up by radiation to the cold surface of the dish. The only possible source of this heat is the energy content of the hot gases, but in order for the walls to receive this heat from the gas the wall temperature must be lower than that of the gas and higher than that of the dish. There exists, therefore, a dynamic equilibrium, heat flowing by conduction from the gas to the fur-

[1] Thesis by A. H. Spaulding, submitted in June, 1914, in partial fulfilment of the requirements for the degree of S.B. from the Massachusetts Institute of Technology. All experimental data in this article are taken from this thesis.

[1] Obtained in a way to be described later.

[2] *Phys. Rev.*, April, **1912**.

nace walls, and by radiation an equal amount passing from the walls to the dish, the temperature of all the elements remaining constant. The thermo-element, or rather its encasing porcelain tube, is subject to approximately the same influence as the wall, and will therefore record, not the temperature of the gas, but that of the solid wall. Indeed there is known no accurate method of measuring the temperature of a hot gas which is interchanging heat with a solid with which it is in contact, since any solid introduced into the gas will, due to this radiation effect, have a temperature intermediate between that of the gas and the body with which it is interchanging heat. This temperature will be determined by the relative rates of conduction and radiation, the first being proportional to the temperature difference, and the second to the difference in the fourth powers of the temperatures.




Call the temperature of the dish $t$, and, in view of the high heat conductivity of fused silica, assume this temperature equal to that of the boiling solution. Designate the temperature of the furnace walls by T, and the unknown temperature of the hot gas by $\Theta$. Call the heat absorbed by the dish, per unit area and time, Q, and the coefficients of heat transfer by radiation and conduction from the furnace walls and the gas to the dish K and $k$, respectively; and $k'$ the conductivity coefficient from gas to furnace walls. Moreover for each unit area of the dish let there be an area of furnace wall equal to A. It is evident then that the following relationships may be expected to hold:

$$Q = K(T^4 - t^4) + k(\Theta - t),$$

and

$$K(T^4 - t^4) = k'A(\Theta - T).$$

From this second relationship,

$$\Theta = T + \frac{K}{k'A}(T^4 - t^4).$$

Substituting this value of $\Theta$ in the first equation,

$$Q = K\left(1 + \frac{k}{k'A}\right)(T^4 - t^4) + k(T - t).$$

In this equation it will be necessary to use an average value of T, since the temperatures show wide variations. The average value chosen is the temperature at the center of the dish less $^2/_3$ the total decrease in temperature from the center to the edge.[1] It is difficult to test the applicability of this formula directly, owing to its complexity, but if it be differentiated with respect to T, for the case of the water runs, where $t$ was constant, there results

$$\frac{dQ}{dT} = 4K\left(1 + \frac{k}{k'A}\right)T^3 + k.$$

If, therefore, the slope of the curve of Fig. IV be plotted against the third power of the absolute temperature,

[1] This method of estimating the average temperature under the dish was derived as follows: As previously stated, the temperature drop from center to edge of the dish was experimentally found to be linear. Calling the radius of the setting R, the temperature at the center T, the drop in temperature between the center and the edge of the dish $\Delta T$, and the temperature at any variable distance $r$, from the center $T_r$, this last quantity is determined by the equation

$$T_r = T - \frac{\Delta T}{R} r.$$

For the moment assume the heat transfer at any point proportional to the temperature difference at that point, and furthermore consider the curvature of the dish so slight that its exposed surface may be taken as a flat plate. Under these conditions the area exposed to the temperature $T_r$, at the radial distance, $r$, from the center of the setting, is $2\pi r dr$, and the heat transfer,

$$dQ_r = k(2\pi r dr)(T_r - t)$$

$$= k(2\pi r dr)\left(T - \frac{\Delta T}{R} r - t\right).$$

Integrating between the limits o and R, and inserting for the total area of the dish, $a = \pi R^2$, this gives

$$Q_{av} = k[(T - {}^2/_3\Delta T) - t].$$

In other words, under these conditions the average temperature to be used in calculating heat transfer is the temperature at the center of the heated area, less two-thirds the total drop in temperature to the edges.

For the case of a spherical dish, as was employed in this work, in a setting such that the exposed surface subtends at the center of the sphere a radial angle of $2\alpha$, the formula for the average temperature to be used in calculating heat transfer which is proportional to the temperature difference, a formula derived exactly similarly to the above becomes

$$T_{av} = T - \Delta T\left[\frac{\alpha\sin\alpha - \cos\alpha}{2(1 - \cos\alpha)}\right].$$

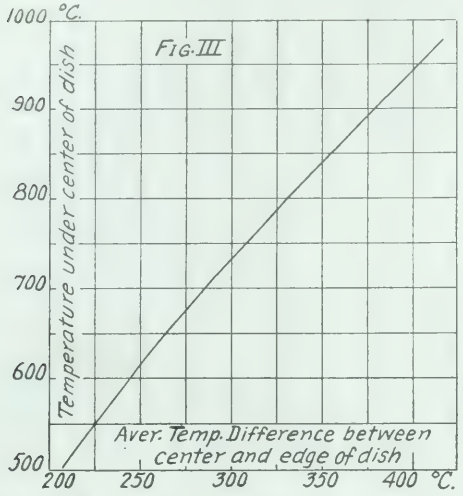
That this formula simplifies to the above for the case of a spherical dish of infinite radius, *i. e.*, for a flat plate, can be shown by successive differentiation of numerator and denominator. Inserting the value of $\alpha$ for the dish employed, the temperature correction is found to be 0.687 times the total drop in temperature, rather than 0.667 times that drop as before.

The flow of heat from furnace walls to the dish is proportional, however, not to the difference in temperature but to the difference of the fourth powers of the temperatures. For the case of such radiant flow to a flat plate, the average temperature is given by the equation

$$T^4_{av} = T^4 - \frac{8}{3}T^3\Delta T + 3T^2(\Delta T)^2 - \frac{8T}{3}(\Delta T)^3 + \left(\frac{\Delta T}{3}\right)^4$$

This equation is derived in exactly the same way as the preceding ones. This formula gives an average temperature slightly higher than the two-thirds rule. Thus for T = 893, $\Delta T$ = 225, and T − $^2/_3\Delta T$ = 673, while this last formula gives $T_{av}$ = 679. For the higher temperature, T = 1223, $\Delta T$ = 410, and T − $^2/_3\Delta T$ = 949, the radiation formula gives 964. These differences are within the experimental error. Having shown for the previous case that the spherical shape does not appreciably affect the correction term, the complicated expressions for radiant flow into the sphere have not been derived, but in all instances the temperature under the center of the dish, less two-thirds the drop to the edges, has been taken as an average.

a straight line should result. This has been done in Fig. V, and from this line the constants $k$ and




$K\left(1 + \frac{k}{k'A}\right)$ obtained, giving in gram calories per sq. cm. per second,

$$Q = \frac{0.000197}{10^8}(T^4 - t^4) + 0.000563(T - t).$$

This equation reproduces the average experimental curve of Fig. IV within 1 per cent. It also reproduces the data on all solutions of zinc chloride and sulfuric acid well within the experimental error (about 10 per cent).

There is no data at hand for the determination of the relative values of the constants $k$ and $k'$, but from the similar nature of the surfaces it is probably allowable to call them equal.[1] Owing to the configuration of the furnace walls employed it is also difficult to decide exactly how much of their surface is capable of heat interchange with the dish by radiation, but the constant A has been carefully estimated for this case as 4.8. This gives for the radiation constant, K, from fire brick to fused silica, the value 0.000163.

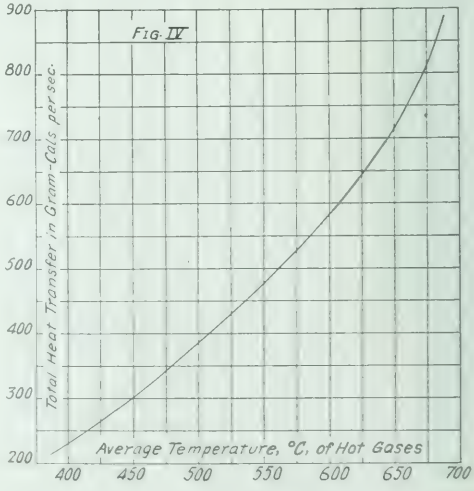
Since the value of K for black body radiation is only 0.000128,[2] this high result proves that there is somewhere an error in the work. To eliminate all possibility of an influence of the gas flame itself upon the heat transmission, the burner was moved from below the furnace to one side and the hot gases led to the setting through a horizontal flue. The two arrangements are shown in Figs. VI and VII. Within the experimental error, no change in performance was found, so the discrepancy must be sought elsewhere.

Inasmuch as the results indicate a higher radiation effect than can correspond to the temperatures, it is natural to suspect that the true average temperatures are higher than the values assumed. The estimation of the average temperature by subtraction of two-thirds the drop in temperature from center to edge from the value at the center is based on the assumption that all parts of the surface of the furnace are equally effective in radiation. In consequence of the configuration of this setting it is evident that those parts of the furnace walls in the center radiate more directly upon the dish, and therefore give up more heat to it, than those at the outside of the furnace. This would mean that, in averaging the temperatures under the dish, those at the center should be given more weight than those near the circumference. This assumption has been tested by using as the average temperature under the dish the arithmetical mean of the temperatures at center and edge; at the highest point on the experimental curve, the temperature at the center being 950° C., this raises the average temperature by 67°, from the previous value of 680° to 747°. At all other points the change is less than this, falling to a difference of only 29° at the lowest point on the curve. The heat transfer was now plotted against this new average temperature, giving a curve similar to Fig. IV; the equation of this curve was determined in exactly the same way as before, giving

$$Q = \frac{0.000136}{10^8}(T^4 - t^4) + 0.00074(T - t).$$

The maximum deviation from the average experimental curve is less than 2 per cent. In this equation $k = 0.00074$, and $K\left(1 + \frac{k}{k'A}\right) = \frac{0.000136}{10^8}$.

We do not know the relative values of $k$ and $k'$, but,

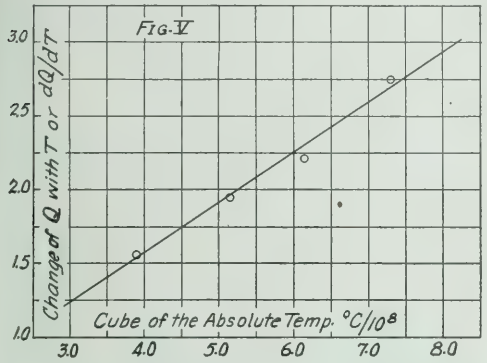



as already stated, A has been estimated as 4.8. Two assumptions will now be made: first, that $k = k' = 0.00074$, on which basis $K = 0.000113$; and second that $k' = 0.75\,k = 0.000555$, giving $K = 0.000106$; the second asumption is probably nearer the truth.

[1] Since the gases flow parallel to the furnace walls, but impinge upon the dish, $k'$ will tend to be less than $k$. On this account we shall also consider the assumed approximation, $k' = 0.75\,k$.

[2] Kurlbaum, W. A., **65** (1898), 746.

Regarding the radiation coefficient, the very fact that the surface is the interior of an enclosed space leads one to expect a high value. The only comparable numerical determination would seem to be that of Wamsler,[1] who found nearly identical values for various inorganic compounds such as metallic oxides, and indeed for all substances investigated other than polished metals. He found for lime mortar a coefficient




of 0.000112, with which the above figures are in close agreement. The general consistency of the results calculated on the basis of the arithmetical mean as the average temperature justify their use as the best data at present available. The results of this work may therefore be generalized in the form of the following equations:

I—The heat given up by a furnace gas, between the temperature of 400° and 1000° C., to a silica dish upon which it impinges is expressed by the formula

$$Q = k(\Theta - t).$$

$\Theta$ and $t$ are the temperatures of the gas and the dish, respectively; if Q is in gram calories per square centimeter per second, while temperatures are in degrees centigrade, $k = 0.00074$, but for Q in B. t. u. per square foot per hour, and Fahrenheit temperatures, $k = 5.5$. Furthermore, it is probable that the same formula gives the heat interchange between gas and any unglazed ceramic material, but that for parallel flow of the gas past the surface the coefficients should be approximately 0.00056 and 4.1, respectively.

II—The heat received by radiation per unit area and time by the cold surface of a silica dish from hot firebrick walls entirely surrounding it is given by the equation

$$Q = K(T^4 - t^4),$$

in which T and $t$ are the absolute temperatures of walls and dish. For Q in gram calories per square centimeter per second, with Kelvin temperatures, $K = 0.000106$, while in B. t. u. per square foot per hour, with absolute Fahrenheit degrees, $K = 0.134$. This expression is also probably valid for heat interchange by radiation between all unglazed ceramic materials.

III—The temperature, T, of the walls entirely surrounding a cold surface which is receiving heat from a hot gas as the only original source of energy, the walls losing heat in no other way than by radiation to this cold surface, is given by the equation

$$K(T^4 - t^4) = kA(\Theta - T),$$

the symbols having the significance given above, and A being the ratio of the hot furnace wall surface to the cold surface absorbing the heat.

IV—The total heat absorbed from a hot gas by a cold surface in a furnace setting is:

$$Q = K(T^4 - t^4) + k(\Theta - t)$$

$$= K\left(1 + \frac{k}{k'A}\right)(T^4 - t^4) + k(T - t).$$

Q cannot be expressed directly in terms of $\Theta$, but T is found from the equation

$$K(T^4 - t^4) = k'A(\Theta - T),$$

best by graphical methods in the case of a large number of problems.

While the utility of this data in the design not only of silica dish evaporators, but in that of most fuel-fired furnaces as well, is evident on its face, three important points have come up in the progress of this work which are not brought out in the preceding discussion. In the first place it can be seen from the last equation quoted above that the greater the area of the furnace walls, the more nearly their temperature approaches that of the gas, and therefore the greater the radiation to the cold surface. Since the heat received by the cold surface directly from the gas by conduction is dependent only on the temperature of the gas, this increased radiation is clear gain in useful heat transmission-capacity of the system. The furnace design should therefore provide for the great-

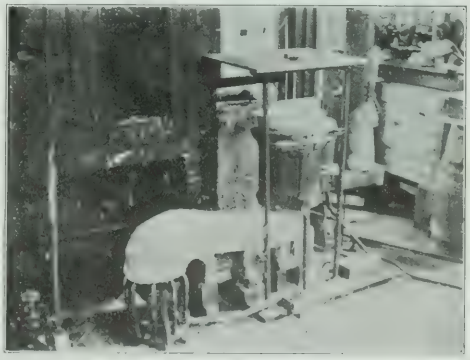


FIG. VI

est possible area of furnace wall, so placed as to get effective contact with the moving gas, and at the same time capable of radiating as directly as may be to the heat-absorbing surface.

This last object will often be difficult of attainment, but if the interior furnace structure be of material of high heat conductivity, heat absorbed on any surface exposed to the gas will be conducted to surfaces

[1] Wamsler, "Mitteilungen über Forschungsarbeiten," Heft 98, 1911.

radiating directly to the cold body, and thus efficiently transmitted to the point desired. The flue space should therefore be filled with an open checkerwork of refractory of high heat conductivity, so designed that the gases will pass freely through the mass and come in effective contact with it, on surfaces as rough as possible, and furthermore so placed that the resistance to flow from absorbing surface to radiating surface will be a minimum.

In the second place, these results suggest an effective method of avoiding one of the serious difficulties in the operation of silica dish evaporators, using counter current flow of hot gases and acid, in the concentration of sulfuric acid. As ordinarily operated, those dishes directly over the fire are so strongly heated both by the hot gases and to an even greater

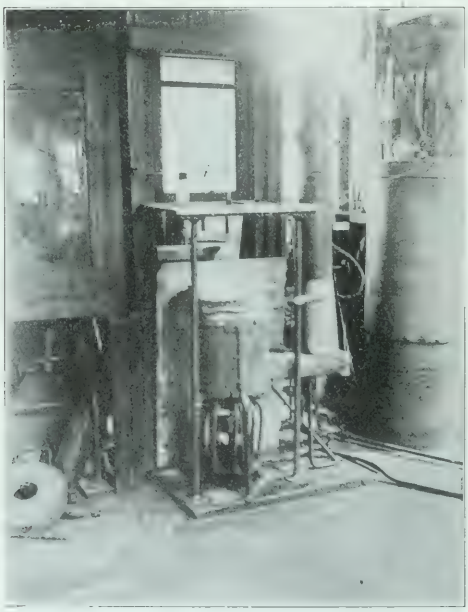


FIG. VII

extent by the direct radiation from the fuel bed itself that bumping and excessive breakage result. The temperature of the fuel bed can be lowered by carrying a thick fire and using insufficient air, producing mainly carbon monoxide by the combustion. If necessary, steam may be injected below the grate to further lower the temperature by the heat absorption of the water gas reaction. The combustible gas thus produced will give up its sensible heat to the lowest dishes in the series, but will not be excessively hot. At various points along the flue, air may now be admitted to complete the combustion. Under operating conditions previously employed this would cut down the evaporative capacity of the system, due to the resistance to flow of heat from gas to dish, but by increasing the heat absorption area of refractory in the flue, this will be avoided, as the heat absorbed from the gas by conduction will be transmitted to the dish in the most efficient manner possible, namely by radiation. Furthermore, this will enable the operator to maintain at every point in the flue, and not merely over the fire alone, the highest temperature the dishes can stand without danger, and thus distinctly increase total evaporative capacity. Not only this, but inasmuch as under these conditions the air supply can be easily controlled, this change will make possible the reduction of the excess air employed, thus improving the recovery of waste heat from the flue gases, and thereby increasing the efficiency of the furnace.

The last point to be emphasized is the fact that the same equation for heat flow expresses within the experimental error the heat transmission in the case of all solutions tested, varying in boiling point from 100° C. for water to 240° C. for zinc chloride. The concentration and viscosity of the solution plays no appreciable part in the phenomena. The reason for this is that the great resistance to flow is found at the boundary surfaces between gas and solid, and in comparison with this the resistance through the dish and from the dish to the solution, whatever its nature, is negligible. It seems therefore justifiable to use this data for the concentration of any liquid in apparatus of the type employed.

SUMMARY

The heat transmission capacity of a silica dish heated in a gas furnace has been experimentally determined, and it is shown that this capacity can be expressed as consisting of the sum of two terms, the first a conduction term proportional to the temperature difference, and the second a radiation term proportional to the difference of the fourth powers of the temperatures. The coefficients of these two terms have been estimated, and expressed in forms directly applicable to the solution of problems in design. The utility of the results in the study of furnaces in general has been pointed out, and suggestions as to desirable modifications in furnace construction and operation have been made. On the other hand, these results are merely a report of progress to date, and further work is under way in which it is being attempted to more accurately control the surface areas involved, to measure the true surface temperatures by means of an optical pyrometer, to estimate the true gas temperatures by carefully controlled air supply and calculation from the known heats of combustion and specific heats, and also by determination of total heat content, and to study the influence of velocity upon the results.

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## THE INFLAMMABLE LIMITS OF MIXTURES OF GASOLINE VAPOR AND AIR[1]

By GEORGE A. BURRELL AND HUGH T. BOYD

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In this report are shown experiments having to do with limits of complete inflammation in mixtures of

[1] Published by permission of the Director of the Bureau of Mines.

gasoline vapor and air. The limits were determined in connection with coöperative work between the Bureau of Mines and the City of Pittsburgh on the prevention of explosions in sewers. Gasoline is so widely used in internal combustion motors and for other purposes that the limits are of interest to users of gasoline generally. Some of the gasoline used was a refinery distillate of 73° specific gravity, Baumé scale. The fractionation analysis as made by Dr. L. W. Dean, of the petroleum laboratory, Bureau of Mines, follows:

FRACTIONATION ANALYSIS OF GASOLINE

| Temp. ° C. | Per cent by weight | Temp. ° C. | Per cent by weight |
|---|---|---|---|
| 50 | 0.90 | 110–120 | 7.30 |
| 50– 60 | 9.00 | 120–130 | 4.90 |
| 60– 70 | 14.50 | 130–140 | 3.20 |
| 70– 80 | 14.40 | Residue | 2.70 |
| 80– 90 | 13.80 | | |
| 90–100 | 12.90 | Total | 94.50 |
| 100–110 | 10.90 | Loss | 5.50 |

The methods of determining the per cent of gasoline vapor in mixtures are those published in THIS JOURNAL.[1]

## INFLAMMABLE LIMITS OF MIXTURES OF GASOLINE VAPOR AND AIR

In preparing mixtures of gasoline vapor and air for the inflammability experiments, the air was shaken with the gasoline to saturation in a 2400 cc. bottle and then enough of the stock mixture withdrawn from the bottle and diluted with air to form a desired mixture. The latter was always analyzed prior to exploding it. No precaution was taken to remove water vapor.

The mixtures were first tested in a Hempel explosion pipette of 100 cc. capacity, using mercury as the confining fluid. Two platinum wires entered near the top of the pipette, across which a spark was made to jump by means of an induction coil driven by five dry cells. Inflammation was deemed complete when, upon ignition of the mixture, flame filled the vessel as far as could be judged by the eye.

THE LOW LIMIT OF INFLAMMABILITY OF MIXTURES OF GASOLINE VAPOR AND AIR; IGNITING SPARK AT TOP OF THE HEMPEL PIPETTE

| No. of test | Percentage of gasoline vapor | Remarks |
|---|---|---|
| 1 | 1.8 | No visible result |
| 2 | 1.9 | No visible result |
| 3 | 1.9 | No visible result |
| 4 | 1.9 | No visible result |
| 5 | 1.9 | No visible result |
| 6 | 2.0 | Complete inflammation |
| 7 | 2.0 | Complete inflammation |
| 8 | 2.0 | Complete inflammation |
| 9 | 2.1 | Complete inflammation |
| 10 | 2.1 | Complete inflammation |
| 11 | 2.2 | Complete inflammation |
| 12 | 2.2 | Complete inflammation |
| 14 | 3.2 | Complete inflammation |

According to the above results complete inflammation occurred when the mixtures contained between 1.9 and 2.0 per cent of gasoline vapor. Mixtures containing less gasoline vapor than the above, of course, underwent some slight burning next the spark, but there was no appreciable propagation of flame in them.

In order to obtain data regarding the influence of the position of the igniting spark on the limits of inflammability, experiments were next conducted under the same conditions as the foregoing, except the igniting spark was placed at the bottom of the explosion vessel.

[1] G. A. Burrell and I. W. Robertson, "The Determination of Gasoline Vapor in Air," THIS JOURNAL, 7 (1915), 112.

THE LOW LIMIT OF INFLAMMABILITY OF MIXTURES OF GASOLINE VAPOR AND AIR; IGNITING SPARK AT BOTTOM OF THE HEMPEL PIPETTE

| Trial No. | Percentage of gasoline | Remarks |
|---|---|---|
| 1 | 2.15 | Complete inflammation |
| 2 | 2.00 | Complete inflammation |
| 3 | 1.94 | Complete inflammation |
| 4 | 1.78 | Complete inflammation |
| 5 | 1.73 | Complete inflammation |
| 6 | 1.62 | Complete inflammation |
| 7 | 1.50 | No inflammation |

All of these mixtures of 73° Baumé gasoline were analyzed before and after explosion.

Some flame occurred near the spark in the mixture analyzing 1.50 per cent, but only about 0.3 per cent of $CO_2$ was formed.

This method, then, gives in the Hempel explosion pipette, firing from below, a low limit between 1.5 and 1.6 per cent as against 1.9–2.0 when fired from above. It also gives a good check on the low limit obtained in the 2800 cc. bottle—1.4–1.5 per cent. There is a difference of only 0.1 per cent. This would tend to show that under the same conditions the initial impulse has almost no effect upon the low limits of complete propagation of flame, as practically the same results were obtained by a very small spark from an induction coil, and a large flash produced by drawing apart two heavy copper wires carrying 220 volts and 6 amperes current.

THE UPPER LIMIT OF COMPLETE INFLAMMATION OF MIXTURES OF GASOLINE VAPOR AND AIR, USING THE HEMPEL PIPETTE; SPARK IGNITION AT TOP

| Test No. | Percentage of gasoline | Remarks |
|---|---|---|
| 1 | 3.5 | Complete inflammation |
| 2 | 4.8 | Complete inflammation |
| 3 | 5.0 | Complete inflammation |
| 4 | 5.2 | Complete inflammation |
| 5 | 5.3 | Incomplete inflammation |
| 6 | 5.4 | Incomplete inflammation |
| 7 | 5.9 | Incomplete inflammation |
| 8 | 6.0 | Incomplete inflammation |
| 9 | 6.1 | Incomplete inflammation |
| 10 | 6.1 | Incomplete inflammation |

According to the above tests the upper limit lies between 5.2 and 5.3 per cent of gasoline vapor. With more than 5.3 per cent there was some burning above the spark, for instance at 5.4 per cent the flame completely filled the small space (about 3 cc. capacity) above the spark but did not extend below it.

Experiments were next tried, using a vessel of larger capacity than the 100 cc. Hempel pipette, namely, one having a capacity of 2800 cc. This vessel was 30 cm. high and 12 cm. in diameter. Two copper wires met near the bottom of the jar, through which an electric current of 6 amperes and 220 volts could be passed. A flash was produced by drawing these wires apart when current was flowing.

THE LOW LIMIT OF COMPLETE INFLAMMATION, USING A 2800 CC. VESSEL IGNITION FROM THE BOTTOM

| Test No. | Percentage gasoline vapor | Remarks |
|---|---|---|
| 1 | 1.4 | Incomplete inflammation |
| 2 | 1.5 | Complete inflammation |
| 3 | 1.5 | Complete inflammation |
| 4 | 2.3 | Complete inflammation |
| 5 | 2.5 | Complete inflammation |
| 6 | 2.8 | Complete inflammation |

According to the above results, the low limit of complete inflammation lies between 1.4 and 1.5 per cent of gasoline vapor. With 1.4 per cent of gasoline vapor a tongue of flame about 1 inch at the base, tapering to a cone, extended one-half through the vessel.

The following data show the high limit as determined in the 2800 cc. vessel, ignition from the bottom upwards:

HIGH LIMIT OF COMPLETE COMBUSTION, USING A 2800 CC. VESSEL

| Test No. | Percentage of gasoline vapor | Remarks |
|---|---|---|
| 1 | 6.0 | Complete inflammation |
| 2 | 6.4 | Incomplete inflammation |
| 3 | 6.5 | Incomplete inflammation |
| 4 | 6.6 | Incomplete inflammation |

According to the above results, the high limit of complete inflammation lies between 6.0 and 6.4 per cent of gasoline vapor.

In commenting upon the difference obtained by the two methods of experimentation, it might be added that the Bureau of Mines and others have found that lower limits are obtained when ignition is effected from the bottom upwards. In the latter case the heated convection currents apparently rise faster than the flame does and transmit heat to the unburned gases prior to their ignition by the flame. As a consequence they receive more heat than when ignition is effected from the top and the mixture inflames with smaller percentages of gas present. Another point brought out by different experimenters is that in small vessels the cooling influence of the walls exerts a marked effect in fixing the limits. For instance, tubes may be of so small bore and hence the cooling influence of the walls so great that flame is not transmitted at all in them. Again, sparks may be so minute as not to ignite the most inflammable mixtures. In such a case the temperature of the spark may be quite above the ignition temperature of the gases, but its duration so short that the heat is dissipated before the gases can be raised to their ignition temperature.

## INFLAMMABLE LIMITS OF VAPOR FROM CLEANERS' NAPHTHA

Further experiments were made to determine whether or not the inflammable limits of gasoline-air mixtures differed for gasoline of different grades, *i. e.*, whether the low limit as determined for gasoline having a specific gravity of 73° Baumé was different from the low limit of a gasoline having a specific gravity of, say, 59–60° Baumé. The gasoline used in the following experiments was 59–60° Baumé cleaners' naphtha. The 2800 cc. explosion vessel described in previous tests was used.

LOW LIMIT OF COMPLETE INFLAMMATION IN 2800 CC. VESSEL OF MIXTURES OF AIR AND GASOLINE VAPOR OF 59–60° BAUMÉ SPECIFIC GRAVITY

| Trial No. | Percentage of gasoline vapor | Remarks |
|---|---|---|
| 1 | 2.4 | Complete inflammation |
| 2 | 2.3 | Complete inflammation |
| 3 | 2.1 | Complete inflammation |
| 4 | 2.0 | Complete inflammation |
| 5 | 1.8 | Complete inflammation |
| 6 | 1.7 | Complete inflammation |
| 7 | 1.5 | Complete inflammation |
| 8 | 1.5 | Complete inflammation |
| 9 | 1.5 | Complete inflammation |
| 10 | 1.4 | Incomplete inflammation |
| 11 | 1.4 | Incomplete inflammation |

According to the above results, complete inflammation, as observed by the eye, took place in a mixture containing 1.50 per cent of gasoline vapor. When a mixture analyzing 1.4 per cent was ignited, inflammation was incomplete, the flame lacking 6 cm. of extending to the top of the explosion vessel.

It was found impossible to obtain a mixture containing too much gasoline vapor to explode at the temperature of the laboratory: 20° C. The highest mixture obtainable, 4.6 per cent of gasoline vapor, completely inflamed. In other words, the vapor pressure of this particular naphtha at 20° C. is 740 × 0.046 = 33 mm. of mercury. It would have been possible, of course, by maintaining higher temperatures all through the experiment, to obtain mixtures of higher gasoline-vapor content.

## EFFECT OF INCREASING THE INITIAL TEMPERATURE ON THE EXPLOSIVE LIMITS

It is interesting to consider the effect of high temperature and pressure, to which mixtures of gasoline vapor and air are subjected in the cylinders of internal-combustion engines. A pressure of about 70.0 pounds per square inch is reached before ignition. The temperature resulting is high because on compression to about 90.0 pounds per square inch pre-ignition sometimes occurs.

The Bureau of Mines found in experimenting with mixtures of methane and air[1] that when the initial temperature was 500° C., the low limit of complete inflammation was about 3.75 per cent. At ordinary temperature under the particular experimental condition adopted, the low limit was 5.50 per cent. Initial pressures up to 5 atmospheres at ordinary temperatures made no difference in the limits.

In the case of gasoline vapor—air mixtures—it was also found that increasing the initial temperature before ignition lowered the low limit very appreciably. Experiments were conducted with an apparatus substantially the same as that used in the methane-air experiments.[1]

The following table shows the shifting of the low limit as the initial temperature was increased. The gasoline was of 73° Baumé gravity, the same as that with which the first experiments were made.

SHIFTING OF THE LOW LIMIT OF INFLAMMATION OF MIXTURES OF GASOLINE VAPOR AND AIR WITH INCREASE OF INITIAL TEMPERATURE—IGNITION FROM BOTTOM

| Temperature ° C. | Values between which the limits lie Percentage of gasoline vapor | Analyses of mixtures after explosion Percentages of gasoline vapor |
|---|---|---|
| 23 | 1.50–1.62 | Complete combustion with 1.50 per cent |
| 200 | 1.42–1.50 | Complete combustion with 1.51 per cent |
| 300 | 1.22–1.28 | Complete combustion with 1.28 per cent |
| 400 | 1.02–1.22 | Complete combustion at 1.22 per cent |

The above table shows that with increasing temperature the lower limit was shifted until, with an initial temperature of 400° C., the limit is between 1.02 and 1.22 per cent of gasoline vapor. A mixture containing 1.00 per cent of gasoline vapor did not explode when it was heated to 500° C. just prior to ignition, but when it was allowed to stand for $^1/_2$ hour at this temperature without sparking it completely burned. At just what time during the $^1/_2$ hour interval combustion was complete was not determined.

The lowering of the low limit as the initial temperature is increased is due to the fact that the higher the initial temperature the less heat will be required to raise the temperature of a given mass of the gas to the ignition temperature and consequently the smaller

[1] G. A. Burrell and I. W. Robertson, "The Influence of Temperatures and Pressure on the Explosibility of Methane-Air Mixtures," THIS JOURNAL, 7 (1915), 417.

is the heat of combustion and the percentage of gasoline vapor required to furnish this quantity of heat.

SUMMARY

Using a 100 cc. Hempel explosion pipette and igniting the mixtures from the top, there was obtained as the lower limit of complete inflammation a value lying between 1.9 and 2.0 per cent of gasoline vapor. The upper limit under these conditions was found to be between 5.2 and 5.3 per cent of gasoline vapor. The gasoline used had a specific gravity of 73° Baumé. Under the same conditions, except ignition of the mixtures from the bottom, there was obtained a value lying between 1.5 and 1.6 per cent of gasoline vapor as the low limit. With the same grade of gasoline, using a 2800 cc. vessel, and with ignition from the bottom, by means of an electric flask produced by pulling two wires apart through which a current of 7 amperes at 220 volts was flowing, there was obtained a value lying between 1.4 and 1.5 per cent of gasoline vapor. The high limit under these conditions lay between 6.0 and 6.4 per cent of gasoline vapor. Appreciably different limits were not obtained with vapor from cleaners' naphtha.

When the initial temperature is increased before igniting the mixtures the low limit is gradually decreased until, with an initial temperature of 400° C., the low limit lies between 1.02 and 1.22 per cent of gasoline vapor.

CHEMICAL LABORATORY, BUREAU OF MINES, PITTSBURGH

## THE INFLUENCE OF TEMPERATURE AND PRESSURE ON THE EXPLOSIBILITY OF METHANE-AIR MIXTURES[1]

By G. A. BURRELL AND I. W. ROBERTSON

Received December 15, 1914

In this paper are shown the results of experiments made to determine the effect of temperature and pressure on methane-air mixtures in changing the low limit of complete propagation of flame in mixtures. Temperatures up to 500° C. and pressures of 5.0 atmospheres above atmospheric pressure were employed.

The apparatus is shown in Fig. 1. *A* is the explosion pipette. It had a capacity of 100 cc. Platinum wires were fused into the upper part. A spark from an induction coil, driven by 4.0 dry cells, was used to ignite the gas mixtures. An electrically heated oven, *D*, surrounded the explosion pipette *A*. The temperatures were measured by means of a platinum-rhodium thermo-couple. Transparent mica plates were used to close the upper end of the oven in order to observe the effects of sparking the mixtures. At *B* is shown a reserve pipette of 200 cc. capacity fastened to the explosion pipette by means of pressure rubber tubing with mercury as the confining fluid.

The apparatus was made ready for use by raising the leveling bottle *C*, thereby completely filling the pipettes *A* and *B* with mercury. The leveling bottle was then lowered until all of the mercury had fallen from *A*, leaving a vacuum therein. The stop-cock between the two pipettes was then closed. The required gas mixture was then drawn into *B* through the free end of the stop-cock and the oven heated to the required temperature, whereupon the gas mixture was introduced into *A* and sparked after two seconds had elapsed. The flame produced, if any, was observed and the products of combustion analyzed.

Preliminary experiments were performed with a thermo-couple inserted in the explosion vessel *A*, to determine the time it took the gas after it was introduced into the evacuated pipette to reach the temperature of the oven. It was found that this took

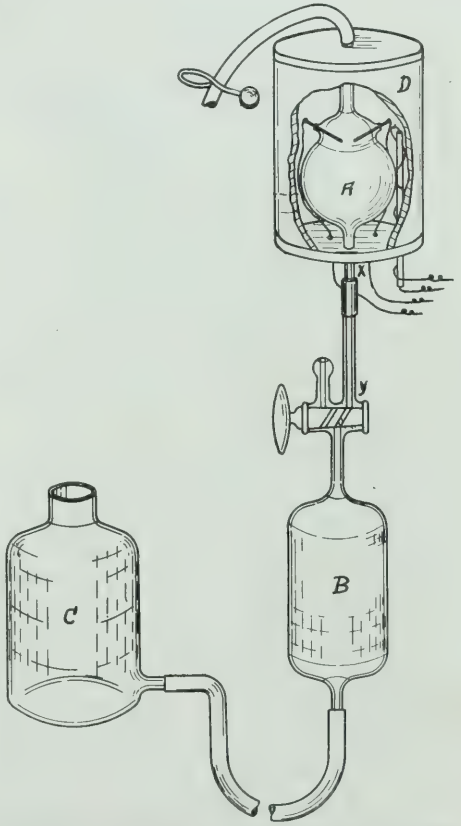


FIG. 1—APPARATUS FOR DETERMINING THE INFLUENCE OF TEMPERATURE AND PRESSURE ON THE EXPLOSIBILITY OF METHANE-AIR MIXTURES

place in less than two seconds after the introduction of the gas.

Methane was prepared from the natural gas used at Pittsburgh by fractional distillation at low temperatures. The natural gas was liquefied at the temperature of liquid air and as much gas pumped from it with a mercury pump as possible. The distillate was reliquefied and pumped again. A trace of nitrogen and pure methane to the extent of about 85.0 per cent of the original volume of the natural gas was obtained in this manner.

The results of the experiments are shown in Table I.

[1] Published with permission of the Director of the Bureau of Mines.

Experiments 1 to 5 show the displacement of the lower limit of complete propagation with the initial temperature at 500° C. and the initial pressure at 1 atmosphere. As far as the eye could judge, there was a complete filling of the explosion vessel with flame when mixtures containing 4.00 to 4.47 per cent methane were sparked. However, a measurable amount of methane remained unburned, probably due principally to the fact that a small amount of gas

TABLE I—EFFECT OF INCREASING THE INITIAL TEMPERATURE ON THE LOW LIMIT OF COMPLETE PROPAGATION OF FLAME IN METHANE-AIR MIXTURES

| Test No. | Temperature ° C. | Pressures. Atmospheres | Analysis of Mixtures Before sparking. CH4 | Air | After sparking. CH4 | CO2 | Observations | Limits per cent CH4 |
|---|---|---|---|---|---|---|---|---|
| 1 | 500 | 1 | 4.47 | 95.53 | 0.58 | 4.08 | Complete propagation | |
| 2 | 500 | 1 | 4.27 | 95.73 | 0.64 | 3.85 | Complete propagation | 4.00 |
| 3 | 500 | 1 | 4.00 | 96.00 | 0.89 | 3.14 | Complete propagation | and |
| 4 | 500 | 1 | 3.75 | 96.25 | 3.45 | 0.42 | No propagation | 3.75 |
| 5 | 500 | 1 | 3.50 | 96.50 | 3.42 | 0.18 | No propagation | |
| 6 | 400 | 1 | 4.75 | 95.25 | 0.75 | 3.74 | Complete propagation | |
| 6a | 400 | 1 | 4.35 | 95.45 | 0.65 | 3.93 | Complete propagation | |
| 7 | 400 | 1 | 4.47 | 95.53 | 4.26 | 0.41 | No propagation | 4.55 |
| 8 | 400 | 1 | 4.27 | 95.73 | 4.12 | 0.23 | No propagation | and |
| 9 | 400 | 1 | 4.00 | 96.00 | 3.88 | 0.20 | No propagation | 4.77 |
| 10 | 400 | 1 | 3.75 | 96.25 | 3.65 | 0.20 | No propagation | |
| 11 | 300 | 1 | 5.15 | 94.85 | 0.82 | 4.36 | Complete propagation | 4.88 |
| 12 | 300 | 1 | 4.98 | 95.02 | 0.71 | 4.13 | Complete propagation | and |
| 13 | 300 | 1 | 4.75 | 95.25 | 4.64 | 0.13 | No propagation | 4.75 |
| 14 | 300 | 1 | 4.27 | 95.73 | 4.17 | 0.21 | No propagation | 5.15 |
| 15 | 200 | 1 | 5.15 | 94.85 | 0.20 | 4.98 | Complete propagation | and |
| 16 | 200 | 1 | 4.98 | 95.02 | 4.84 | 0.18 | No propagation | 4.98 |
| 17 | 25 | 1 | 5.40 | 94.60 | 5.40 | 0.00 | No propagation | 5.46 |
| 18 | 25 | 1 | 5.46 | 94.54 | 5.47 | 0.00 | No propagation | and |
| 19 | 25 | 1 | 5.56 | 94.44 | 0.12 | 5.46 | Complete propagation | 5.56 |

was contained in the tube *xy* of the pipette outside of the electric oven and did not burn. When the methane in the mixture was dropped to 3.75 and 3.50 per cent, no propagation was observed, although some methane was burned, as was shown by the carbon dioxide found upon analysis.

According to these results, the low limit of complete propagation is between 3.75 and 4.00 per cent when the initial temperature is 500° C. and the initial pressure 1 atmosphere. At 400° C. and at atmospheric pressure a mixture containing 4.55 per cent methane completely propagated flame, as far as could be judged by the eye, although 0.75 per cent methane remained unburned. When the methane content was lowered to 4.47 per cent propagation could not be observed. The same was true of mixtures containing 4.27, 4.00, and 3.75 per cent methane.

Experiments 17, 18 and 19 were performed to obtain the low limit of complete propagation of methane-air mixtures under ordinary conditions of temperature and pressure. This value lies, it will be noted, between 5.46 and 5.56 per cent methane. Undoubtedly a small amount of carbon dioxide was formed in the case of Experiments 17 and 18, but not enough to detect by the method of analysis used. In each test an analysis was made of the mixtures before and after sparking. The sum of the carbon dioxide and methane should equal the methane present before sparking. The analyses agreed quite well. A curve representing the results of the experiments is shown at Fig. 2.

The variation of the limits of explosibility with temperature and pressure may be explained on purely thermal grounds.

If one heats an explosive mixture of methane and air, the number of collisions between the molecules increases with rising temperature and the speed of reaction increases until finally a violent reaction and appearance of flame follows. The temperature at which this kind of a reaction takes place is called the ignition temperature. The ignition temperature of methane-air mixtures was found to be between 650° and 750° C. by Dixon and Coward.[1] A slow combustion effect is possible, however, below the ignition temperature, depending on the nature of the source of ignition and length of time the gas is heated. But in order that flame may be propagated throughout the gas mixture, the heat of reaction of a layer of gas near the igniter must be sufficient and its rate rapid enough to raise the temperature of the adjacent layer to the ignition temperature. Obviously the higher the initial temperature the less heat will be required to raise the temperature of a given mass of the gas to the ignition temperature, and consequently the

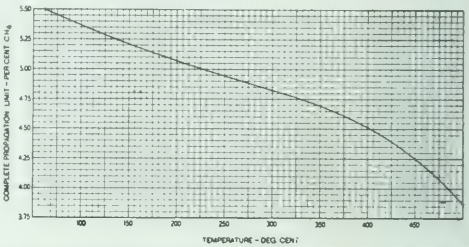


FIG. 2—EFFECT OF INCREASING THE INITIAL TEMPERATURE ON THE LOW LIMIT OF COMPLETE PROPAGATION OF FLAME IN METHANE-AIR MIXTURES

smaller is the heat of combustion and the percentage of methane required to furnish this quantity of heat.

## SLOW COMBUSTION OF METHANE-AIR MIXTURES AT HIGH TEMPERATURES WITHOUT SPARKING

A few experiments were performed to show the extent of burning when various mixtures of methane and air were subjected to high temperatures without sparking.

TABLE II—RESULTS OF EXPOSURE OF METHANE-AIR MIXTURES TO HIGH TEMPERATURES WITHOUT SPARKING

| Temp. ° C. | Pressure Atmos. | Analysis before ignition CH4 | Air | Analysis after ignition CH4 | CO2 | Exposed Min. |
|---|---|---|---|---|---|---|
| 500 | 1 | 4.27 | 95.73 | 4.21 | 0.10 | 1/2 |
| 500 | 1 | 4.27 | 95.73 | 3.89 | 0.40 | 30 |
| 500 | 1 | 4.60 | 95.40 | 3.74 | 0.90 | 30 |

The results, given in Table II, show that no appreciable combustion effect occurred in experiments previously cited between the time the gas mixtures were introduced into the pipette and the time they were sparked. In the experiments previously described, not longer than 2 seconds was required for the mixtures to attain the temperature of the oven after introduction into the exhausted pipette. It will be observed that as much as one-half minute exposure to a temperature of 500° C. resulted in only a small amount of carbon dioxide.

## EFFECT OF INCREASING THE INITIAL PRESSURE ON THE EXPLOSIBILITY OF METHANE-AIR MIXTURES

Some experiments were made with the apparatus shown in Fig. 1 to determine the effect of initial pres-

[1] H. B. Dixon and H. F. Coward, "The Ignition Temperature of Gases," *Chem. News*, **99** (March 19, 1909), 139.

sures higher than ordinary on the explosibility of methane-air mixtures. The first experiments were made with pressures up to five atmospheres, by raising the level bottle of the apparatus high enough to put the gas under this pressure. It was found that increased pressure up to five atmospheres had no effect in changing the low limit of complete propagation. In other words, the value, about 5.50 per cent methane, is true at five atmospheres pressure.

SUMMARY

When the initial temperature of methane air mixtures is 500° C., the low limit of complete propagation of flame of the mixtures is between 3.75 and 4.00 per cent methane. As the initial temperature is lowered from 500° C., the low limit is raised until at ordinary temperatures it is about 5.5 per cent methane. Differences in the initial temperature of as much as 200° C. higher, shift the low limit only from 5.50 per cent to between 4.98 and 5.15 per cent methane.

The results are important in that they show that pressure and temperature conditions may vary over rather a wide range without affecting the explosibility of methane-air mixtures. Inconsistent results that have been obtained in the laboratory by different investigators on the limits of inflammation of methane-air mixtures cannot be explained on the basis of slight variations in temperatures and pressures. They are better charged to the nature of the source of ignition, method of ignition, size and shape of the containing vessel, and in some cases, inaccuracies in mixing and analyzing the gases.

Since the low limit of complete inflammation for methane-air mixtures is not changed at pressures as great as five atmospheres, it can be stated that even in the deepest coal mines the low limit is not altered from the limit at ordinary temperatures.

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## THE VARIATION IN COMPOSITION OF NATURAL GAS FROM DIFFERENT SANDS IN THE SAME FIELD[1]

By G. A. BURRELL AND G. G. OBERFELL
Received December 15, 1914

In working on the composition of natural gases from different parts of the country, the authors have found that natural gases from different sands in the same field may differ appreciably in composition. Invariably the gas from the shallower sand has contained less of the heavier paraffin hydrocarbons than that from the deeper sands. The most striking variation yet encountered has had to do with natural gases from two different sands in a gas field near Trafford City, Westmoreland County, Pa. and not far from Pittsburgh. The compositions of these gases follow:

| GAS FROM | Murraysville sand | | | Elizabeth sand | | | |
|---|---|---|---|---|---|---|---|
| Depth of sand.... | 1700 ft. | | | 2295 ft. | | | |
| Rock pressure..... | 190 lbs. per sq. in. | | | 1000 lbs. per sq. in. | | | |
| CONSTITUENTS | $CO_2$ | $CH_4$ | $N_2$ | $CO_2$ | $CH_4$ | $C_2H_6$ | $N_2$ |
| Percentages..... | Trace | 98.8 | 1.2 | Trace | 94.0 | 5.2 | 0.8 |

It will be noted that from the shallow sand there was collected a sample of almost pure methane, while in the deeper sand there is contained in addition to methane an appreciable proportion of the higher members of the paraffin series of hydrocarbons. If one were to assume a common source of origin for the natural gases in the two sands, then by some process of separation the gas in the upper sand has been freed of its ethane and higher paraffins.

It should be added that the paraffins were analyzed by burning them in oxygen, not by fractional distillation; hence in the case of the gas from the deep sand, only the two predominating paraffins are shown. Undoubtedly small proportions of propane, the butanes, etc., were also present, as in the case of other natural gases containing methane and ethane.

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[1] Published by permission of the Director of the Bureau of Mines.

## A SIMPLIFIED FERROUS SULFATE METHOD FOR THE DETERMINATION OF VANADIUM IN STEEL

By GEORGE T. DOUGHERTY
Received October 17, 1914

In the application of Johnson's[1] or similar methods for the determination of vanadium in steel, considerable difficulty is often experienced in producing a colorless or "old rose" shade with ferrous sulfate in the solution containing an excess of permanganate after the preliminary oxidation of the vanadium. To obviate this difficulty the following method has been developed, in which this oxidation of the vanadium is effected by a sufficient quantity of nitric acid alone or with ammonium persulfate.

METHOD—Treat 2 to 4 g. of the drillings in a 500 cc. Erlenmeyer flask, with 60 cc. of water and 10 cc. concentrated sulfuric acid. After heating the solution nearly to boiling, until the reaction is complete, add 40 cc. of nitric acid (sp. gr. 1.20) and boil thoroughly for 10 minutes to oxidize the iron and vanadium and to expel the last traces of nitrous fumes. Cool the solution, add 60 cc. of cold sulfuric acid (1:2) and dilute in a 600 cc. beaker to 450 cc. Add 3 cc. of a freshly prepared 1 per cent solution of potassium ferricyanide, and titrate rather rapidly, with constant stirring, with 0.05 *N* ferrous ammonium sulfate, to the appearance of the first dark blue color. The end point can best be observed by looking through the side of the beaker toward the bottom of the beaker placed directly before a window. Deduction of a blank of 0.4 cc. of the ferrous solution has been found necessary, and is independent of the weight of the sample, the presence of chromium, and of the carbon content up to 0.5 per cent C.

For steels with over 0.50 per cent C, the blanks are higher; and, moreover, with 4 g. samples of such steels, the end point is rendered indistinct by a turbidity which appears toward the end of the titration. This difficulty may be avoided by adding to the solution immediately after the boiling with nitric acid as above, 60 cc. of 1:2 sulfuric acid and 5 to 8 g. of ammonium persulfate (which in the absence of silver nitrate will not oxidize the Cr and Mn), and continuing to boil for 15 minutes, so that all nitrous oxides and hydrogen peroxide are expelled. (Before this second boiling, wash down with hot water loose specks of the per-

[1] C. M. Johnson, "Analysis of Special Steels."

sulfate which stick to the glass.) Cool, dilute and titrate as above. After such treatment the blank is 0.35 (instead of 0.4 cc.) for steels with under 0.5 per cent C, and 0.5 cc. for 0.60 to 0.70 C, and 0.6 cc. for 0.90 to 1.25 C steels. The blanks are the same with or without the persulfate treatment for steels of over 0.50 per cent carbon.

The ferrous ammonium sulfate solution may be standardized against 0.1 *N* permanganate, the strength of which has been determined with sodium oxalate. The iron value of the permanganate multiplied by 0.917 gives the vanadium value.

By this method the following results were obtained, the chromium in expts. 9, 10, 13 and 14 being added as $K_2Cr_2O_7$ before the solution of the steel.

The following steels were employed:

A—U. S. Bureau of Standards Sample No. 24, containing 0.15 per cent V, 0.35 per cent C, and a trace of Cr.
B—U. S. Bureau of Standards Sample No. 30, containing 0.21 per cent V, 0.37 per cent C, and 1.35 per cent Cr.
C—A steel casting containing 0.215 per cent V, 0.30 per cent C, and no Cr.
D—A plain steel containing 0.85 per cent C.
E—A plain steel containing 1.25 per cent C.

TABLE I—VANADIUM DETERMINATIONS BY SIMPLIFIED METHOD

| Expt. | Sample | Weight of sample Grams | Persulfate added Grams | Vanadium found Gram |
|---|---|---|---|---|
| 1 | A | 2 | 0 | 0.148 |
| 2 | A | 4 | 0 | 0.146 |
| 3 | B | 2 | 0 | 0.206 |
| 4 | B | 4 | 0 | 0.208 |
| 5 | C | 2 | 0 | 0.216 |
| 6 | C | 4 | 0 | 0.216 |
| 7 | C + D | 2 + 2 | 0 | 0.222 |
| 8 | C + E | 2 + 2 | 0 | 0.210 |
| 9 | C + D + 1.3% Cr | 2 + 2 | 0 | 0.210 |
| 10 | C + E + 1.3% Cr | 2 + 2 | 0 | 0.200 |
| 11 | C + D | 2 + 2 | 7 | 0.216 |
| 12 | C + E | 2 + 2 | 7 | 0.216 |
| 13 | C + D + 1.3% Cr | 2 + 2 | 7 | 0.216 |
| 14 | C + E + 1.3% Cr | 2 + 2 | 7 | 0.210 |

From these results it is apparent that in general for such materials, the method is accurate to 0.01 per cent vanadium.

If chromium also is to be determined, it is determined in a separate portion of the sample, using any of the usual volumetric methods.

AMERICAN STEEL FOUNDRIES, CHICAGO

## THE EFFECT OF CERTAIN ORGANIC COMPOUNDS ON WHEAT PLANTS IN THE SOIL—PRELIMINARY PAPER

By FRED W. UPSON AND A. R. POWELL

Received March 20, 1915

In recent years our knowledge of the chemical nature of soil organic matter has been greatly extended through the work of a number of investigators, chief among whom are Jodidi and the several workers in soil fertility investigations of the United States Bureau of Soils. A very complete historical account of the work on soil organic matter and of the older views regarding it has been presented by Schreiner and Shorey[1] and by Jodidi.[2] Through the work of these investigators and their co-workers, we have come to regard the soil organic matter not as consisting of three of four compounds of rather indefinite properties, but as being made up of a large number of different organic compounds which result from plant and animal residues through the agency of the various chemical processes which are taking place in the soil. From various soils there have been isolated and identified up to the present time, more than half a hundred definite organic compounds. Among the various classes of organic compounds represented are acids, aldehydes, alcohols, amino acids, resins, esters, glycerides, hydrocarbons, sugars, amines and other nitrogenous compounds. The methods by which these compounds have been isolated and identified are somewhat involved and need not be considered here.

The toxic effect on wheat plants of the various organic compounds which have been isolated from various soils has been extensively studied by Schreiner[1] and his co-workers. With two exceptions,[2] the work

1 2 3 4

PLATE I

by these investigators on the toxic effect of organic compounds has been determined by growing plants for short periods in distilled water cultures containing the various compounds. The organic compounds studied are either those which have been isolated from the soil or those which may result through the breaking down of plant and animal residues.

Many of the compounds studied have been shown to be more or less toxic to wheat plants in comparatively low concentrations, 10–200 parts per million of solution. Some few have been found beneficial to the growth of wheat plants in water solution. In many cases the addition of fertilizer salts to the culture solution has partially or completely overcome the toxic effects of the organic compounds.

While a knowledge of the effect of these compounds on the growth of wheat seedlings in water solution is of the greatest importance, nevertheless we should

[1] *Bull.* **53**, Bur. of Soils, U. S. Dept. Agr., p. 21.
[2] *Biochem. Bull.* **3**, 17.

[1] A summary of the effect of various organic compounds on growth is given in *Bull.* **87**, Bur. of Soils, U. S. Dept. Agr., p. 70.
[2] Schreiner and Skinner have studied the effect of cumarin (*Bull.* **77**, Bur. Soils, p. 16) and of salicylic aldehyde, U. S. Dept. Agr. (*Bull.* **108**, 5, 12), on wheat plants in the soil.

not assume from results obtained in this manner that these compounds will exhibit the same behavior toward plants growing in the soil. Conditions are much more complex in the soil. Adsorption and other surface effects, aeration, the effect of chemical compounds and the action of microörganisms are all factors which are of little importance in the water culture, but which play a much more prominent rôle in the soil.

Extensive work on the behavior of these organic compounds toward plants in the soil, is necessary before we are able to draw final conclusions in regard to the relation of these substances to soil fertility.

## EXPERIMENTAL PART

The present paper deals with the behavior of vanillin, salicylic aldehyde, cumarin, quinone and dihydroxystearic acid toward wheat plants in the soil.

Vanillin is of special interest because it exists in many plants in the form of a glucoside. Vanillin or substances which give rise to it have been reported in oats,[1] asparagus shoots[2] and other plants. Quite[3] recently it has been isolated from ungerminated wheat seeds and from seedlings five days old. It has recently also been isolated from Florida soils.[4]

Vanillin has been shown by Schreiner, Reed and Skinner[5] to be toxic to wheat seedlings grown in distilled water solution, 500 parts per million being sufficient to cause death in nine days. It was noticeably toxic in much lower concentrations. Schreiner and Skinner[6] have shown also that vanillin is much less toxic in water solution in the presence of fertilizer salts.

EXPERIMENT 1—The soil used in this experiment came from a meadow which has long been in blue grass. It is a black silt loam of excellent texture and rich in organic matter. Approximately 1800 g. of dry soil were mixed with the required amounts of vanillin, potted and brought to the proper moisture content with distilled water. After standing 24 hours, ten wheatseeds were planted in each pot. Complete germination was secured in each. After the plants were well sprouted each pot was thinned to five plants. The experiment lasted from October 20 to November 28th (39 days). At the end of this time the pots were opened, the soil very carefully removed from the roots and the green and dry weights of the whole plant determined. The results are shown in Table I, A.

TABLE I—RESULTS WITH VANILLIN

| No. | Treatment | A | | | B | | | C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Green weight | Dry weight | Relative growth | Green weight | Dry weight | Relative growth | Green weight | Dry weight | Relative growth |
| 1 | Soil untreated | 19.2 | 2.21 | 100 | 48.1 | 7.58 | 100 | 51.0 | 6.4 | 100 |
| 2 | Same + 250 p. p. m. vanillin | 19.2 | 2.20 | 100 | 51.5 | 7.43 | 107 | 51.8 | 6.39 | 101 |
| 3 | Same + 500 p. p. m. vanillin | 18.8 | 2.09 | 98 | 47.7 | 7.20 | 99 | 58.2 | 7.13 | 114 |
| 4 | Same + 1000 p. p. m. vanillin | 18.6 | 2.16 | 97 | 48.4 | 7.46 | 101 | 50.1 | 6.57 | 98 |

The roots were not visibly injured in any way even in the highest concentration of vanillin. A photograph serves to show this more clearly. Plate I shows the plants from Experiment 1: Nos. 1, 2, 3 and 4 show the plants from the untreated soil and from the soil containing 250, 500 and 1000 parts per million vanillin respectively.

EXPERIMENT 2—This is a duplicate of the first experiment except that the plants grew till December 23rd (64 days). The results are shown under B in Table I.

EXPERIMENT 3—This experiment was carried out in the same manner as Experiments 1 and 2 except that the vanillin was added to the soil in water solution. This experiment ran from October 30th to December 29th (60 days). The results are given under C in Table I.

EXPERIMENT 4—Another experiment was carried out using soil from a field which has been under cultivation for about thirty years. It is a silt loam of excellent texture, but much less fertile than the soil used in the previous experiments. The plants grew from November 30th to February 3rd. Three plants were grown in each pot, the green weights of the tops only being recorded (Table II).

TABLE II—RESULTS WITH VANILLIN

| Treatment | No. | Green weight | Relative growth | No | Green weight | Relative growth |
|---|---|---|---|---|---|---|
| Soil untreated | 1 | 6.5 | 100 | 4 | 6.69 | 100 |
| Same + 500 p. p. m. vanillin | 2 | 6.39 | 97 | 5 | 6.59 | 99 |
| Same + 1000 p. p. m. vanillin | 3 | 5.9 | 90 | 6 | 6.49 | 97 |

These experiments show that vanillin is not appreciably toxic to wheat plants when present in the soil even in quantities as high as 1000 parts per million. Vanillin is therefore, to say the least, much less toxic in the soil than in water cultures. Even with the addition of fertilizer salts in the most favorable combinations, solutions containing only 50 parts per million of vanillin gave a relative growth of wheat plants[1] of 88.

Salicylic aldehyde has very recently been found in a soil by Schreiner and Skinner.[2] These investigators have also determined its effect on corn and wheat in distilled water cultures and also in the soil. They find that in distilled water, growth of wheat is reduced by the presence of 25 parts per million salicylic aldehyde, 69 per cent and that in concentrations of 50, 100 and 200 parts per million this substance produced death.[3] Much the same effect was produced on corn grown in nutrient solutions: 10 parts per million of the aldehyde gave a relative growth of 60 after 25 days, whereas 200 parts per million gave a relative growth of only 10.

The effect of salicylic aldehyde on wheat and corn in soil in pots was also determined.[4] Salicylic aldehyde in 50 parts per million gave a relative growth of wheat of 61, after 22 days and in concentrations of 100 and 200 parts per million caused death: 50 parts per million of the aldehyde reduced the growth of corn in soil 24 per cent and in quartz sand 60 per cent. These experiments were carried out in paraffined wire pots described in Circular 18 of the Bureau of Soils.

## EXPERIMENTS WITH SALICYLIC ALDEHYDE

For these experiments the soil selected was the same as the one used in Experiment 4 with vanillin. Pots holding about 1800 g. of soil were employed. The aldehyde was dissolved in water and added to the soil in the proper proportions.

[1] de Rawton, *Compt. rend.*, **125**, 797.
[2] von Lippman, *Ber.*, **18**, 1335.
[3] Sullivan, THIS JOURNAL, **6**, 920.
[4] Shorey, *J. Agr. Res.*, **1**, 357.
[5] Bur. Soils, U. S. Dept. Agr., *Bull.* **47**, 31.
[6] *Ibid.*, *Bull.* **77**, 20.

[1] Schreiner and Skinner, Bur. Soils, U. S. Dept. Agr., *Bull.* **77**, 21.
[2] U. S. Dept. Agr., *Bull.* **108**, 1 (1914).
[3] *Ibid.*, **108**, 3; Skinner, *Biochem. Bull.* **3**, 390; *J. Am. Soc. Agron.*, **6**, 108
[4] U. S. Dept. Agr., *Bull.* **108**, 5.

EXPERIMENT 5—This experiment with salicylic aldehyde was carried out in the same manner as the vanillin experiments. Ten wheat seeds were planted in each pot and the plants thinned to five after they were well sprouted. The experiment ran from November 22nd to January 2nd. Section A of Table III shows the weights of the tops only.

TABLE III—RESULTS WITH SALICYLIC ALDEHYDE

| | | A | | | B | | |
|---|---|---|---|---|---|---|---|
| No. | Treatment | Green wt. G. | Dry wt. G. | Relative growth | Green wt. G. | Dry wt G. | Relative growth |
| 1 | Soil untreated | 6.7 | .85 | 100 | 12.7 | 2.51 | 100 |
| 2 | Same + 10 p. p. m. salicylic aldehyde | 6.8 | .89 | 102 | 12.1 | 2.29 | 95 |
| 3 | Same + 25 p. p. m. salicylic aldehyde | 6.2 | .77 | 93 | 11.8 | 2.30 | 93 |
| 4 | Same + 50 p. p. m. salicylic aldehyde | 5.7 | .73 | 85 | 12.2 | 2.42 | 96 |
| 5 | Same + 100 p. p. m. salicylic aldehyde | 6.2 | .75 | 93 | 12.3 | 2.47 | 97 |

EXPERIMENT 6—This experiment is a duplicate of Experiment 5, except that it ran till January 28th. The results are shown under B in Table III.

EXPERIMENT 7—The same method was used as in the preceding experiments, except that higher concentrations of the aldehyde were used and the experiment ran from January 15th to March 6th. A of Table IV gives the results.

TABLE IV—RESULTS WITH SALICYLIC ALDEHYDE

| | | A | | | B | | |
|---|---|---|---|---|---|---|---|
| No. | Treatment | Green wt. G. | Dry wt. G | Relative growth | Green wt G. | Dry wt. G. | Relative growth |
| 1 | Soil untreated | 8.5 | 1.6 | 100 | 4.5 | .33 | 100 |
| 2 | Same + 100 p. p. m. salicylic aldehyde | 7.8 | 1.55 | 92 | 3.8 | .25 | 84 |
| 3 | Same + 200 p. p. m. salicylic aldehyde | 8.4 | 1.73 | 99 | 3.3 | .20 | 73 |
| 4 | Same + 500 p. p. m. salicylic aldehyde | 8.0 | 1.59 | 94 | 4.4 | .34 | 98 |

EXPERIMENT 8—The effect of salicylic aldehyde on corn was also determined. The experiment ran from February 3rd to March 6th. Two plants were grown in each pot and the method was the same as the one used in the wheat experiments. The results are given under B in Table IV.

Our experiments indicate that salicylic aldehyde is much less toxic to wheat and corn plants in the soil than in water cultures. The toxic effect on wheat, even in a concentration of 500 parts per million, is practically negligible. This does not agree with the results of Schreiner and Skinner.[1] In order to determine whether this difference was due to the method or to the soil we repeated the experiment, using the paraffine wire pots according to the method of Schreiner and Skinner.[1]

EXPERIMENT 9—Wheat was grown for twenty-two days in paraffined pots. At the end of this time the tops only of the six plants from the check pot weighed 0.98 g. while those from the pot treated with 100 parts per million of the aldehyde weighed 1.09 g. The soil which we used was a silt loam of loose texture and fairly high in organic matter, while the one used by Schreiner and Skinner is described as "a heavy clay loam."

Our experiments show that the effect of salicylic aldehyde on the growth of wheat and corn is different for different soils. We are of the opinion that aeration and absorption are important factors in overcoming the effect of the aldehyde. It is probable that the explanation of our results is to be found in the fact that the soil used was of a looser texture and more absorptive than the one described by Schreiner and Skinner.

Preliminary experiments on the behavior of cumarin, quinone and dihydroxystearic acid toward wheat plants in the soil indicate that the effect is entirely different from the effect of these substances in water solutions. Quinone in concentrations below 500 parts per million in soil is beneficial to the growth of wheat. The other two substances are somewhat more toxic in the soil than is vanillin. A complete series of experiments with these compounds is in progress. Experiments are also in progress to determine the fate of these compounds and also of vanillin and salicylic aldehyde, in the soil.

[1] *Loc. cit.*

## CONCLUSIONS

The behavior of vanillin and of salicylic aldehyde toward wheat plants in the soil is shown to be quite different from the behavior of these substances in water cultures.

The behavior of salicylic aldehyde is shown to be different in different soils.

The necessity for more extended experiments of the nature of those here reported, has been demonstrated.

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## THE ENGINEERING PROPERTIES OF SOILS

By R. O. E. Davis[1]

Received February 6, 1915

The engineering properties of soils are of interest to all peoples living under civilized conditions, and engineering questions concerning the soil are of importance next to that of productiveness. The construction and maintenance of drainage, irrigation or commercial canals, the proper foundations for architectural structures, the construction and operation with safety of mines and quarries, and the protection afforded by levees and embankments are all dependent directly in most cases and indirectly always on these engineering properties. Attention has not been given to the subject in proportion to its importance. Lately, however, engineers and engineering societies have evidenced a growing interest in the subject, as it is realized that while the engineering features of the superstructures have been worked out with much care and detail, the properties of the soil on which the foundation rests are very little understood.

The statement has been made that nothing is known of these properties. This, however, is rather misleading; the facts are that the properties that the engineer has to deal with are mainly the physical properties of the soil and these have been studied systematically for some years, mainly from the agricultural standpoint. So it is well to see in what way the two studies are related so that needless work may be avoided.

Approaching the problem from the engineering standpoint, the properties of the soil on which the engineer wishes information are the rigidity of the soil, its cohesiveness, its penetrability, and its porosity. These are the properties that determine the weight which the soil will support under structural conditions, the height to which a retaining wall of soil will stand without additional support, the resistance

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offered to the driving of piles or similar operations, and the rates at which water is lost from irrigation ditches and canals. These same physical properties of the soil determine the resistance of a soil to erosion by wind or water, regulate the rate of water movement as a supply to the plant, determine the resistance offered by the soil to tillage operations and to the expansion or growth of plant roots. While important to know these properties in engineering operations, the studies carried on from an agricultural viewpoint have resulted in generalizations that must be regarded if the engineering investigations are not to result in much unnecessary duplication.

### PHYSICAL NATURE OF SOIL

Soil is made up of solid particles mostly mineral in character, a varying amount of water within the interspaces of the soil and generally gases occupying part of the interspace. The relative proportions of these constituents are constantly changing, but the actual amount of solid material remains more or less constant. Even this, however, is not actually true; the movement of wind or water over the surface causes a translocation of the solid soil-material, and the movement of water within the soil is constantly causing the removal or deposition of the solid phase of the soil A more serious change in the soil as a result of the changing moisture content will be referred to later. It is sufficient to state here that the soil is constantly changing in actual composition, and the properties are also changing; that is, the soil problem is not static but dynamic.[1] If we consider more in detail the physical properties we shall see in what manner this is true.

### SOIL TEXTURE

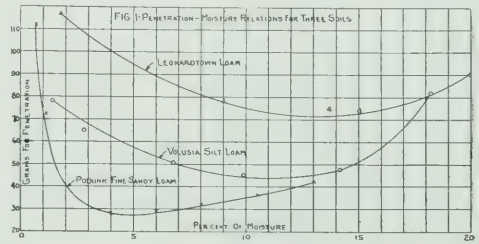
The texture of soil is the factor upon which many of the physical properties are dependent. The soil texture is determined by the mechanical composition and by the crumbing of the soil. Mechanical composition refers to the relative amounts of different sized particles composing the soil. A soil made up mostly of sand or larger sized particles has larger interstices than a soil composed of smaller particles, under conditions in which crumbing does not take place. Accompanying the presence of the smaller grades the phenomenon of crumbing occurs. This is the grouping of the small silt and clay particles into larger aggregates, the result of which is a more open and porous soil. The actual amount of interspace is not increased greatly but the size of the spaces is materially enlarged. This is closely related to the moisture content as will be shown later.

The amount of water which a soil may contain is measured by the pore space. In the case of heavy clay soils, where the amount of pore space is great, the capacity for absorbing water is very large. The rate at which water will move through a soil depends upon the size of the pore spaces which is directly dependent on the size of the soil particles or kernels.

[1] This has been emphasized by Cameron in several articles, especially in the article, "The Dynamic Viewpoint of Soils," THIS JOURNAL, 1 (1909), 806.

### MINERALOGICAL COMPOSITION

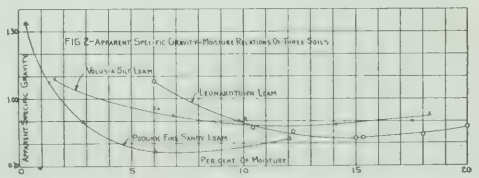
The mineralogical composition of the soil has an effect upon the engineering properties of the soil that is both chemical and physical. The chemical factor is the ease with which the minerals are broken down or changed chemically, due to the weathering conditions, or the action of soil water and soil atmosphere. These are exactly the same conditions that are important from an agricultural standpoint. The physical factor is due to the particular shape or condition of surface of the soil minerals connected with various mineral compositions. This question is one of vital importance in the erosion of soil. The presence, for example, of much micaceous material in the soil is




presumed to cause the particles to move over each other more easily than when these are absent. This is also vitally important to the engineer in selecting foundations or building embankments.

### MOISTURE CONTENT

While the textual relations of the soil and its mineralogical composition are important in studying the physical properties, probably the most important single factor in determining the physical condition of the soil is the moisture content. It is not stating the case too strongly to say that the soil is constantly changing and that these changes are mainly due to the soil moisture. There are surface changes taking place due to the action of wind, and these changes are large; but the changes resulting from water ex-



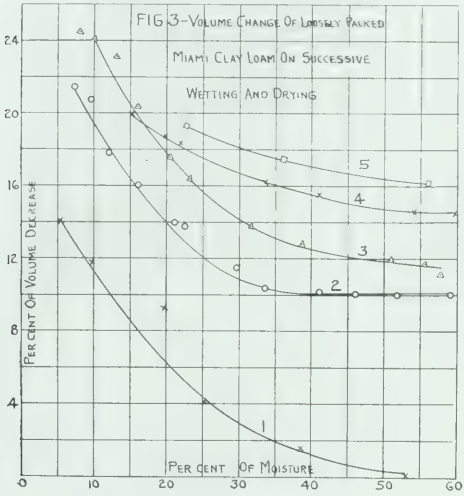

tend throughout the mass of the soil wherever the rainfall is sufficient, and the aggregate of these changes is very large.

Experiments have shown[1] that the magnitude of any physical measurement of the soil changes with a change in moisture content. The degree of the change varies with the mechanical composition of the soil, the variation in soils of fine texture being more gradual with changing moisture content, than that in soils of a coarser texture. However, the change in dimen-

[1] Cameron and Gallagher, *Bull.* **30**, Bureau of Soils, Dept. of Agric. (1908).

sion of any physical property of a soil varies with the moisture content, reaching a maximum or minimum value at a definite moisture content for any specific soil. As examples, the volume or the penetrability of a soil changes with a change in moisture content.

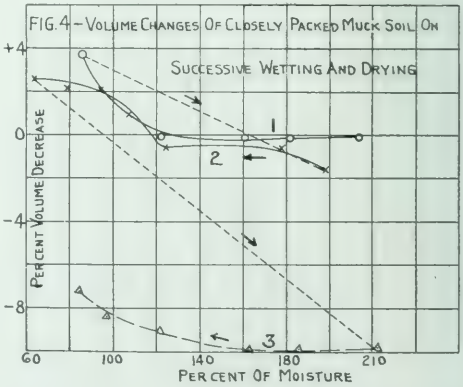
Figs. 1 and 2 show the curves[1] for the apparent specific gravity and the penetrability of several soils, in which these values vary with the change of moisture content. From the penetration curves it will be noted that the penetration reaches a minimum value with Podunk fine sandy loam at about 6 per cent moisture, with Volusia silt loam at 13 per cent and with Leonardtown loam at 15 per cent. The apparent specific gravity is at its minimum value at 6 per cent moisture for Podunk fine sandy loam, at 12 per cent for Volusia soil and at 14 per cent for the Leonardtown loam.




Since the soil as a whole is always either being wet or drying out, in undergoing these processes the physical properties change within certain limits, as already pointed out. The most important of these changes from an engineering standpoint is the change in volume. If water is added to a loose soil and then the soil is allowed to dry out, it will be found that the dry soil will be in a more compact state than the soil to which water was first added. By repeating the process it will be found that the change in volume results always in the soil occupying more volume when wet than when dry. However, the change in volume becomes smaller each time, approaching a limiting curve for the volume changes. Those changes are shown in Fig. 3 for a clay loam soil. The curves in Fig. 3 show the percentage volume decrease of a loosely packed soil on successive wetting and drying. The curves are numbered in the order of the wetting. There is a decrease of 14 per cent in volume on the first drying, but when re-wetted the volume shows an increase of only 4 per cent. This is followed by a shrinkage of nearly 12 per cent. The change becomes less with each cycle, approaching limiting values.

On the other hand, if the soil is compacted as much as it is possible to do by mechanical means and then wetted, the volume will increase; but on drying out, while shrinkage takes place, the dry volume will be larger than the volume of the originally compacted soil. Again the changes in volume show a hysteresis effect approaching a limiting curve, as shown in Fig. 4. In this case the soil was first compacted and then wetted. The compacted condition is taken as the zero volume. The first curve shows a decrease in volume on drying, but on rewetting there is an increase in volume over the previous condition of the soil with the same amount of moisture. The direction of change on wetting is indicated but the actual path followed is not shown. This, then, explains natural packing. Regardless of the condition of the soil, by several successive wettings and dryings the soil particles so arrange themselves that the changes in volume approach a limiting curve. This is the process that the soil follows under natural conditions, so that this process of "natural packing" produces a soil of a definite volume for a given moisture content. Whether we start with a loosely packed or a compacted soil, on continued wetting and drying there are changes in volume and a hysteresis effect until a state is reached in which the expansion on wetting is just equal to the contraction on drying. This is the state of natural packing. Within narrow limits the change of volume on contractions is not greatly dependent on the packing of the soil.

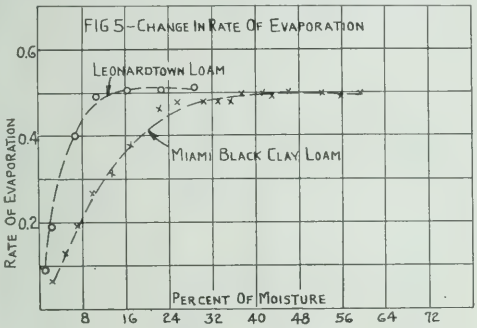
Still another property of the soil influenced by the moisture content is that of the rate of evaporation of the water contained therein. Measurements of the rate of evaporation for several soils show that there is a fairly rapid increase in the rate of evaporation from the dry condition up to the critical moisture content, and that the rate then becomes nearly constant. The change in the rate curve corresponds to the maximum or minimum of other physical properties. The curves reproduced in Fig. 5 show more




[1] Reproduced from *Bulls.* **80** and **82**, Bureau of Soils, U. S. Dept. of Agric.

clearly how this change in rate of evaporation takes place.

From the consideration of the changes taking place in the soil it is evident that the conditions of the soil are not constant. The composition as well as the physical properties of the soil is constantly changing and these changes must be considered in any study of soil conditions. The largest and most important changes in the soil are wrought by a changing water content. The influence of these changes follow a definite law and with this understanding of the influence




of moisture variation, it remains to investigate the amount of such changes due to specific soil conditions.

SUMMARY

The engineering properties of the soil are the properties of interest from the physical standpoint and are identical with those physical properties of importance to agricultural operations.

The factors influencing the physical properties are mechanical composition, mineralogical composition and moisture content. All of these are constantly changing, but the greatest variation occurs in the moisture relations of the soil.

A study of the moisture relations has demonstrated the fact that all of the physical properties change with a changing moisture content and with any given soil there is a particular moisture content at which the properties either reach a maximum or minimum value; this moisture content is the critical moisture content of the soil.

The soil, if allowed to become wet and dry out several times, reaches a condition of compactness known as "natural packing." This compactness varies with the moisture content just as the other physical properties do.

The study of the engineering properties of the soil will consider the changes due to specific soil conditions, but must recognize the dynamic soil conditions.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON

## LITHIUM IN SOILS

By L. A. Steinkoenig

Received January 6, 1915

Lithium is very widely, though not abundantly, distributed in nature. It has been found in a large number of sedimentary rocks examined by A. Hilger,[1] in a great number of primary rocks, granites, syenites and gneisses, by L. Dieulafait,[1] and in many varieties of marble, calcareous rocks and English chalk by Kirchoff and Bunsen.[2]

Lithium is also very often found in mineral waters and salines. It has been found in the larger bodies of water: in the Dead Sea, by Dieulafait[3] and in the waters of the Mediterranean Sea, Red Sea, Indian Ocean, Chinese Sea, Atlantic Ocean, Antarctic Ocean and the Northern Ocean by the same author,[4] the concentration of lithium being great enough in the waters of the Mediterranean to make it easy to detect in the residue from one cubic centimeter of water.

Being so widely distributed in rocks one would expect to find lithium in the soil and plants supported by the soil. Beet[5] and tobacco plants take up considerable quantities of this element from the soil. Lithium was found in tomatoes, chick peas and Iris germinica by Passerine[6] and in a great number of plants growing exclusively in Austria by Tschermak.[7] Bunsen and Kirchoff found lithium in the ash of the wood of trees grown on a granite soil and in the ash of all kinds of cereals grown in the valley of the Rhine.

Lithium has also been found in the blood and muscles of man and ruminant animals by Kirchoff and Bunsen and in nearly all the organs of the human body by Herrmann.[8]

Lithium has been known to be present in soils, for a long time, but there are few quantitative estimates of this element. It was found present in all soils examined by Robinson.[9]

The lithium was obtained together with the sodium by the J. Lawrence Smith method and the excess of platinum used to precipitate the potash removed by treatment with hydrogen sulfide. The lithium and sodium salts remaining in solution are filtered and concentrated to small volume.

The lithium was determined by means of a Hilger wave length spectroscope using the line of 6708.2 wave length. The intensity and duration of the line, compared with that of a standard solution, served to measure the content of lithium. The method of comparing the spectra of unknown and standard was very similar to that of Truchot, with the use of platinum spiral and addition of sodium chloride to standards as described by Skinner and Collins.[10]

A blank determination showed small amounts of lithium in reagents but not enough to interfere with the determination. To determine whether appreciable amounts of lithium are volatilized during heating twice to drive off ammonium salts, standards were made by adding lithium, in amounts occurring in soils, to powdered quartz. No loss of lithium occurred

[1] *Ann. chim. phys.*, [5] **16**, 377–391.
[2] *Chem. News*, **98**, 151–2.
[3] *Compt. rend.*, **94**, 1352–1354.
[4] *Ann. chim. phys.*, [5] **16**, 377–391.
[5] von Lippmann, *Ber.*, **30** (1897), 3037–3039.
[6] *Staz. Sper. Agrar.*, **20**, 471–476.
[7] *Zeit. Landw. Versuchs-Wesen. Oesterr.*, **2**, 560–572.
[8] *Pflüger's Archiv.*, **109** (1905), 26–50.
[9] *Bull.* **122**, Bureau of Soils, U. S. Dept. Agriculture, 1914.
[10] Skinner and Collins, *Bull.* **163**, Bur. of Chem., U. S. Department of Agr. (1912).

| Soils Analyzed for Lithium | Per Cent Lithia Soil | Subsoil |
|---|---|---|
| **Soils of River and Flood Plains Province** | | |
| Cahaba Fine Sandy Loam, Clay County, Ga | 0.002 | 0.004 |
| Cahaba Very Fine Sandy Loam, Minden, La | 0.001 | 0.002 |
| **Soils of Glacial and Loessial Province** | | |
| Memphis Silt Loam, Grenada Co., Miss | 0.002 | 0.002 |
| Memphis Silt Loam, Smooth Phase, Grenada Co., Miss | 0.001 | 0.002 |
| Carrington Loam, Lawville, Wis | 0.002 | ... |
| Gloucester Stony Loam, 3 mi. E. Marlboro, N. H | 0.003 | ... |
| Volusia Silt Loam, 3½ mi. S. W. Naples, N. Y | 0.003 | ... |
| **Soils of Coastal Plains Series** | | |
| Ruston Fine Sandy Loam, Minden, La | 0.002 | 0.003 |
| Susquehanna Clay, Clark Co., Miss | 0.008 | 0.007 |
| Susquehanna Fine Sandy Loam, Smith Co., Texas | 0.003 | 0.003 |
| Orangeburg Sand, Terrel Co., Ga | 0.002 | 0.003 |
| Norfolk Fine Sandy Loam, 3 mi. S. W. Murphy, Colquit Co., Ga | 0.003 | 0.003 |
| Susquehanna Fine Sandy Loam, Colquit Co., Ga | 0.002 | 0.003 |
| Portsmouth Fine Sandy Loam, Colquit Co., Ga | 0.003 | 0.004 |
| Tifton Fine Sandy Loam, Bellville, Ga | 0.002 | 0.004 |
| **Soils of the Limestone Valley and Upland Province** | | |
| Hagerstown Loam, 1 mi. N. W. Conshohocken, Pa | 0.010 | ... |
| **Soils of Great Plains Province** | | |
| Oswego Silt Loam, 2 mi. N. W. Manhattan, Kan | 0.003 | ... |
| Colorado Sands, Greeley, Col | 0.002 | ... |
| **Soils of Piedmont Plateau Province** | | |
| Louisa Loam, Trevilians, Va | 0.003 | ... |

during the analysis of these standards. Approximately the same amount of sodium chloride as the soil samples contained was added to the standards.

The soils were taken from six different areas. The results of the analyses are given in the accompanying table.

Lithium, although occurring in small amounts, was found present in all soils examined and in many cases in larger amounts than rubidium[1] is usually found. The content of lithium does not seem to follow that of any other element in the soil. Nearly the same amount of lithium is found in soil and subsoil but in most cases the proportion found in the subsoil is greater.

Bureau of Soils
U. S. Department of Agriculture, Washington

# LABORATORY AND PLANT

## SAND BLAST FOR MARKING GLASSWARE

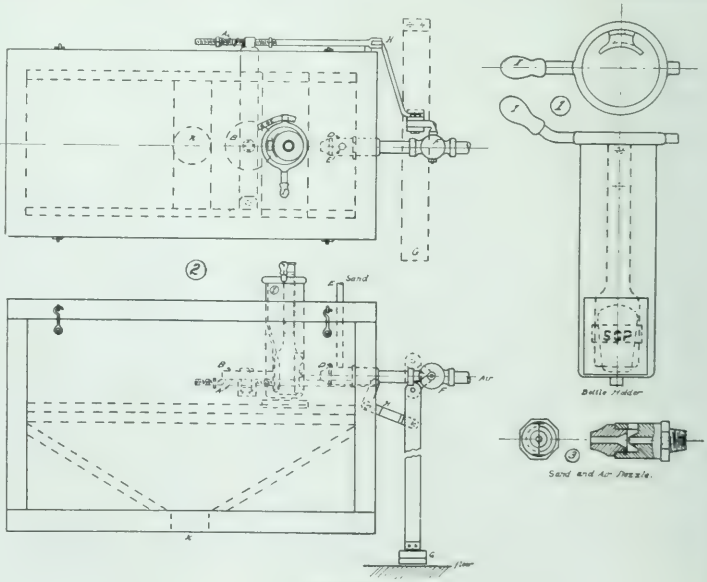
By George Spitzer and L. S. Trachsel

Received March 19, 1915

Sometime ago it became necessary for the senior writer to devise a means for marking glassware. The main objects desired were rapidity, economy and durability. Where large quantities of glassware are to be marked rapidity is very essential. The method of using an emery wheel or emery paper answers the purpose quite well where only "spot etching" is required and the glassware is sufficiently strong to withstand the pressure of the rapidly moving emery wheel or emery paper. When lettering is to be done other methods are resorted to, and the so-called diamond ink or hydrofluoric acid method is sometimes used. Before employing either hydrofluoric acid or diamond ink for effective etching it is necessary that the glassware be warmed and free from grease or dirt. The rubber stamps used for applying the etching agent clog up with the paste, making frequent cleaning necessary and also making the whole operation very slow and sometimes unsatisfactory. In addition the etching done by the hydrofluoric acid is fine-grained and soon becomes very faint if the glassware is handled to any great extent. This is true when grease or greasy substances come in contact with the etching.

To overcome these difficulties an effort was made to devise a sand blast, embodying the features necessary for rapid work, economy in various relations and one that would give durable markings. In this we believe we have succeeded, in a great measure, and it is hoped that perhaps others who may have occasion to make use of the sand blast may find some suggestions in our description and drawings.

The sand blast devised by the writers has given excellent results in marking Babcock test bottles. It is easy to manipulate, economical and rapid. From the drawing it will be seen that the manipulation is very simple; the bottle to be marked is placed in a cylindrical receptacle (bottle holder), the bell-crank presses the bottle against the stencil, the air cock is opened and the sand forced against the stencil. At the same time the cylinder is rotated by the hand sufficiently to expose the letters to the blast; when the turn is made the foot-lever is released which cuts off




Sand Blast

[1] *Bull.* **122**, Bureau of Soils, U. S. Dept. Agriculture, 1914.

the air blast, also prevents the sand from escaping, and the glassware is then withdrawn. From the construction of the apparatus very little sand is blown out during the marking, even though high pressure is used.

Where large quantities of bottles are to be marked the cost of marking becomes an important factor from the financial point of view, not only for time consumed, but also with reference to cost of the material. During the past year over twenty thousand (20,000) bottles have been marked at a cost of less than ten cents for sand and two dollars ($2.00) for stencils, in addition to the cost of compressing the air. The last item is to be considered and varies in different locations. In places where steam power is available, as in factories, creameries etc., the expense is scarcely to be considered after the initial cost of installing an air compressor. Where only a limited number of bottles are to be marked a hand compressor will answer quite well; for rapid work the pressure need not exceed 20 to 25 lbs. per sq. in.

It has been possible for an experienced man to mark six to eight gross per hour, in a very satisfactory manner. The sand blast requires no previous cleaning of glassware, as is frequently the case when marking with hydrofluoric acid.

### DESCRIPTION OF DRAWINGS

Fig. 1 is a brass receptacle of such dimensions as will accommodate the bottle to be etched or marked. This receptacle has a guide opposite the opening containing the stencil. The stencil is held in front of the piece of glassware to be marked, by two clamps.

Fig. 2 shows plans of and elevations of the air-tight box which encloses all the etching mechanism. The spring (A) through the medium of the roller (B) forces the guide and the bottle against the stencil. This rotation is obtained by pressing the foot-lever (G) and is communicated through the bell-crank and rod (H). The spring (A) is adjusted to obtain the proper pressure of the bottle or piece of glassware against the stencil. The sand is blown from the nozzle (D) and forced against the stencil. The receptacle is rotated by means of the handle (I) sufficiently to bring each letter of the stencil normal to the blast of sand. The sand enters the nozzle (D) through the opening (E) by gravity. The compressed air enters through the valve (F), which is controlled by the foot-lever (G), this one lever operating the valve (F) and spring (A) simultaneously. The sand entrance to the nozzle is so located that no sand escapes when the air pressure is removed. All the motions necessary to mark each piece of glassware are controlled by the foot-lever simultaneously, except the rotation of the receptacle, the speed of which depends upon the depth to which the glassware is to be marked. All the sand blown into the box escapes through the opening (K) into a container. The sand is returned to the sand box supplying the sand to the nozzle. This sand box is placed two or three feet above the apparatus and the sand is carried by means of rubber tubing or small glass pipe to the opening (E) of the nozzle.

The fundamental design of this apparatus can be made use of in marking various kinds of glassware. Stencils can be easily made containing a greater number of letters or rows of letters. Stencils having plain openings may be used in etching laboratory glassware, beakers, necks of flasks, etc., or for "spot" etching.

PURDUE UNIVERSITY, LAFAYETTE, INDIANA

## A MODERN HYDRATED LIME PLANT

By RICHARD K. MEADE

Received March 23, 1915

One of the newest hydrated lime plants is that of the Dutchess County Lime Company, at Dover Plains, N. Y. This plant was completed in the fall

FIG. 1—PLANT OF THE DUTCHESS COUNTY LIME CO., DOVER PLAINS, N. Y.

and has now been in operation for about four months. This company, however, has been in existence for several years, operating two small kilns about two

FIG. 2—LIME KILNS DURING CONSTRUCTION

miles from the town of Dover Plains, hauling their lime to the railroad with teams and bringing the coal and other supplies to the plant by the same means.

The stone found on the property is a high-grade magnesian limestone of which the following analyses give a good idea.

| Analyses of Limestone | From old quarry | From new quarry |
|---|---|---|
| Silica | 0.74 | 0.88 |
| Iron oxide and alumina | 0.92 | 0.90 |
| Lime | 31.04 | 30.74 |
| Magnesia | 21.03 | 21.11 |
| Loss on ignition | 46.34 | 46.64 |

The lime has been sold for years in New York City, Albany, Poughkeepsie and other cities along the line of the New York Central R. R. and enjoys the reputation of being a very high-class building lime. About a year ago, the company decided to build a new plant consisting of both kilns and hydrating equipment and commissioned the writer to prepare plans and specifications for this plant. It was decided also to locate the plant on a part of the property adjacent to the railroad, where the same quality of stone as at the old plant is found and to extend a siding from the railroad to the plant. At the new site, the stone lies to the south of the plant in a hill, having quite a considerable elevation, while an ideal location for the mill was found on a level plateau immediately adjacent to the hill and easily reached from the railroad. Work was begun upon the plant last winter and completed in the late summer.

The general layout of the plant is shown in Fig. 1. The kilns are located at the end nearest the quarry; next comes the cooperage and barrelling department, then the boiler room and the hydrating plant in the order named and finally a storage for hydrated lime, which latter is not yet completed.

The kiln building is designed to receive five kilns, two of which are already in place. These kilns are of the general type found throughout Maryland and Southern Pennsylvania (Fig. 2). They have been modified, however, so as to obtain both increased output and economy over the latter. The kilns are equipped with two fire boxes, one on each side and a cooling cone below. They also have a storage for stone in the upper part of the kiln. The capacity of the kilns on the stone found at Dover Plains will average about 12 tons per day. The fuel ratio is about 1 of coal to 4 of lime.

Arrangements have been made to install a belt conveyor to carry the lime from the kilns to the hydrating plant but at the present time the lime will be wheeled from one to the other.

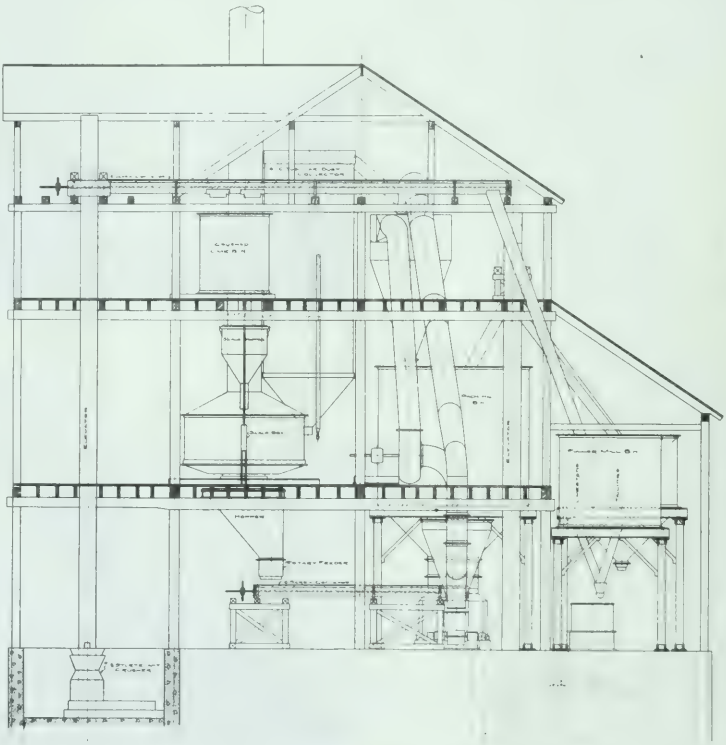


Fig. 3.—Side Elevation, Hydrating Plant, Dutchess County Lime Co.

On entering the hydrating plant, the lime is first passed through a Sturtevant open-door crusher (see Figs. 3 and 4). This reduces the lime to such a size that it will all pass through a one-half inch screen, which is fine enough for hydrating purposes. From the crusher the lime is elevated to the third and top floor of the building into a large steel bin which holds about 20 tons of lime and is provided at the bottom with a spout and gate, the latter being opened and closed by a lever. Below the spout is located the weighing hopper and beneath this, the Clyde hydrator (Fig. 5), which rests on the second floor: the scale box and indicator to the water tank are also on this floor, so that all the operations of the hydrator are controlled at one point. The lime is weighed out in batches of 200 lbs. and dumped directly from the scale hopper into the hydrator. The water is measured in a tank beside the lime bin and is sprayed on the lime after the latter is introduced into the hydrator. The process of

hydration lasts about 20 minutes, although it is probable that when the plant is pushed for capacity this time can be shortened to 15 minutes, as this lime hydrates very rapidly—particularly so for a magnesian lime.

After passing through the hydrator, the lime is dumped into a large steel bin or hopper, capable of holding comfortably the charge from the hydrator, and provided at the bottom with an automatic feeder which serves to regulate the supply of lime going from the hydrator to the pulverizer and is so adjusted as to empty the hopper before the new charge from the hydrator is ready to be dumped. The lime falls from the feeder into a screw conveyor which carries it to the pulverizer.

For treatment of the lime after passing through the hydrator, the Raymond system is used. The lime first goes to a No. 1 automatic Raymond pulverizer (Fig. 6), located on the ground floor; this mill is equipped with a throwout which separates from the hydrate any large pieces of core or unhydrated lime left in the product of the hydrator. From the pulverizer the fine product is sucked up by means of a No. 11 fan, and blown into a 7 ft. dust collector located above the packing bin, as shown in Fig. 3.

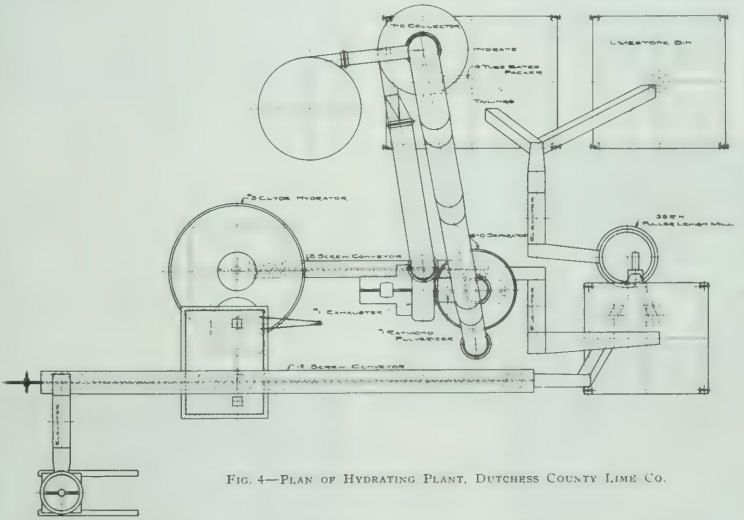



Fig. 4—Plan of Hydrating Plant, Dutchess County Lime Co.

It will be noticed that for the hydrating part of this plant only one elevator is used, namely that for carrying the lime from the crusher to the lime bin. This is a feature of all the plants which the writer has designed, thus greatly simplifying the installation.

In connection with the cyclone dust collector there is also a tubular collector with 18 ft. tubes. This is designed to catch the dust in the exhaust from the Raymond system. The product obtained from this is so fine that all of it will pass a 100 mesh screen, and on account of this extreme fineness, it is suitable for the manufacture of grease and for other uses where a superfine hydrate free from grit is necessary.

Space has been left in the building, and all arrangements made for adding another hydrator and separating system whenever it is desired to double the capacity of the plant, which has been designed with this end in view.

From the dust collector, the hydrate, as we have said, falls into a bin above the packing machine. This latter is of steel plate supported on steel columns and holds 40 tons of hydrate. A novelty in its construction is a partition dividing it into two parts. By an arrangement of slides, hydrate may be packed from either side with the same packing machine. This feature is designed to allow two grades of hydrate to be manufactured at once, the uniform product being obtained from the Fuller mill as explained further on. The packing is done by the Bates packer and Bates valve bags are used (Fig. 7). This packer is now being equipped with a dust catching system which will remove practically all of the dust and will make the plant almost dustless. This system consists of a suction fan connected with a pipe running along behind the packing machine. Branches with openings extend to the tubes of the machine and the spill from the tubes is sucked away through the pipe. The dust is discharged into the dust collector of the Raymond system.

A feature of this plant is the equipment for pulverizing limestone. For this purpose a 36 in. Fuller mill is employed and with it almost any fineness desired can be obtained. Where the limestone is desired for agricultural purposes the mill is provided with a $\frac{1}{4}$ inch mesh woven wire screen. This gives a product sufficiently fine for farm requirements. At this fineness the mill will grind about 5 tons of the Dover Plains dolomite per hour. The limestone to be pulverized is passed through the same crusher used for the lime, goes up the same elevator and into a screw conveyor which carries it to a bin over the Fuller mill. As the capacity of the crusher is 8 to 10 tons per hour, this is amply large enough to take care of both the hydrator and the pulverized limestone department by hydrating first on lime and then on stone. The discharge from the Fuller mill is taken up by an elevator to another bin and it may be packed from this into bags by hand or it can be spouted directly from the discharge of this elevator into the cars.

There is also an elevator leading from the throwout of the Raymond mill. This takes the tailings from the latter up to the bin above the Fuller mill (which latter

bin has a special compartment for these tailings) where they can be mixed with limestone and ground for agricultural purposes or they can be mixed with fresh hydrate ground and elevated into one of the compartments of the hydrate packing bin. The idea of this latter arrangement is to allow the making of a very fine hydrate by adjusting the Raymond mill to reject all but the finest hydrate. The coarse material so rejected is then ground in the Fuller mill and sold as second-grade or mason's hydrate. The two compartments in the packing bin are to allow the two grades of hydrate to be manufactured simultaneously.

Figs. 3 and 4 show the general arrangement of the hydrating plant.

Power for driving the plant is obtained from an Atlas-Corliss engine which can develop about 135 H. P. Steam for this is supplied from two water tube boilers which have a rated capacity of about 60 H. P. each. The machinery installed at the present time requires about 75 H. P., the additional power available being intended for the plant after its capacity has been doubled.

Coal for the boilers is brought in on the south side of the plant on an elevated track and dumped into a pocket opposite the boiler, while the coal pockets

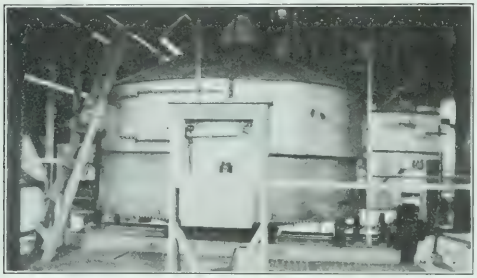


FIG. 5—THE HYDRATOR

for supplying the lime kilns are located further on along the same trestle. The coal is elevated to the firing floor by the use of a bucket elevator. The cars to be loaded are brought in on the north side of the plant and the platform from the bagging machine is on a level with the car floor.

The kiln building is 60 ft. x 53 ft. and is of steel covered with corrugated iron. The firing floor is of concrete and steel and all of the ground floors throughout the buildings are concrete. The hydrator building is 60 ft. x 53 ft., of frame covered with galvanized iron and the construction throughout is of heavy mill-type. At the present time, a storehouse 53 ft. x 100 ft. is being built. This is of light steel construction and will be covered with galvanized iron. This storehouse is designed to hold hydrated lime in bags. It is the intention, however, very shortly to put in a steel tank storage in which the hydrate will be stored in bulk as manufactured and then conveyed back to the plant for packing, as desired for shipment.

The bins are all of steel and with the exception of the crushed lime bin are all supported on latticed columns. All the elevators are encased in steel and are of the chain bucket type. The conveyors are of

FIG. 6—RAYMOND PULVERIZER

the screw type and work in steel troughs. The main shafting is supported on concrete piers, and clutches are used to make the operation of the plant more flexible. The hydrated lime plant can be operated at its full capacity with but five men and it is believed that for quality of product and ease of operation it will not be surpassed by any hydrated lime plant in the country.

All plans and specifications for the hydrated lime plant were prepared by the writer, who also drew plans

FIG. 7—BATES VALVE BAG PACKING MACHINE

for the general arrangement of the entire plant, selected the mill site, prospected the store deposits, etc. The construction work was in charge of Mr. Ambrose Allen, superintendent of the plant.

202 NORTH CALVERT STREET
BALTIMORE, MD.

## A NEW TYPE OF APPARATUS FOR THE REDUCTION OF IRON SOLUTIONS BY METALLIC ALUMINUM

By C. L. Schumann

Received January 12, 1915

The use of aluminum in the form of a sheet for the reduction of iron from the ferric to ferrous state was first recommended by W. H. Seamon.[1] Aluminum wire in the form of a spiral in a large test tube was worked out independently about the same time at the University of Michigan by Professor E. D. Campbell. Since that time the method has been widely used on account of its convenience and accuracy. A modification has been proposed with the view of eliminating the error resulting from the oxidation of the iron during the transfer from the reduction tube to the titrating flask.

The writer has found a very convenient form in an aluminum chain made from heavy aluminum wire attached to a glass rod of such length that it projects up into the neck of an Erlenmeyer flask (see sketch). The reduction and titration may be thus carried out in the same flask, the chain being easily removed and washed after the reduction is complete. This method has the additional advantage of requiring only a small depth of liquid.

The chain is weighed before and after use to correct for the iron present in the aluminum. A large number of determinations may be in progress at the same time, for experiment has shown that differences in time of reduction introduce no appreciable error.

University of Michigan, Ann Arbor

## THE USE OF LIGHT FILTERS WITH THE TASSIN METALLOGRAPHIC APPARATUS

By Frederick H. Getman

Received January 23, 1915

In the course of certain investigations now in progress in this laboratory it became necessary to employ photomicrographic apparatus for the examination of metallic surfaces. In order to secure satisfactory illumination, the Tassin electric illuminator[2] was used

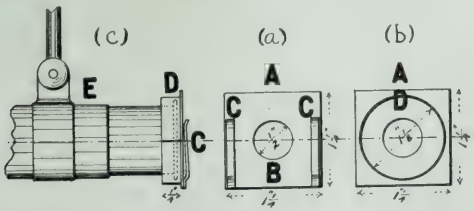



Fig. I

in connection with a Bausch and Lomb microscope and photomicrographic camera. While more or less satisfactory results were obtained with ordinary isochromatic photographic plates it was found to be almost impossible to secure negatives showing much contrast and sharply defined detail.

To overcome this defect a very simple accessory to the Tassin apparatus was devised as shown in Fig. I (*a*) and (*b*). Through the center of a sheet of brass, A ($^1/_{32}$ in. thick and $1^1/_4$ in. sq)., a $^1/_2$ in. hole, B, was bored. To one side of A was soldered a brass ring, D ($1^1/_8$ in. in diameter and $^1/_4$ in. deep),

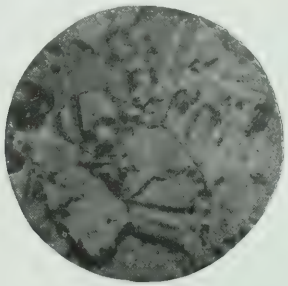


Fig. II—Taken with Ordinary Isochromatic Plate

the center of the ring being concentric with the hole B. To the opposite side of A were fastened two spring clips, CC, $^1/_8$ in. wide and $^7/_8$ in. long. This device was then slipped over the lens in front of the vertical illuminator as shown in Fig. I (*c*), the ring D being split in order to hold A securely in place.

After focusing on the ground glass screen in the usual manner, a Wratten and Wainwright gelatine light filter of the desired color was slipped under the

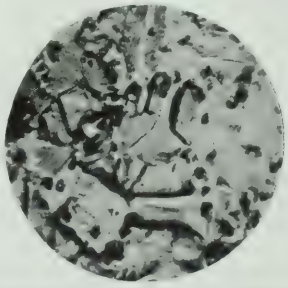


Fig. III—Taken with W. and W. Panchromatic Plate and B Filter

spring clips CC, and the exposure made with a Wratten and Wainwright panchromatic plate, the time of exposure being determined by means of appropriate factors for each screen. The Wratten and Wainwright A, B and C screens gave a sufficient range of colors for all ordinary purposes, but if it is desired to obtain a record of the true color ratios of a heat-tinted specimen the $K_3$ screen should be used.

The accompanying photomicrographs (Figs. II and III) of a polished brass surface, etched with nitric acid, and magnified 200 times, may be taken as typical of the results obtained when the Wratten and Wainwright filters and plates are used in conjunction with the Tassin apparatus.

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[1] *West. Chem. Met.*, **4**, 105.
[2] Tassin, This Journal, **6** (1914), 95.

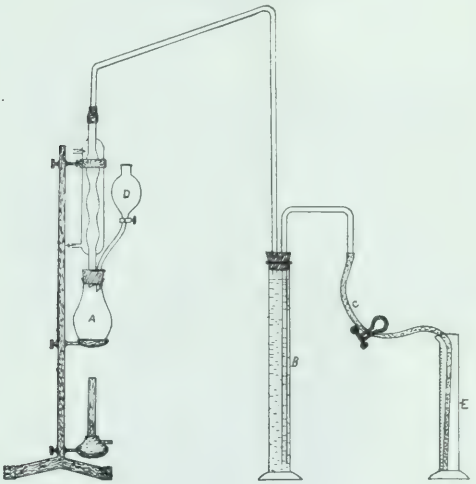
## A METHOD FOR THE DETERMINATION OF CARBON DIOXIDE IN BAKING POWDER AND CARBONATES

By H. W. Brubaker

Received December 7, 1914

The following is the result of an attempt to devise a method for the determination of the available carbon dioxide in baking powders, which is simple in principle, requires an apparatus easy to construct, and manipulate, consumes little time and gives reasonably accurate results. The method was devised for the use of a class of girls in household chemistry. It is adapted not only to the determination of carbon dioxide in baking powder but also in carbonates, bicarbonates and minerals such as limestone and dolomite.

The principle of the method, in brief, is the liberation of the carbon dioxide, causing it to displace its own volume of a saturated solution of sodium chloride into a graduated cylinder and measurement of the volume of the solution displaced. A saturated solution of salt is used because carbon dioxide is not readily dissolved in it and tests show that under the conditions of the experiment the amount of absorption is so small that it may be neglected. A saturated solution of salt is also used, instead of water, in the decomposition of the baking powder. The principle of collecting carbon dioxide over a saturated solution of sodium chloride is used by Jago in determining the strength of yeast.




### PROCEDURE

One gram of the baking powder is placed in the flask *A*. Water is circulated through the condenser for several minutes. The cylinder *B* is nearly full and the delivery tube *C* is full, to the open end, of a saturated solution of salt, the pinch clamp being closed. The stopcock in the funnel *D* is now closed and exactly 25 cc. of a saturated solution of salt placed in the funnel. The pinch clamp on the delivery tube is now opened and the salt solution run in from the funnel by opening the stopcock, care being taken not to admit any air. The carbon dioxide begins to be liberated at once and the salt solution is driven over into the graduated cylinder *E*. The decomposition of the baking powder is completed by heating with the gas burner until the solution has boiled for two or three minutes or until the rise of the salt solution in the cylinder *E* is seen to have stopped. The flame is then turned out and the apparatus allowed to stand until it has cooled to room temperature again. The cooling of the flask *A* can be hastened, if desired, by lowering the ring and bringing a beaker of cold water up under the flask until it is immersed in the water. When the apparatus has reached room temperature the salt solution in *E* and *B* is leveled up by raising *E*. The pinch clamp is then closed; the cylinder *E* is lowered to the table, the delivery tube removed and the volume of salt solution in *E* read. Subtract 25 cc. from this volume to compensate for the 25 cc. of salt solution which were run into the flask *A* to decompose the baking powder. Correct the remaining volume to 0° C. and 760 mm. pressure. As 5.1 cc. of carbon dioxide gas at 0° C. and 760 mm. pressure weigh 0.01 g., which is one per cent of 1.0 g., the per cent of carbon dioxide in the baking powder may be found by dividing the corrected volume by 5.1.

Note: In making the correction for aqueous tension I have used that for pure water which is two or three mm. too high in each case. The effect of the small error thus introduced into the results here recorded is to make them too low.

### RESULTS

The purpose of the condenser in the apparatus is to prevent any water from distilling over into the cylinder *B* and thus diluting the salt solution. Table I shows some results obtained with various baking powders:

Table I—Analyses of Baking Powders for $CO_2$

| Sample Baking powder | Vol. $CO_2$ Cc. | Temp. ° C. | Barometer Mm. | Per cent $CO_2$ |
|---|---|---|---|---|
| Royal A 1 | 65.0 | 20 | 740 | 11.30 |
| 2 | 66.0 | 20 | 740 | 11.47 |
| Royal B 1 | 66.4 | 21 | 742 | 11.43 |
| Calumet A 1 | 78.3 | 22 | 740 | 13.47 |
| 2 | 77.9 | 23 | 740 | 13.34 |
| Calumet B 1 | 82.0 | 29 | 745 | 13.69 |
| K. C. 1 | 65.0 | 24 | 745 | 11.14 |
| 2 | 64.5 | 25 | 745 | 11.02 |

In order to ascertain whether an appreciable amount of carbon dioxide is absorbed by the salt solution during a determination, 90 cc. of carbon dioxide were run into the apparatus at 22° C. and 740 mm. and allowed to stand 2 hours and 40 minutes, at the end of which time the volume was 90.3 cc. and the temperature 23° C., the pressure having remained the same. The increase in volume is very close to that which would result from the increased temperature.

In applying this method to the determination of carbon dioxide in carbonates such as sodium carbonate and precipitated calcium carbonate the sample was decomposed by means of a dilute solution of hydrochloric acid which was saturated with sodium chloride. The absorption of carbon dioxide by the acid solution is appreciable and must be allowed for.

This is done by decomposing one sample with 10 cc. of the acid solution, then running a second determination, using 15 cc. of acid. The difference in the amounts of carbon dioxide obtained in the two cases being due to the absorption by 5 cc. of acid solution, the proper correction is made on either determination. When decomposing precipitated carbonates with hydrochloric acid no heating is necessary, hence the time consumed in each determination is very short, but two or three minutes being required for the liberation of the carbon dioxide. In running two samples of calcium carbonate in this way, the whole process, including the weighing of the samples, required only ten minutes.

Table II shows some of the results obtained on carbonates. In Determinations 1 and 2 heat was used. In Determination 3 no heat was used. The sample of sodium carbonate used in determinations 4 and 5 was found to contain 4.46 per cent of moisture. The theoretical amount of carbon dioxide in this sample

TABLE II—ANALYSIS OF CARBONATES FOR $CO_2$

| Detn. No. | Sample | Wt. taken Gr. | Decomposed by cc. acid | Vol. $CO_2$ Cc. | Temp. ° C. | Bar. mm. | Per Cent $CO_2$ Found | Per Cent $CO_2$ Theoretical |
|---|---|---|---|---|---|---|---|---|
| 1 | $CaCO_3$ | 1/4 | 5 | 62.5 | 23 | 737 | 43.98 | 44.00 |
| | | 1/4 | 10 | 61.0 | 25 | 737 | | |
| 2 | $CaCO_3$ | 1/4 | 3 | 64.0 | 24 | 739 | 43.88 | 44.00 |
| | | 1/4 | 8 | 63.5 | 25 | 739 | | |
| 3 | $CaCO_3$ | 1/2 | 8 | 127.0 | 25 | 735 | 43.98 | 44.00 |
| | | 1/2 | 13 | 124.65 | 25 | 735 | | |
| 4 | $Na_2CO_3$ | 1/2 | 7 | 116.0 | 25 | 734 | 39.95 | 39.65 |
| | | 1/2 | 12 | 113.88 | 25 | 734 | | |
| 5 | $Na_2CO_3$ | 1/2 | 7 | 116.0 | 25 | 734 | 39.95 | 39.65 |
| | | 1/2 | 12 | 113.88 | 25 | 734 | | |
| 6 | Dry $Na_2CO_3$ | 1/2 | 7 | 118.2 | 24 | 742 | 41.38 | 41.50 |
| 7 | Limestone | 1/2 | 10 | 111.5 | 25 | 744 | 38.18 | 38.45(*a*) |
| | | 1/2 | 15 | 113.5 | 28.3 | 742 | | |

(*a*) By difference; see text.

is therefore 39.65 per cent. Some of this sodium carbonate was now dried and Determination 6 made upon the dry sample with the result shown. Allowing for the same absorption as in Determination 5, which is 2.97 cc., gives a total volume of 121.17 cc. under the above conditions of temperature and pressure which correspond to 41.38 per cent of carbon dioxide.

Determination 7 was made on a sample of limestone. It was necessary to use heat to completely decompose the sample with the acid solution. I had no gravimetric determination of carbon dioxide in this limestone against which to check the result. However, according to the figures of another analyst, the limestone contains 12.28 per cent $SiO_2$, 1.15 per cent $Al_2O_3 + Fe_2O_3$, 46.74 per cent CaO and 1.38 per cent MgO, making a total of 61.55 per cent, which leaves for carbon dioxide 38.45 per cent. This makes no allowance for potassium and sodium which may be present in very small quantities. The result is undoubtedly a close approximation to the actual percentage of $CO_2$ present.

NOTE (Jan. 11, 1915): Since sending this paper for publication I have found a convenient way of obviating the necessity of making a correction for the absorption of carbon dioxide in those cases where the sample is decomposed by dilute acids. This makes it unnecessary therefore, to decompose more than one sample of the substance for one determination. The procedure is as follows: Just before making the determination pour 30 or 40 cc. of dilute hydrochloric acid (1 acid : 3 water) on 0.5 g. of precipitated calcium carbonate. When the effervescence has ceased, and the acid solution has become clear, pipette 10 cc. of this into the bulb of the separatory funnel and proceed with the determination. This method of saturating the acid with carbon dioxide requires but a moment and makes it unnecessary to correct for any absorption whether the sample is decomposed by heating or at room temperature. The following determination will illustrate the accuracy of this method of procedure:

| | |
|---|---|
| Wt. of limestone taken | 0.5 g. |
| Volume of salt solution displaced | 138.18 cc. |
| Temperature, 22° C. Barometer | 739 mm. |
| Volume corrected to 0° C. and 760 mm | 112.3 cc. |
| Per cent $CO_2$ found | 44.03 |
| Theoretical per cent $CO_2$ | 44.00 |

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# ADDRESSES

## THE FIXATION OF ATMOSPHERIC NITROGEN[1]

By W. S. LANDIS

It is now some three years since I have occupied this side of the lecture table, and I can assure you this is a most delightful occasion to me, not only because I can here omit the tedious routine of taking an attendance record of my class, but also because it is my first opportunity to tell the chemical and engineering professions something about the interesting work I have been engaged in since giving up university teaching.

I am going to assume that you are all more or less familiar with the use of nitrogen in one or more of its various combinations, for to catalogue even a partial list of the most common commercial nitrogen compounds would read like a few pages out of Mr. Olsen's "Chemical Annual," or from the "Chemiker Kalender." I am not even going to bore you with statistics of consumption of the nitrogen compounds, because the very complex nature of these statistics would make them difficult of comprehension if merely read from prepared tables, and I believe our time can be better occupied along other more interesting lines intimately connected with our subject. I shall add only that in tonnage alone the nitrogen compounds stand well at the head of the list of the world's trade in heavy chemicals, nitrate of soda and sulfate of ammonia being produced in 1913 to the value of $200,000,000.

Not including atmospheric nitrogen, whose utilization is yet in its infancy, we are practically dependent for our supply of this valuable element upon the nitrate deposits of Chile, and its recovery as a by-product from our fuels. The Chilean deposits have been so frequently and fully described elsewhere that we can omit reference to the same here. The end of this source of supply is, however, in sight, and it will be only a few years until Chilean nitrate will pass into history along with our anthracite coal and the Saxon silver-lead ores.

The recovery of ammonia as a by-product from fuel is entirely different, since for many centuries to come, we shall have an ever-increasing source of this element in the coke oven and the gas producer, from which it is obtained in one of its most valuable forms of combination, ammonia. This source

[1] Presented before the Washington Section of the A. C. S. on March 17, 1915, and before the Philadelphia Section of the A. C. S., March 18, 1915.

supply is, however, somewhat unsatisfactory, inasmuch as it is wholly a by-product of the coal distillation industry, a ton of coal yielding only 5 to 6 pounds of ammonia, and by-products as a source of primary supply have many limitations. This is well illustrated by the present status in Germany, from which country I have lately returned. There is in that country just now a considerable shortage of nitrogenous fertilizer because the Government has confiscated all stores of nitrate for military purposes (the fertilizer industry there consumes about 800,000 tons of nitrate per year). The coke ovens which we should expect would normally come to the rescue in such a crisis are, however, largely closed down because industrial Germany is at a standstill, and no one wants coke. Ammonium sulfate production is, therefore, correspondingly decreased just at a time when agriculture needs it most, and its lack is felt acutely. Since my return I have learned that the use of coal has been prohibited in Germany in order to force the use of coke, and thus increase the supply of ammonia and tar.

We come very near having the same conditions arising in this country, for were the farmer in position to take his normal fertilizer requirements there would be a great sulfate shortage, as our own industrial depression has closed down many of our coke ovens, and we would have no ready means of meeting even a normal demand for sulfate. We thus see the disadvantage of a by-product source of such an important element as nitrogen, and why inventors have been so actively engaged in finding a substitute for the Chilean nitrate and the coke-oven ammonia.

Naturally the inexhaustible store of atmospheric nitrogen has presented itself most prominently in this search for a new source, and it is upon the activities of the inventors in that field that I wish particularly to speak tonight.

Neglecting the many proposals which have merely wasted much paper and ink in describing impossible methods for the fixation of our atmospheric nitrogen, I shall devote my attention solely to the successful, and at the present time commercially developed efforts in this field. We can classify these successful attempts into three groups:

I—Direct synthesis of nitrogen and hydrogen to ammonia.

II—Combustion of nitrogen and oxygen in the electric arc.

III—Combination of nitrogen with metals or carbides.

The only commercial process today belonging to Group I is the so-called Haber Process. Dr. Bernthsen described this process at the Eighth International Congress of Applied Chemistry,[1] and exhibited a small working model of the apparatus. I am sorry that I can add but little to the technical information he there presented, but the owners of this process have maintained the greatest secrecy with respect to its commercial development, and but little is known regarding the details in the commercial world.

As you will recall, this process consists in passing a mixture of three volumes of hydrogen and one volume of nitrogen, at a pressure of upwards of 150 atmospheres, over a suitable catalyzer operating at a temperature of some 500 to 700° C. A single passage of this mixture through the apparatus causes a transformation of 2 to 6 per cent of the nitrogen to ammonia, which is recovered from the apparatus by condensation, and the rest of the uncombined gases are again returned to the cycle.

Too much honor cannot be shown the courageous chemists who have succeeded in placing this process on a commercial working basis. The difficulties seem almost insurmountable. The catalyzer, which has taken various forms and compounds, principally metals and carbides, poisons very readily, and hence extreme care must be taken in the purification of the gases. Purity which the average chemist would classify as C. P. finds no place in this industry, as that would lack almost as much of meeting the requirements of the process as would the use of crude chemicals in the analytical laboratory. It took years of work to find a suitable metallic container for the high pressure gas mixture, because of the permeability of most ordinary materials. However, most of these difficulties have been overcome, and I have been reliably informed that the Badische Plant at Oppan supplied its allotted quota of sulfate to the German Sulfate Sales Company last year, but I greatly doubt that they did it at a profit if it was made from synthetically produced ammonia, with sulfate prices as low as they were in the early part of 1914.

FIG 1 —GENERAL VIEW OF FACTORIES, AMERICAN CYANAMID COMPANY

This process, as ordinarily understood, is not supposed to involve the use of any considerable quantity of electric power, which is not quite true, but does require a large amount of highly skilled labor, for the units are small and complicated. This particularly suits it to the Rhine location, but renders its value in the United States rather questionable. I personally cannot see a future for its operation under American conditions, particularly in view of the competition of the much cheaper Cyanamid process which furnishes the same end product—ammonia.

[1] THIS JOURNAL, 4 (1912), 760.

At Oppan the Badische must dispose of large quantities of waste sulfuric acid and have at their disposal by-product hydrogen; hence local conditions favor this process above all others.

The second group of processes embraces those oxidizing the nitrogen of the atmosphere in the electric arc. It is well known that when air is heated to temperatures of above 1800° C. and rapidly cooled, the nitrogen oxidizes to NO and remains in that form. At this temperature, however, the reaction velocity is very low and commercial working requires that temperatures of above 3000° C. be used, at which temperature the reaction velocity becomes quite considerable.

Three types of apparatus are in commercial use for performing this reaction:

1—The drum furnace with disc arc—Birkeland-Eyde.

2—The long tube furnace with spiral arc—Schonherr.

3—The narrow furnace with fan-shaped arc—Pauling.

There are numerous other proposed types of apparatus which are claimed to be far superior to the above, as reference to patent literature in particular will show, but the above listed three furnaces are the only ones in actual every-day operation.

The products obtained by passing air through the arc of any of these furnaces consists of a highly heated gas containing

FIG. II—ONE OF THE TRANSFORMER ROOMS

from 1 to 2 volume per cent of nitric oxide. On cooling down to temperatures of approximately 600° C. this nitric oxide unites with free oxygen to form nitrogen peroxide, $NO_2$; on further cooling of this nitrogen peroxide to below 140° C. it polymerizes to $N_2O_4$. When brought into contact with water and oxygen, this reacts, forming a mixture of equal molecular parts of nitric and nitrous acids. By subjecting the nitrous acid to further action of the peroxide this is also changed to nitric acid with the liberation of nitric oxide, which again passes through the cycle. Thus by suitable cooling of the nitric oxide in the presence of air and water one ultimately attains a product which consists almost quantitatively of nitric acid, and actual operating results of the large furnace plants have shown a steady recovery of about 90 per cent of the nitrogen oxides in the form of nitric acid or nitrate salts, the remainder being received as nitrite or not absorbed.

In general, the handling of the nitrose gases from the arc furnaces is now well standardized, and the design of a condensation plant is almost as well understood today as that of a sulfuric acid plant. After passing the various systems of cooling apparatus, consisting of steam boilers, evaporators, etc., the gases enter aluminum condensers where the temperature is reduced to approximately 100° C. They then enter a preliminary oxidation chamber so proportioned that they remain at least $1^1/_2$ minutes, and the preliminary oxidation to peroxide takes place. The gases next pass into a series of four or five stoneware or granite towers where they are washed with water by a counter current system, remaining in the tower system for from 3 to 5 minutes. Of the nitrogen oxidized, 90 per cent is here condensed as nitric acid, the most concentrated acid being obtained in the first tower, and averaging from 30 to 35 per cent $HNO_3$. After passing these condensing towers the gases usually enter a final tower fed with caustic soda liquor, where a further 3 to 5 per cent of the oxidized nitrogen is recovered as sodium nitrite. The remaining 5 per cent passes out into the air unabsorbed.

As above mentioned, these towers deliver a 30 to 35 per cent nitric acid; this can be further concentrated to 50 per cent nitric acid, using the heat of the hot gases issuing from the arc furnace to perform the necessary evaporation. It is not possible to carry this evaporation much above 50 per cent for economical reasons, and where higher concentration of nitric acid is demanded special complicated concentration processes must be employed.

Dilute nitric acid, as obtained from the towers, finds little use in industrial processes, and it is difficult to transport. Most of the nitric acid plants, therefore, either concentrate it to 96 per cent acid by special means, or convert it into calcium nitrate for fertilizer use, or into ammonium nitrate for explosive purposes. In the latter case most of the ammonia used today in the nitric acid plants, operating on the arc system, is obtained from Cyanamid. It is quite probable that calcium nitrate will soon disappear from the fertilizer market, as it certainly cannot be sold at a profit in competition with Chilean nitrate or ammonium sulfate, even when the latter is made from Cyanamid.

As we shall see later, these arc processes require enormous quantities of cheap electric energy, and must be located near such power centers. We have no cheap power in the United States, and there is no immediate prospect of our having an arc process in continuous large scale operation within our borders. Our Western powers are far from markets and transportation of the nitric acid as such to the East is almost out of the question.

I should like to dwell more at length upon the details of recovery of 95 per cent of the available products from the gas issuing from the arc furnace, which contains at its maximum concentration only 2 volume per cent of the same. But my time is rapidly passing and I want to give you at least a glimpse of the third group of the nitrogen fixation processes, the one in which I myself am most actively connected.

This third group of processes embraces fixing nitrogen by metals or carbides, and has reached its highest development in the Cyanamid process, which last year produced throughout the world, in the fourteen factories at present in operation, some 300,000 tons of material, carrying over 20 per cent nitrogen.

The inventors of the Cyanamid process originally attempted the synthesis of cyanides by subjecting barium carbide to the action of nitrogen, which, as is well known, forms barium cyanide. On attempting to use the cheaper calcium carbide in place of barium carbide, Professors Frank and Caro found that instead of obtaining a cyanide they obtained a new material, which proved to be calcium cyanamide. It was found later that this material could be utilized directly in agriculture, and from this discovery has grown the enormous Cyanamid industry which has proven itself to be the cheapest method of fixing atmospheric nitrogen at present in existence.

Reference to the literature existing upon the manufacture of Cyanamid seems to lead one to suppose that it is a comparatively simple matter to carry out the reaction so frequently written:

$$CaC_2 + N_2 = CaCN_2 + C.$$

This might be true to a limited extent were this the only reaction that we chemists at Niagara have to contend with, but I

can merely say to you that even this reaction itself is so complicated that while it is well known that it is a reversible one, no one has yet succeeded in correctly establishing its equilibrium constants. A laboratory study of this reaction has been carried out in this country by Professor Thompson, and abroad by Professor Haber, but neither of them has succeeded in mastering it, because of the peculiar difficulties that arise in a study of it.

Naturally, if the highly skilled chemical laboratories met with these difficulties, we can assume that practice runs against a few of them itself. But aside from the fundamental absorption reaction, as written above, there are a number of other complications that arise in this industry which we have to meet with in our every-day work, and which I shall call to your attention to show that the actual carrying out of the Cyanamid process requires something more than writing the reaction on a piece of paper.

The fertilizer industry, into which most of our material at present goes, is a rather peculiar one, and probably has more peculiar fads and precedents than almost any other highly developed industry in the country. Naturally, to sell them material one must take into account all of the peculiarities of the industry, and must satisfy them, a fact which further complicates the Cyanamid industry itself. As there may be fertilizer men present here tonight in the audience, I am not going to expose them to the engineering profession, but will dismiss mention of these peculiarities, and you can assume that inasmuch as Cyanamid is being produced and sold at the rate previously mentioned we have succeeded somewhat in meeting their fancies.

The first stage of the Cyanamid process involves the production of calcium carbide. To produce day after day a high-grade calcium carbide that meets the peculiar requirements of the cyanamid industry is quite an art in itself. There are no journeymen carbide workmen in our country, and we had to start out and develop our own furnaces and methods of operation. We had to seek sources of raw materials for this manufacture, which are quite different even from those which meet the requirements of the manufacture of lighting carbide, and we have to operate our furnaces in a certain peculiar way in order to combine these raw materials into a product of such structure and grade that we can make Cyanamid out of it successfully. You will recall that Moissan in his early work found that he could not nitrify certain kinds of carbide, showing that there are conditions existing in our carbide manufacture that are different from those in the manufacturing of lighting carbide.

Our next great problem is to grind this special grade of calcium carbide so that it passes a hundred mesh screen. Naturally this must be done without slaking the carbide, as hydrated lime does not make good Cyanamid. Now 100 mesh carbide dust, when exposed to the atmosphere on a damp day or thrown out on damp ground, is almost as explosive as low-grade dynamite, so that it is quite a problem to grind this carbide to the required degree of fineness and have a mill left at the end of the day's run.

Next comes the production of nitrogen. It is a comparatively simple matter for the chemist to make a few cubic centimeters of high-grade nitrogen in his laboratory, but if one were to call upon him for 2,000,000 cu. ft. of a practically pure nitrogen per day, such as we make at Niagara, he would probably have to do considerable research to find out just how this enormous quantity of such high-grade material could be made. In the early days of the Cyanamid process, when the Niagara plant started, liquid air machinery was in a rather backward state of development, and we were forced to make our nitrogen by passing air over copper. The original plant was later enlarged, and I am sorry that my pictures do not include it. It was a long step from the combustion tube of the chemical laboratory to our present plant, using retorts containing 5 tons of copper mass, but the problem has been successfully solved, and the new plant has been in operation with a minimum of trouble for some years. In the early days of the industry at Niagara we could draw upon natural gas for reducing our copper oxide, so as to re-vivify it, but this gas supply has since failed and we were forced to put up our own coal gas plant, shown in Fig. II. Even this coal gas plant is not a standard one, inasmuch as we

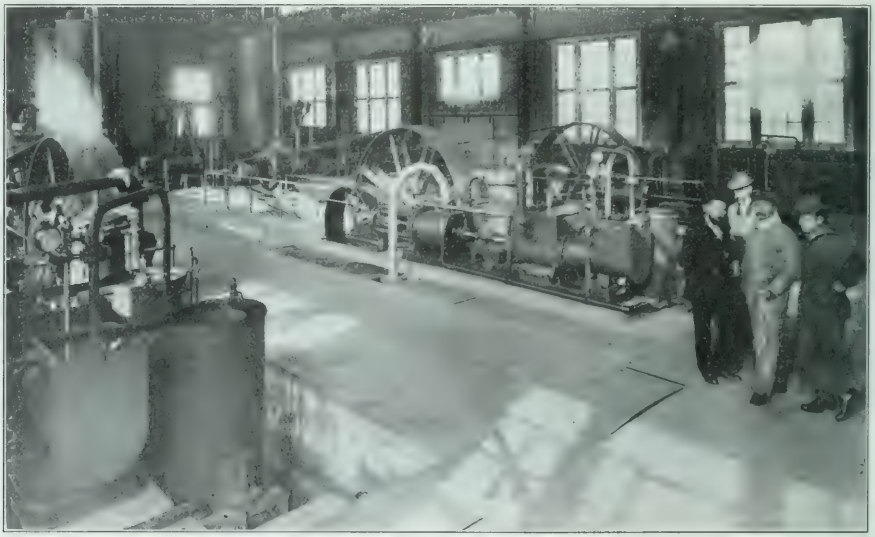


FIG. III—PART VIEW OF LIQUID AIR PLANT, AMERICAN CYANAMID COMPANY

are coking coal, not only for the production of gas, but also to furnish the coke for our carbide furnaces. We are running at temperatures in our retorts and obtaining qualities of coke and gas that the average city gas plant would not consider as possible of attainment, and it was only after considerable experiment that we ourselves demonstrated that our theories were correct in this respect and succeeded in finding gas engineers liberal-minded enough to incorporate our ideas into a working plant.

Eventually we had to install purification apparatus for taking out the impurities in the nitrogen, as it came from the copper retorts, and have equipped ourselves with soda towers for removal of carbon dioxide, refrigeration plants for drying, lime tanks for purification, etc., and have even developed this plant so highly that we have included a causticizing plant for recovery of our spent alkali.

After the development of the liquid air machinery, both in the way of capacity and reliability, the problem of producing pure nitrogen was much simplified, and our latest addition at Niagara includes what was probably the largest liquid air plant in the world at the time it was built, a year ago. This plant alone throws to waste almost thirty gallons of liquid air an hour, just to keep the apparatus flushed out and in good working order, not to speak of the thousands of cubic feet of rich oxygen-nitrogen mixture.

After one has overcome the difficulties in the production of a proper grade of nitrogen and of carbide, the next step is exposing these two to mutual reaction at a proper temperature, which is done in small individual ovens, holding from $^1/_2$ to $2^1/_2$ tons of carbide. The reaction itself is reversible, and particular precautions must be taken to keep it always running in the right direction until the carbide has all been nitrified. It would take several evenings to present the complex physical and chemical difficulties met in this phase of our work. The product removed from these ovens is a black, hard cake, which analyzes 22 per cent nitrogen and about 1 per cent un-nitrified carbide. This material, which we call Lime Nitrogen, is next finely ground and stored in silos. The carbon set free in the reaction previously indicated is in the form of graphite, and it is not an easy proposition to find a satisfactory mill that will grind this material fine and at the same time not blow itself up from liberated acetylene derived from the presence of any uncombined carbide, or wear itself out grinding the lime nitrogen-graphite mixture. Extreme precautions are taken in this part of our operation, both in the mills themselves and in the elevating and conveying apparatus connected with them to avoid dangerous explosions, and I can truthfully say that in the years I have been connected with the Company not a single injury has resulted from such explosions in our plant.

To prepare the lime nitrogen for agricultural purposes the finely ground material is partly hydrated to insure decomposition of the carbide it contains, and is then oiled to render it dustless, and stored in bulk, or packed immediately into sacks and shipped to the fertilizer mixer.

Calcium cyanamide tends to transform itself into a large number of organic compounds when subjected to the action of water, particularly at temperatures above normal, and, therefore, this hydration has proven an extremely complex problem, because we desire to avoid any such transformation, as agricultural experiments have shown that the calcium cyanamide in its unaltered form yields the best crop results.

But agricultural uses are not the only purposes to which the Cyanamid can be applied, as it is a very simple matter to convert the Cyanamid into ammonia by the exothermic reaction

$$CaCN_2 + 3H_2O = 2NH_3 + CaCO_3.$$

If lime nitrogen is mixed in a slurry with water and subjected to the action of heat and high pressure it is converted quantitatively into ammonia. In this country this use of Cyanamid was not developed on large scale outside our experimental laboratory until the beginning of this year, but while I was in Germany I saw in the yards of a big manufacturing concern some 60 autoclaves, each capable of converting 10 tons of Cyanamid per day into ammonia. This equipment was waiting railroad cars to move it out, and was in no sense experimental, because three similar plants have been in operation in Germany for at least three years. The cost of this transformation is hardly appreciable, and the purity of the product is quite high, requiring merely passing through a self-acting rectifying column for the removal of steam.

The ammonia so produced abroad is at present being converted into a high-grade sulfate and a pure nitrate, and we are at work now in this country on producing a new fertilizer material, "Ammo-Phos," consisting largely of ammonium phosphate; my experimental laboratory is at present working day and night trying to meet initial demands for this new material. Agricultural results during the past season have been so phenomenal that our friends will not await the completion of a large plant for meeting the requirements, but have insisted on our converting our laboratories into a miniature factory.

Our product contains over 13 per cent $NH_3$ and 45–50 per cent $P_2O_5$, or over 60 per cent plant food, the bulk of the remainder being chemically combined water, and when mixed with the high-grade potash salts available, will make a complete fertilizer some 6 times as concentrated as the average grade sold today.

It is also possible to transform Cyanamid into urea, and I have made in my experimental laboratory a great deal of pure salt in a comparatively easy and simple manner.

Similarly, Cyanamid can be converted into Dicyandiamid—by simple treatment with hot water. This material has been proposed for use as a deterrent in explosives, but I think it offers a much better field for transformation into the Guanidines.

Such transformations of Cyanamid abroad have received a great deal of attention, and there are numerous derivatives on the market. Just a few months ago I saw a sample of Creatine which had been made in a chemical laboratory from Cyanamid, and we feel that we are not very far from the synthetic production of foods when we can reach such a point in our chemical synthesis.

When a special grade of Cyanamid is melted down with a flux, such as common salt, it combines the free carbon present with the cyanamide radicle, forming cyanide. The resulting product of this fusion contains about 25 per cent of its full weight in equivalent potassium cyanide; this crude form of cyanide dissolves very readily in water and filters rapidly from the insoluble, after which the solution is ready for metal extraction, or other uses to which cyanide in its dissolved form can be put. Large scale experiments have been tried out in a number of the big cyanide plants scattered at various places throughout the world, and in every respect this material has shown an exactly equivalent value to the higher grade cyanides. The transformation of the cyanamide nitrogen into cyanide nitrogen is almost quantitative, and the fusion experiments can be carried out without difficulty and at a low cost. We have here, therefore, a crude form of cyanide which can be prepared very cheaply and which could be readily delivered to the consumer at a price approximately one-third under the present prices of the higher grade cyanide. Abroad this material has been made in large quantities and transformed into the pure cyanide, running approximately 127 per cent potassium cyanide equivalent, but we believe that with proper propaganda work our own cyanide users would find the low-grade material quite acceptable, provided it could be delivered to them at a cost sufficiently low to enable them to perform the extra dissolving and filtering operation which it involves over the use of the present high-grade alkali cyanides.

Cyanamid itself forms an excellent case-hardening material,

and we have prepared a number of mixtures which are in steady use at our plant for performing this operation upon various machine parts which we are using. It works extremely rapidly at very low temperatures, but we have not yet succeeded in overcoming certain fads in large scale use of this material, and it has not met with any general introduction. We found that the case hardener is more concerned with the color of his hardening powders than he is with the actual work they perform, and as the colors and odors of our cyanamid products are rather fast we have not found it interesting to us to meet some of these peculiarities of the case-hardening trade. While abroad I saw these case-hardening materials being prepared by the hundreds of tons for use in the manufacture of armament and war materials, and the small factory engaged in their production has been swamped with orders ever since its inception.

The arc processes have shown themselves capable of producing nitric acid or nitrates. Cyanamid itself is an entirely different product, but it is quite easy to produce ammonia from it, and there has recently been evolved abroad a most successful method of oxidizing this ammonia to nitric acid, so that in case of competition with the Birkeland-Eyde process we are not entirely limited to the fixation of nitrogen, but can furnish this nitrogen in exactly the same form that the arc processes can, and at considerably less cost. Our raw materials are cheap—coke, limestone, air. We use only one-fifth the electrical power that the arc processes do per unit of nitrogen fixed in the form of Cyanamid, respectively ammonia, and by the addition of a very small percentage more power we can convert our Cyanamid into nitric acid. We require about the same quantity of labor to fix a unit of nitrogen in Cyanamid as the arc process does in nitric acid, but since there is only a small fraction more labor used to transform Cyanamid nitrogen into nitric acid we do not feel this is a great handicap when one considers our smaller power consumption. On the American continent where water power is so expensive and so scarce this difference readily off-sets the additional labor necessary to make nitric acid from Cyanamid. Further, our Cyanamid is easily transported and can be changed to ammonia or nitric acid at the end of its journey at the expenditure of a very small amount of steam and labor, so that we have the additional advantage in transportability of stable raw material, and subsequent conversion at the point of direct use. These commercial transformation units are small, and can be set up to supply even small amounts of ammonia or acid in a quite cheap and efficient plant. Practically all sulfuric acid plants in Germany have installed them since nitrate disappeared from trade.

There is no comparison between the initial investment required for a Cyanamid plant and for an arc plant, if one includes power development. The Cyanamid plant, per unit of nitrogen fixed, requires an investment of only about one-fourth that required by the arc process, and for a Cyanamid-ammonia plant about one-half that required by the Haber process. Even the combination of the Cyanamid-ammonia-nitric acid process requires an investment of only one-third to one-half that for the arc process. In each case we are assuming exactly the same quantity of fixed nitrogen in the forms above designated. Where electrical power is expensive, as in the United States, there is no question regarding the superiority of the Cyanamid process for the fixing of atmospheric nitrogen, particularly for fertilizer purposes, and we eventually hope that the future development of our nitric acid process will enable us to compete in every line of nitrogen compounds with all other competitive sources.

I have brought with me some moving pictures of our Niagara Plant, showing the arrangement of the whole and some details of the various units comprising it. It is manifestly impossible in a plant such as ours to obtain pictures of every operation, but I have brought the most representative views of the operation of fixing nitrogen. When one considers that we have at Niagara a 12 kiln lime plant, 25,000 H. P. of carbide furnaces, a liquid air plant which was the largest in the world a year ago, a gas plant of sufficient size to serve the average town of 25,000 inhabitants, a nitrogen retort plant, an ammonia refrigeration plant, a causticizing plant, a nitrification plant, a hydration plant, and innumerable crushers, mills, silos and feeding machinery, it is rather difficult to include them all in a few hundred feet of motion picture film.

# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

## RECOVERY OF TOLUENE FROM GAS

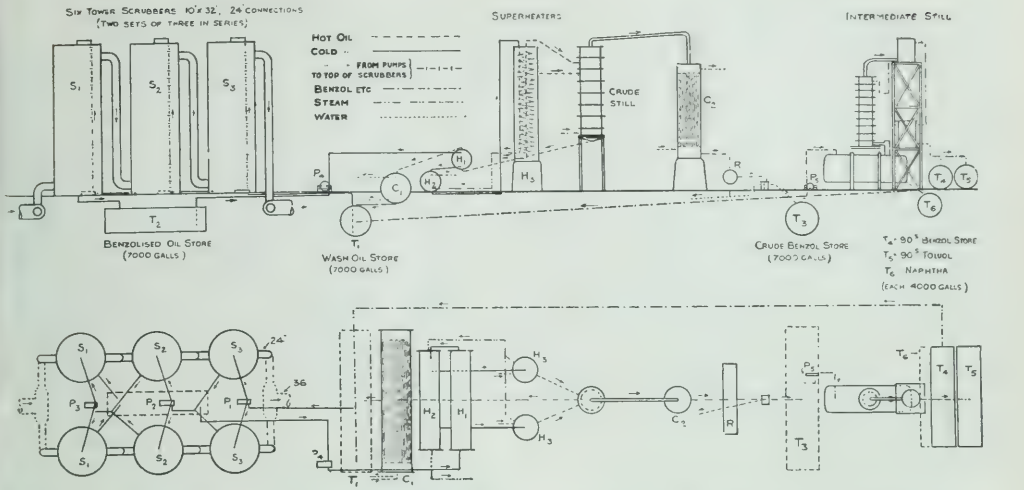
In the course of the proceedings at the conference on coal supplies held in Manchester in February, Mr. Macintosh Williams, who attended on behalf of the War Office Committee on the Supply of High Explosives, referred to the shortage of toluol and to the action taken by the committee with the object of obtaining the necessary quantity to meet requirements. He stated that satisfactory arrangements had been made with the tar distillers; the coke-oven manufacturers were approached, and did what they could. Subsequently an appeal was made to the larger gas undertakings to make arrangements to wash the toluol out of their gas, and, in case of need, replace it with benzol if this was necessary to preserve the illuminating and calorific power. They thought that if the wash oil employed for washing or scrubbing the gas was first pre-benzolized, it would take up only the toluol content of the gas and leave the benzol content to a certain extent intact. Birmingham had made experiments, and found that if the oil was pre-benzolized to the extent of 5 per cent, it was possible to extract nearly 80 per cent of the toluol content, and leave more than two-thirds of the benzol content still in the gas. If this were the case, it would materially assist the Government.

Dr. W. B. Davidson, the engineer-in-charge of the Nechells station of the Birmingham Gas Department, had drawn up a sketch of the plant which he thought might be adopted to effect the object in question. There is from twenty to forty times as much toluene in the gas made from a ton of coal as there is in the tar produced from this bulk of raw material; and probably at least 2 lbs. of pure toluene, making 4 lbs. of trinitrotoluene, can be readily recovered per 10,000 cubic feet of coal gas.

The stream of cooled debenzolized oil coming from the crude still is mixed with a small stream (about 5 per cent by volume) of benzol in tank $T_1$ and is then pumped at the required rate (about 1300 gallons per hour) by pump $P_1$ to the top of scrubbers $S_3$; then by pump $P_2$ from the bottom of $S_3$ to the top of $S_2$; and finally by pump $P_3$ from the bottom of $S_2$ to the top of $S_1$.

The oil now benzolized runs from the bottom of $S_1$ to the store-tank $T_2$, whence it is pumped by $P_4$ in a continuous stream through the heater $H_1$, where heat interchange takes place between the cold oil and the hot oil leaving the crude still; then through the exhaust steam heater $H_2$; then through the superheater $H_3$ (containing a closed high-pressure steam-coil) to the crude still, where it meets a current of high temperature steam, which deprives it of its crude benzol.

The hot debenzolized oil is drawn off and caused to flow first through $H_1$, and afterwards through a water condenser, $C_1$, to the store-tank $T_1$. The crude benzol vapors and steam are condensed in the water condenser $C_2$. The condensate flows to a receiver, R, whence it passes through a separator, the crude benzol being stored in the tank $T_3$.




ELEVATION AND PLAN OF PLANT FOR THE EXTRACTION OF TOLUOL FROM COAL GAS—CAPABLE OF DEALING WITH 800 TONS OF COAL OR 10,000,000 CU. FT. OF GAS PER DAY

A charge of about 1600 gallons of crude benzol is pumped by $P_6$ daily into the intermediate still where it is distilled by steam with the production of commercial benzol, commercial toluol and residual xylol and heavier oils. The commercial benzol is mixed with the wash oil, together with an additional quantity corresponding to the amount of toluol, etc., permanently removed from the gas. The commercial toluol is redistilled in a second still for the production of pure toluol.

If the wash oil contains much naphthalene, it may be necessary to return the xylol to the gas, to prevent naphthalene stoppages in the district services.

Gas oil will probably prove the most suitable oil for washing purposes, as it is generally ready to hand, contains no naphthalene and readily absorbs crude benzol.

## COST OF HYDROGEN GAS

In the course of the report of the British Comptroller and Auditor-General upon the Army Services appropriation account for the year ended March 31st last, which has been issued as a White Paper, it is stated, in connection with expenditure at the Royal Aircraft Factory, that the cost of hydrogen gas showed an increase from $4.60 per 1000 cu. ft. in 1912–13 to $5.25 in 1913–14 [*J. Gas Lighting*, **129** (1915), 442]. The output during the latter year was 2,023,607 cu. ft. as compared with 3,493,296 cu. ft. in 1912–13.

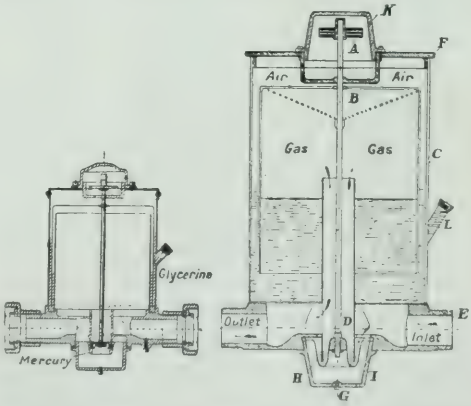
## GAS PROGRESS IN TURIN

Notwithstanding the cost of coal and the outbreak of war, the Societa Anonima dei Consumatori di Gas-Luce, of Turin, Italy, states in its last annual report that gas affairs in that city are not only satisfactory but progressive. During the twelve months covered by the report, 21,750,465 cubic meters of gas were sold, which was an increase of over 500,000 cubic meters on the sales of the previous year. Gas-meters, likewise, have gone up in number—from 45,000 to 47,000. In spite of keen electricity competition, the board of directors are convinced the future offers splendid prospects—especially in respect of the use of gas for heating purposes.

Early in 1913 the price of coal was $5.75, c. i. f. at Savona. Later it rose to $6.12, while during 1914, it dropped first to $5.40 then to $5.00. The Company was fortunate enough, at the outbreak of war, to have their coal stores well stocked —even considerably above their contractual obligations with the municipality of Turin. All the coke is readily sold; so much so that efforts are being made to use, in the producers, coke dust mixed with tar, and coke dust briquettes made on the gas-works. Old scrubbers have been replaced by modern vertical centrifugal washing apparatus, and old benches of retorts have given place to new.

## EXPLOSION FROM A DEFECTIVE GAS SERVICE GOVERNOR

A communication by Mr. Reinhard, manager of the Leipzig Gas Company was published in the *Journal für Gasbeleuchtung* of Jan. 30th, describing an explosion that occurred in a spacious




cellar of a bookseller's establishment and a basement restaurant adjoining it. The explosion and resultant fire were attended with loss of life. There were six gas-meters located in the cellar for supplies to various parts of the whole building—four being 50-light meters in an open cupboard, one of the remaining two

being a 200-light, and the other a 5-light meter, both standing exposed on the floor of the cellar. On the outlet of the 50-light meter for the supply of the restaurant, there was a Hahn governor having $1^1/_2$-inch connections. This governor, which, as far as could be traced, had been installed more than nine years previously, was of an antiquated type.

The old pattern contains considerably less glycerine to seal the bell and so far as could be traced in this instance the glycerine had not been renewed nor the governor inspected, during the past nine years. Investigations on this governor made by Reinhard after the explosion showed that nearly the whole of the glycerine had disappeared—presumably evaporated—and that there was also a deficiency of mercury. It is not known whether the governor was originally filled with neat glycerine or with glycerine and water. It is clear, however, that the gas on the night in question blew the seal of the governor and the explosive mixture of gas and air in the cellar, which had a cubic content of about 11,650 cubic feet, was ignited by a young cook who brought a naked flame into the cellar. The explosion was very violent, and caused wide-spread damage. In view of the disastrous results, Reinhard has thought it useful to draw attention to the defective character of the governor and the way in which the defect has been minimized in the more recent type.

## ENGLISH FOREIGN TRADE IN JANUARY

The English foreign trade of last January is compared with that of January, 1913, in the following table made from data published in *Z. angew. Chem.*, **28** (1915), III, 83:

| Imports | Value | Per cent change compared with Jan., 1913 |
|---|---|---|
| Wheat | $ 2,160,000 | +56.6 |
| Wheat flour | 4,710,000 | +56.8 |
| Barley | 1,270,000 | —21.7 |
| Oats | 1,300,000 | —46.5 |
| Corn | 10,110,000 | +226.9 |
| Raw cotton | 31,500,000 | —36.2 |
| Cotton manufactures | 2,480,000 | —45.3 |
| Flax | 1,590,000 | —27.7 |
| Raw hides | 3,430,000 | +81.6 |
| Iron and steel | 2,820,000 | —52.3 |
| Raw jute | 2,620,000 | —63.7 |
| Lard | 3,050,000 | —8.4 |
| Leather | 8,590,000 | +127.5 |
| Preserved meats | 3,330,000 | +173.5 |
| Saltpeter | 380,000 | +26.5 |
| Petroleum | 4,310,000 | —19.9 |
| Rice | 2,080,000 | +145.1 |
| Raw sugar | 12,000,000 | +229.3 |
| Refined sugar | 6,800,000 | +22.3 |
| Tea | 9,300,000 | +73.7 |
| Tobacco | 3,420,000 | —24.1 |
| Raw wool | 22,300,000 | +7.7 |
| **Exports** | | |
| Coal and coke | $11,000,000 | [illegible] |
| Cotton yarn | 3,350,000 | [illegible] |
| Cotton cloth | 23,950,000 | [illegible] |
| Other cotton manufactures | 3,440,000 | —48.8 |
| Iron and steel | 13,000,000 | —45 |
| Jute products | 661,000 | —51.8 |
| Linen yarn | 170,000 | —67 |
| Linen cloth | 1,999,000 | —34.4 |
| Machinery | 8,090,000 | —50.8 |
| Raw wool | 712,000 | —94.6 |
| Woolen yarn | 405,000 | [illegible] |
| Woolen cloth | 4,350,000 | [illegible] |

## AMERICAN FOREIGN COMMERCE

A remarkable illustration of the maritime supremacy of Great Britain is afforded by an analysis of the foreign commerce of the United States in the American fiscal year 1914. Vessels flying the British flag carried 53.45 per cent of the imports and exports of the United States during that period according to *Engineering*, 99 (1915), 308. The corresponding proportion carried by German shipping was 13.79 per cent; by American shipping, 9.26 per cent; by French shipping, 4.64 per cent; by Dutch shipping, 4.10 per cent; by Norwegian shipping, 3.49 per cent; by Japanese shipping, 2.14 per cent; by Italian shipping, 1.94 per cent; by Austrian shipping, 1.57 per cent; by Belgian shipping, 1.27 per cent; and by all other shipping, 4.35 per cent. The analysis extending in the fiscal year 1914 to American imports and exports represented an aggregate value of $3,785,469,000.

## RUSSIA'S FOREIGN TRADE IN 1914

Russia's foreign trade during last year amounted in the aggregate to a sum of $813,000,000, against $1,213,000,000 for the year 1913, the decrease for 1914 amounting to 32.7 per cent [*Engineering*, 99 (1915), 273]. The imports and exports were:

| | 1913 | 1914 |
|---|---|---|
| Imports | $560,000,000 | $423,000,000 |
| Exports | $652,000,000 | $390,000,000 |

The imports, consequently, show a decrease of 24.55 per cent, while the corresponding figures under the exports are reduced as much as 39.73 per cent. In 1913 Russia had a surplus on the export side of $92,000,000 as against a deficit of $33,000,000 for 1914; in other words, the commercial balance of the country for last year has deteriorated by $125,000,000, as compared with the preceding year. The figures for the months after the declaration of war do not appear to have been made available yet. They are not only responsible for the unsatisfactory balance, but have also neutralized the increase as compared with 1913, which the first six months of 1914 manifested. The figures for the first six months of 1914 and 1913 were:

| | 1913 | 1914 |
|---|---|---|
| Imports | $259,000,000 | $312,000,000 |
| Exports | $260,000,000 | $310,000,000 |

There was consequently an increase of about 22 per cent on the imports during the first half of last year and 20 per cent on the exports, as compared with the corresponding figures for the previous year. The value of the ruble is taken as $0.46. [1 ruble = 51.5 cents according to latest Treasury Department Circular.]

## SWEDISH FOREIGN TRADE IN 1914

In 1914 Sweden's foreign trade amounted to 146,300,000 kroner, or 8.7 per cent less than in 1913 [*Z. angew. Chem.*, **28** (1915), III, 106], imports decreasing 77,100,000 kroner, or 9.1 per cent, and exports decreasing 69,200,000 kroner or 8.45 per cent. The decrease in the imports of raw material amounted to 33,200,000 kroner; of the exports, iron showed the greatest falling off. [1 kroner = $0.268.]

## THE GRÄNGESBERG IRON-ORE DEPOSITS, SWEDEN

A Swedish expert has recently investigated the Grängesberg iron-ore deposits, and pronounced their content to be much larger than was formerly believed. Only a few years ago the aggregate capacity of these deposits was put at some 60,000,000 tons, and the area within which they were found at 72,800 square meters. Now, however, the quantity, as regards only the phosphoric ore, is reckoned to be three or four times as much [*Engineering*, 99 (1915), 255]. The surveying and examination work undertaken at Grängesberg is the greatest of its kind ever undertaken in Sweden, and it has been going on ever since 1906. The examination has revealed the presence of 180,000,000 tons pure ore, and it is now proposed to extend the boring to 1000 meters. Approximately an aggregate of 250,000,000 tons pure phosphoric ore may be reckoned upon. With the present production of about 840,000 tons annually, the deposits are calculated to last some 200 to 300 years. Further investigations are expected to reveal the presence of additional iron-ore deposits in this mining district.

## MANUFACTURE OF EXPLOSIVES IN NATAL

It is reported that Messrs. Kynochs, Ltd., will shortly cause great extensions to be made to their dynamite factory at Umbogintwini. This manufacture will mean a very large consumption of wattle wood.—E. G. ANDERSON.

## SCOTCH OIL TRADE

The *Oil and Color Trades Journal*, **47**, No. 855, states that not for many years have the Scotch oil companies experienced such a brisk demand or as good prices for all their products as is being

experienced at the present time. All classes of oil, sulfate of ammonia, and paraffin wax are being dispatched as soon as they are manufactured, and there are no stocks on hand. The shutting out of German competition in the sulfate of ammonia trade has brought prosperity to the Scotch industry. When the war broke out the price was around $50 per ton as compared with $70 at present. Paraffin wax has also risen about $45 per ton, lubricating oils $5 per ton, and burning oil $0.02 per gallon. These constitute almost record prices in the history of the industry during the past 10 or 15 years, and everything points to their being continued during the current year. Another excellent feature is the large amount of fuel oil taken by the admiralty at a price very remunerative to the Scotch companies.—A.

### COMMERCIAL VEHICLES DRIVEN BY STEAM

Some time ago a new form of steam omnibus was sanctioned for use in London, in which solid fuel in the form of ordinary gas coke was used. The results have been so encouraging that no less an authority than Professor Vivian Lewes has predicted that everything points to steam challenging the supremacy of petrol or petrol substitutes for commercial motor traction. According to the *Mechanical World*, **47**, No. 1471, the virtue of the steam vehicle using solid fuel is the cheapness in cost of running. Experimental working has shown the cost of fuel, where the stops are not frequent, to work out at 2 cents per 17 ton-miles, which is about half the cost with petrol, even when the latter is purchased in large quantities at 20 cents per gallon.

The uncertainty as to the price of petrol is undoubtedly the cause of many traders holding back from substituting mechanical for animal haulage, and there is some force in the argument that coke, being a home production, is not likely to be affected as to price in the same way as oil.—A.

### CHLORINE IN COAL

Mr. A. de Waele in a paper before the English Society of Public Analysts gave particulars of a case of abnormal corrosion of the tube of an economizer, and traced the corrosion to the presence of chlorine in the coal used. The average chlorine content of the coal obtained from the Midland coals of the brine district was 0.22 per cent.—A.

### BRITISH-MADE TUNGSTEN

Before the war all the tungsten powder used in the manufacture of high-class steels for shell steel, armor, and cutting tools used in engineering works and armament factories, was imported from Germany, and a serious condition arose when the supplies were cut off. A British firm has now been established to capture the industry, the combine company representing all the great steel firms of Sheffield, and also Armstrong, Whitworth & Company. Such good progress has been made that supplies on a commercial scale will be produced in a few weeks' time at the company's factory at Widnes.—A.

### NEW SOUTH WALES STEEL WORKS

With reference to the completion of the Broken Hill Steel Proprietary Company's works at Newcastle, N. S. W., it appears from the Bulletin of January 14th, of the South Australian Official Intelligence Bureau at Adelaide, quoted by the British *Board of Trade Journal*, that the South Australian Government has already accepted a tender from the company for the supply of 2000 tons of 60-lb. steel rails and 140 tons of fish-plates. The rails will be manufactured on the basic open-hearth method, and the Sandberg process applied. The acceptance of the tender means that for the first time in the history of the South Australian Railways, rails of Australian manufacture will be used. In connection with the utilization of some of the large iron-ore deposits in South Australia, it is interesting to note that a shipment of 2800 tons of ironstone was recently dispatched to the Broken Hill Proprietary Company's iron and steel works. The ironstone was obtained from Iron Knob, some 41 miles from Port Augusta, where the largest deposit in that State is situated. This is contained in two great ore bodies known as the Iron Knob and Iron Monarch, the latter being the larger of the two. The ore from the Iron Knob has, during the last 12 years, been used by the Proprietary Company for fluxing purposes at its smelting works at Port Pirie, and its average content of metallic iron has been found to be over 68.5 per cent. The extent of the deposits has not yet been actually determined, but on the assumption that the average depth of ore is no more than 100 ft., it has been calculated that over 21,000,000 tons of ore are available.

### SEGER CONES

Seger cones were at one time solely manufactured by the Prussian Government at the Royal Porcelain Works at Charlottenburg, and were imported into Great Britain in considerable quantities for use by pottery manufacturers in standardizing the fire of ovens and kilns. It is reported that Dr. Mellor, principal of the Pottery Section at the North Staffordshire College, has brought to a successful finish experiments directed towards carrying on the manufacture of these cones in England. The governors of the college have authorized the manufacture and the laboratories and are already turning out Seger cones at the rate of 1000 per day.—A.

# SCIENTIFIC SOCIETIES

## FIFTIETH MEETING AMERICAN CHEMICAL SOCIETY NEW ORLEANS, MARCH 31 TO APRIL 3, 1915

### PROGRAM OF PAPERS

#### GENERAL PUBLIC MEETINGS, APRIL 1

**Addresses of Welcome.** MR. MARTIN BEHRMAN, Mayor of New Orleans, AND PRESIDENT ROBERT SHARP, Tulane University.

**Response.** CHARLES HOLMES HERTY, President of the American Chemical Society. (See *this issue*, p. 371.)

**Opening Address. The Industrial Resources and Opportunities of the South.** ARTHUR D. LITTLE (See *this issue*, p. 373.)

**Symposium on the Contributions of the Chemist to American Industries.** DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS (See below and also *April issue*, pp. 273-304.)

**The Stassfurt Potash Industry.** (Slides and Moving Pictures.) H. A. HUSTON.

**Evening Address. The Chemist's Contribution to the Industrial Development of the United States A Record of Achievement.** BERNHARD C. HESSE. (See *April issue*, p. 273.)

#### AGRICULTURAL AND FOOD CHEMISTRY DIVISION

FLOYD W. ROBINSON, *Chairman* GLEN F. MASON, *Secretary*

1. **The Importance of Checking Foreign Organisms in Breadmaking.** ROBERT WAHL.
2. **On the Composition and Properties of an Oil from the Seeds of Martynia Louisiana.** E. H. S. BAILEY AND W. S. LONG.
3. **Action of Milk on Colloids.** EDWARD GUDEMAN, PH.D.
4. **The Relation of Index of Refraction, Specific Gravity and Solids in Tomatoes and Tomato Pulp.** W. D. BIGELOW.
5. **The Influence of one Feedingstuff upon the Digestibility of Another.** H. S. GRINDLEY, W. J. CARMICHAEL AND C. I. NEWLIN.
6. **Chemical Investigations at the Texas Experiment Station.** G. S. FRAPS.
7. **Individuality of Pigs as to the Completeness with which they Digest their Feed.** W. J. CARMICHAEL, C. I. NEWLIN AND H. S. GRINDLEY.
8. **The Influence of Litters on the Fermentation of Manure.** W. E. TOTTINGHAM.
9. **Bread: Weight of an Akron (Ohio) Loaf.** CHAS. P. FOX.
10. **Tamarind Syrup.** W. C. TABER.

11. **A Survey of the Frozen Egg Industry of Chicago.** DAVID KLEIN.

12. **Fertilizers for Field Crops in the Southwest of Alabama.** (Lantern.) F. W. ZERBAN.

### FERTILIZER CHEMISTRY DIVISION

J. E. BRECKENRIDGE, *Chairman* F. B. CARPENTER, *Secretary*

1. **The Availability of Organic Nitrogen.** J. E. BRECKENRIDGE.

2. **Results of Some Co-operative Work on Determination of Sulfur in Pyrites. Some Observations on Details of Manipulation, Sources of Error, and on Barium Sulfate as Precipitated under Different Conditions.** H. C. MOORE.

3. **The Activity and Availability of Insoluble Nitrogen in Fertilizers Determined by Chemical and Vegetation Tests.** F. R. PEMBER AND B. L. HARTWELL.

4. **The Determination of Potash in Fertilizers.** B. B. ROSS.

5. **Effect of Lime and Limestone upon Acid Phosphate.** G. S. FRAPS.

6. **Report of Committee on Research and Methods of Analysis.**

7. **Report of Committee on Fertilizer Legislation.**

### BIOLOGICAL CHEMISTRY DIVISION

CARL L. ALSBERG, *Chairman* I. K. PHELPS, *Secretary*

1. **The Control of Cottonseed Products.** C. L. ALSBERG.

2. **Emetine, the Specific Remedy of Pyorrhoea Alveolaris.** C. C. BASS.

3. **Saw Palmetto, a Biochemical Study.** CHARLES MANN.

4. **Volatile Oils of Some Species of Solidago.** EMERSON R. MILLER AND J. M. MOSELEY.

5. **Volatile Oils of Several Species of Eupatorium.** E. R. MILLER.

6. **The Volatile Oil of Achillea millefollium L.** E. R. MILLER.

7. **Some Volatile Oils from the Genus Pycnanthemum.** E. R. MILLER.

8. **Artificial Photo Synthesis by Chlorophyl.** W. J. V. OSTERHOUT.

9. **The Role of Chlorine in Plant Nutrition.** W. E. TOTTINGHAM.

10. **Nitrification Studies.** G. S. FRAPS.

11. **The Form of Nitrogen in Nitrogenous Materials as an Index to Nitrifiability.** C. B. LIPMAN.

12. **The Formation of Creatinine by Bacteria.** M. X. SULLIVAN.

13. **The Amount of Creatinine in Plants.** M. X. SULLIVAN.

14. **Toilet Papers, a Source of Infection.** EDWARD GUDEMAN.

15. **A Simple Colorimetric Method for the Determination of Free Reducing Sugars and Total Carbohydrate in Miscellaneous Food Products.** ADOLPH BERNHARD.

16. **The Reducing Action of Certain Carbohydrates on Distillation.** J. P. ATKINSON.

17. **A Precipitant for Ammonia.** SARA S. GRAVES.

18. **Phenols and Phenol Derivatives in Urine.** W. DENIS.

19. **On the Physiological Activity of Combined Hydrochloric Acid.** J. H. LONG.

20. **On Combinations of Proteins with Halogen Acids.** J. H. LONG.

21. **On the Rate of Evaporation of Ether from Oils and its Application in Oil-Ether Colonic Anesthesia.** CHARLES BASKERVILLE.

22. **The Free Amid Nitrogen and the Free Amino-acids Nitrogen of Feedingstuffs.** H. S. GRINDLEY AND E. C. ECKSTEIN.

23. **Quantitative Determination of the Amino-acids of the Mixed Proteins of Feedingstuffs.** H. S. GRINDLEY, W. E. JOSEPH AND M. E. SLATER.

24. **Nitrogen Distribution According to the Van Slyke Method in Soils and Their "Humic Acids."** R. S. POTTER AND R. S. SNYDER.

25. **Amino Acid Nitrogen in Soils Variously Treated.** R. S. POTTER AND R. S. SNYDER.

26. **A Study of Urinary Mucin.** MAX KAHN.

27. **On Cystine.** M. KAHN AND F. G. GOODRIDGE.

28. **Biochemical Studies of Mercaptan.** F. G. GOODRIDGE.

29. **Metabolism Studies of Multiple Myeloma with Bence-Jones Albumose.** M. KAHN AND FRANCIS HUBER.

30. **Study of the Mineral Metabolism of Diabetics.** M. KAHN AND S. SCHNEIDER.

31. **Mineral Metabolism of Two Cases of Haemophilia.** A. F. HESS AND M. KAHN.

32. **A Study of the Ethereal Sulfates of the Urine in Various Diseases.** JACOB ROSENBLOOM.

33. **A Modification of Gerhardt's Test for Diacetic Acid.** JACOB ROSENBLOOM.

34. **The Influence of Low and High Protein Intake on the Excretion of Acetone, Diacetic Acid, and Beta-oxybutyric Acid in Diabetes.** JACOB ROSENBLOOM.

35. **On the Adjustment of the Reaction of Bacteria Culture Media.** W. M. CLARK.

36. **Final Hydrogen Ion Concentration of Cultures of *B. Coli*.** W. M. CLARK.

37. **Relation of Propionic Fermentation to the Development of "Eyes" in Ementhaler Cheese.** E. H. WALTERS AND W. M. CLARE.

38. **On the Factor to be Used for the Calculation of the Phosphoric Acid in Neumann's Method.** S. L. JODIDI.

39. **On the Factor to be Used for the Calculation of Phosphoric Acid in Neumann's Method. I. The Factor as Influenced by the Water Used for Washing the Yellow Precipitate.** S. L. JODIDI AND E. H. KELLOGG.

40. **The Quantitative Estimation of Alantoin.** ROBERT E. SWAIN AND E. R. HARDING.

41. **The Influence of Certain Sugars on the Growth and Respiration of Vetch.** LEWIS KNUDSON.

42. **The Influence of Certain Inorganic Substances on the Digestion of Starch by Penicillium camemberti.** W. J. ROBBINS.

43. **Differentiation of Organisms of the Colon Group by Means of Indicators.** W. M. CLARK AND H. A. LUBS.

44. **Studies on the Saponins of Chlorogalum pomeridianum and of Agabe lechuguilla.** C. C. JOHNS AND ARNO VIEHOEVER.

45. **On the Alkaloids of Amianthium muscaetorium.** C. C. JOHNS AND ARNO VIEHOEVER.

### INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION.

GEO. P. ADAMSON, *Chairman* S. H. SALISBURY, JR., *Secretary*

**Symposium on the Contributions of the Chemist to American Industries:** (See *April issue*, p. 273.)

1. **The Wine Industry.** CHARLES S. ASH.
2. **The Copper Industry.** J. B. F. HERRESHOFF.
3. **The Corn Products Industry.** E. T. BEDFORD.
4. **The Asphalt Industry.** JAMES LEWIS RAKE.
5. **The Cottonseed Oil Industry.** DAVID WESSON.
6. **The Cement Industry.** G. S. BROWN.
7. **The Sugar Industry.** W. D. HORNE.
8. **The Incandescent Gas Mantle Industry.** SIDNEY MASON.
9. **The Textile Industry.** FRANKLIN W. HOBBS.
10. **The Fertilizer Industry.** H. WALKER WALLACE.
11. **The Soda Industry.** F. R. HAZARD.
12. **The Leather Industry.** WILLIAM H. TEAS.
13. **The Flour Industry.** J. A. WESENER AND G. L. TELLER.
14. **The Brewing Industry.** GASTON D. THEVENOT.
15. **The Preserved Foods Industry.** R. I. BENTLEY.
16. **The Potable Water Industry.** WILLIAM P. MASON.
17. **The Celluloid and Nitrocellulose Industry.** R. C. SCHUPPHAUS.
18. **The Glass Industry.** A. A. HOUGHTON.
19. **The Pulp and Paper Industry.** F. L. MOORE.

20. **The Chemists' Contribution to the Industrial Development of the United States—A Record of Achievement.** B. C. HESSE (see THIS JOURNAL, **7** (1915), 293–304).

21. **The Chemists' Corporation: A Plan to Make Research Possible and Enable the Investigator to Profit by the Results.** ALEXANDER SILVERMAN.

22. **The Chemist and Industrial Water Purification.** WILLIAM M. BOOTH.

23. **What the Chemist Has Done for the Portland Cement Industry in the United States.** W. C. HANNA.

24. **The Industrial Chemist in His Relation to Fire Prevention.** FREDERICK DANNERTH.

25. **The Influence of Free Fatty Acids on the Flash and Fire Points of Fats and Oils.** A. LOWENSTEIN AND J. J. VOLLERTSEN.

26. **The Influence of Pyridine on the Ammonia Determination of Concentrated Ammoniacal Liquor.** A. LOWENSTEIN AND J. J. VOLLERTSEN.

27. **The Potash Supply.** EDWARD HART.

28. **The Constituents of Portland Cement Clinker.** (Lantern.) G. A. RANKIN.

29. **A Study of the Quality of Platinum Ware with Special Reference to Losses on Heating.** G. K. BURGESS AND P. D. SALE.

30. **A Study of Some Recent Methods for the Determination of Total Sulfur in Rubber.** J. B. TUTTLE AND A. ISAACS.

31. **Gas Washing Apparatus with Enclosed Filter.** E. R. WEAVER AND J. D. EDWARDS.

32. **A Simple Stone-Frame Chemical Hood.** E. R. WEAVER.

33. **Apparatus for the Determination of Sulfur in Gas.** E. R. WEAVER AND J. D. EDWARDS.

34. **The Determination of Oil and Resin in Varnish.** E. W. BOUGHTON.

35. **Tetraphosphorus Trisulfide.** W. O. MITSCHERLING.

36. **Discussion of Symposium.**

### ORGANIC CHEMISTRY DIVISION

F. B. ALLAN, *Chairman* C. G. DERICK, *Vice-Chairman and Secty.*

1. **The Classification and Nomenclature of Organic Compounds.** EDWARD KREMERS.

2. **Dimethylsulfate as a Methylating Agent.** VICTOR P. LEE.

3. **Some Derivatives of Coumarin.** FRANCIS D. DODGE.

4. **The Isolation of a Blue Hydrocarbon $C_{15}H_{18}$ from Milfoil Oil.** L. F. Augspurger.

5. **A Possible New Terpene from Monarda punctata.** Miss Nellie Wakeman.

6. **The So-called Alpha and Beta Isomeric Resin Acids.** C. H. Herty and D. H. Killeffer.

7. **The Structure of Certain Hydronaphthoic Acids.** Oliver Kamm and C. G. Derick.

8. **The Correlation of Ionization and Structure in Unsaturated Acids.** C. G. Derick and Oliver Kamm.

9. **Some Tests for Qualitative Organic Analysis.** Oliver Kamm.

10. **Qualitative Organic Analysis.** W. F. Moncreiff, Jr. and J. T. McGill.

11. **Recent Progress in the Study of the Quinone-Phenolate Theory of Indicators.** E. C. White and S. F. Acree.

12. **A Theory of the Mutarotation of Sugars and Their Derivatives by Acids and Alkalis.** S. F. Acree.

13. **On the Reactions of Both the Ions and Molecules of Acids, Bases and Salts. A Reinterpretation of the Reactions of Sodium Methylate and Sodium Ethylate with 1,2-Dinitrobenzene, 1,2,4-Dinitrochlorobenzene, and with 1,2,4-Dinitrobromobenzene.** S. F. Acree.

14. **Alkaloidal Tartrates. I. Strychnine Tartrate.** G. D. Beal and H. F. Lewis.

15. **A Comparison of the Optical Rotatory Powers of the Alpha and Beta Forms of Certain Acetylated Derivatives of Glucose.** C. S. Hudson and J. K. Dale.

16. **The Isomeric Alpha and Beta Octacetates of Maltose and Cellose.** C. S. Hudson and J. M. Johnson.

17. **The Isomeric Pentacetates of Mannose.** C. S. Hudson and J. K. Dale.

18. **The Isomeric Pentacetates of Galactose.** C. S. Hudson and H. O. Parker.

19. **The Crystalline-*d*-Fructose Pentacetate.** C. S. Hudson and D. H. Brauns.

20. **The Existence of a Third Pentacetate of Galactose.** C. S. Hudson.

21. **Some Derivatives of Chlor-Methyl Ether.** Friend E. Clark and Samuel F. Cox.

22. **Hop-Seed Oil.** Norman A. Dubois.

23. **Research on Purines. XVII. On a New Synthesis of Alkyl-amino-Purines. On 2-Oxy-8-thiopurine, 2-Oxy-8-methyl-mercaptopurine, and 2-Oxy-6,9-dimethyl-8-thiopurine.** C. O. Johns.

24. **Researches on Thioamino-Acids. On Thiohippuric Acid and Phthalyl-α-aminothioacetic Acid.** C. O. Johns.

25. **Citral, and its Determination.** B. G. Feinberg.

26. **The Preparation of Trimethylene Oxide.** C. G. Derick.

27. **The Use of Trimethylene Oxide in the Grignard Reaction. The Synthesis of Normal Primary Hexyl Alcohol.** C. G. Derick and E. H. Vollweiler.

28. **The Synthesis of δ-Acetyl-valerianic Acid and Adipic Acid.** C. G. Derick and R. W. Hess.

29. **The Ionization Constants of Certain Ketoparaffine Monobasic Acids.** C. G. Derick and St. Elmo Brady.

30. **On the Decomposition of Tertiary Amyl Esters.** M. A. Rosanoff and M. M. Harrison.

### PHARMACEUTICAL CHEMISTRY DIVISION

F. R. Eldred, *Chairman* A. P. Sy, *Secretary*

1. **The Stability of Nitroglycerin Tablets.** Wilbur L. Scoville

2. **Variation Clause of the Food and Drugs Act.** J. H. Beal.

3. **The Composition of Oil of Cassia.** Francis D. Dodge and Alfred E. Sherndal.

4. **The Chemistry of the Daturas. II. The Alkaloidal Content of Datura Leaves.** H. A. Langenhan.

5. **A Possible Explanation of the Reduction Phenomena Observed in Elixir Phosphate of Iron Quinine and Strychnine when Exposed to Light.** N. R. Mueller.

6. **Discussion of Papers 4 and 5.** Prof. Edward Kremers.

### PHYSICAL AND INORGANIC CHEMISTRY DIVISION

G. A. Hulett, *Chairman* R. C. Wells, *Secretary*

1. **A Colorimetric Determination of Acetylene.** E. R. Weaver.

2. **The Ternary System $K_2O$–$SiO_2$–$H_2O$ from 300–700°.** (Lantern.) George W. Morey.

3. **Rubidium Ammonosodate and Ammonopotassiate.** E. C. Franklin.

4. **Distillation of Liquid Air in a Magnetic Field.** R. S. McBride

5. **A Systematic, Rapid, Electroanalytical Procedure for the Separation and Determination of Silver (Arsenic), Copper, Bismuth, Antimony, Tin, Lead, and Cadmium.** E. P. Schoch and Denton J. Brown.

6. **The Influence of the Potassium Ion upon the Potential of the Ferrocyanide-Ferricyanide Electrode.** E. P. Schoch and W. A. Fielding.

7. **The Rates of Solution of Metals in Ferric Salts and in Chromic Acid.** R. G. Van Name and D. U. Hill.

8. **The Electrolytic Preparation of Solid Alkali Amalgams in Quantity.** Paul M. Giesy and James R. Withrow.

9. **The Analysis of Silicates and Carbonates for Their Ferrous Iron Content.** O. L. Barnebey.

10. **The Permanganate Determination of Iron in the Presence of Fluorides.** O. L. Barnebey.

11. **The Phenomenon of Passivity in Connection with Ferrous Alloys of Different Composition and Structure.** H. W. Mosbley.

12. **The Thermoelectric Properties of Carbon.** William C. Moore.

13. **Potassium Chloride Concentration Cells.** D. A. MacInnes and Karr Parker.

14. **The Precipitation of Lead Chloride in Qualitative Analysis.** J. P. Montgomery.

15. **Radium Content of Gulf of Mexico Water.** Stewart J. Lloyd.

16. **Studies in the Measurement of the Electrical Conductivity of Solutions.** W. A. Taylor.

17. **Electrolytic Rectification of Alternating Currents.** William J. Van Sicklen.

18. **The Changes of Mass and Weight Involved in the Formation of Complex Atoms.** William D. Harkins and Ernest D. Wilson.

19. **The Structure of Complex Atoms.** William D. Harkins and Ernest D. Wilson.

20. **Nuclear and Valence Electrons.** William D. Harkins and Ernest D. Wilson.

21. **A Periodic Table which Plots the Atomic Weights of the Ordinary and the Isotopic Elements.** William D. Harkins and Ernest D. Wilson.

22. **A Connection between Planck's Quantum Hypothesis, the Magneton, and the Balmer Series Formula.** Ernest D. Wilson and William D. Harkins.

23. **Cuprous Salts of Oxygen Acids and a New Method for Preparing Cuprous Salts.** Lloyd C. Daniels.

24. **A Rational Process of Fractional Distillation.** M. A. Rosanoff.

25. **Equilibria in the Systems of Methyl Alcohol, Ketones, Water, and Inorganic Salts, Part I.** G. B. Frankforter and Lillian Cohen.

26. **Equilibria in the Systems of Propyl Alcohols, Water, and Salts.** G. B. Frankforter and Sterling Temple.

### WATER, SEWAGE AND SANITATION SECTION

Earle B. Phelps, *Chairman* H. P. Corson, *Secretary*

1. **The Use of Benzidene for Sulfates in Water Analysis.** F. W. Bruckmiller.

2. **The Determination of Arsenic in Filter Alum.** Edward Bartow and A. N. Bennett.

3. **The Manufacture of Filter Alum at the Columbus Water Softening and Purification Works.** C. P. Hoover.

4. **The Determination of the Biochemical Oxygen Demand by the Saltpeter Method in Stockyards, Tannery, and Corn Products Wastes.** Arthur Lederer.

5. **Ventilation Studies.** Earle B. Phelps.

6. **The Purification of Sewage by Aeration in the Presence of Activated Sludge.** Edward Bartow and F. W. Mohlman.

7. **The Sanitary and Mineral Properties of the Public Water Supplies of Georgia.** Ray C. Werner.

8. **Analytical Methods for Sewage Works Operation.** W. L. Stevenson and Others.

9. **The New Orleans Water Purification Works.** John L. Porter.

10. **Rat Proofing of Wharves as an Anti-Plague Measure.** H. P Letton.

11. **A Comparison of Methods for Determining Putrescibility or Oxygen Demand.** F. E Hale and T W. Melia.

12. **A Sanitary Survey of Lake Michigan, Together with a Study of Stream Pollution along the Wisconsin Shore.** E. J. Tully.

13. **Report of the Committee on Standard Methods of Analysis for Potable Water and Sewage.**

## EXCURSIONS

Water Purification Plant—Of the public works which have successfully overcome the natural difficulties that beset the city of New Orleans, none are more important than those of sewerage, water and drainage. These include 427 miles of sewers, with nine pumping stations; 312 miles of storm water

drainage arteries, with seven great pumping stations; and 532 miles of water mains, with a purification plant and pumping station on each side of the Mississippi River, which take its muddy water and render from it a crystal-clear and highly-safe and desirable water supply, and distribute it to the entire populated area of the city under 70 lbs. pressure, thus giving a magnificent fire protection as well.

These great works of sewerage, water and drainage, so widely scattered, have involved an expenditure of over $30,000,000.

This plant, as it stands, has a capacity to purify and deliver to the city 60,000,000 gallons of water a day, with ample reserve pump and boiler capacity to take care of any probable accident to pumps or boilers which may put a portion of them out of service for repair. The machinery and boiler equipment are of the most modern and efficient design known to waterworks practice, and the coal consumption is below that of many plants for smaller cities which do not pump one-third as much water as is now being handled at this plant. The universal use of water meters for all water consumers has resulted in the prevention of waste of water; the present requirements of the city call for an average delivery of only 17,000,000 gallons of water per day. The plant, however, includes a sufficient area of ground and is laid out with a view of economical extension to a capacity of at least 168,000,000 gallons per day, which should serve a population of nearly 2,000,000.

Water is taken from the Mississippi River, three-quarters of a mile away, through a 48-inch suction line, which is laid level and with its top 2 feet below extreme low water in the river, and lifted by the low-lift pumps, through the head or controlling, house, into one of the two grit reservoirs, in passing through which it deposits about 10 per cent of the heavier suspended matter which it contains. From the grit reservoir the water passes through the head house again, and, in proportion to the amount of water passing and its condition, lime and sulfate of iron are added to it, after which it passes through one of the two sets of chemical mixing passages, which afford a runway back and forth and up and down of about a mile, during which any deposit is prevented by the motion of the water. This keeps the chemical solution thoroughly mixed with the water until the full chemical reaction required has taken place. Then once more the water passes through the head house, going this time to one of the two sets of settling reservoirs, through which its passage is very slow, for the express purpose of causing the deposit of the now coagulated masses of clay and precipitating lime and magnesia which were originally contained in solution in the water, as well as of the iron and lime which were added to bring about this precipitation. The result is that when the water has reached the outlet of the settling reservoirs and is ready once more to pass through the head house to the filters nearly all of the suspended matter and a large amount of the chemicals which were in solution in the river water, together with those which were added in the treatment, have been left behind in the settling reservoirs, and the remainder, about fifty parts per million out of an average of 750 parts of suspended matter contained in the raw river water, are in such changed condition that they are easily removed by the filters, which yield an effluent entirely free from suspended matter and containing less than half as much lime and magnesia and only about 1 per cent as many bacteria as the river water originally contained. The resultant water is bright and sparkling in appearance and safe and desirable for every use.

The filters are of the so-called mechanical or rapid type. They are, however, merely gravity sand filters, designed to handle large quantities of water and to be very easily and cheaply cleaned. In filtering, the water enters above the sand layer, passes through it and is collected by a system of drains into one effluent pipe for each of the ten filter units, which effluent pipe is automatically throttled to prevent a too rapid flow through the filters. As the suspended matter in the water accumulates in the sand layer, the latter is gradually choked up, until finally the filter will not pass as much water as is required of it with the throttle on its effluent pipe wide open. This stage is reached in from 100 to 300 hours of service under present operating conditions in New Orleans, and then the filter has to be cleaned. The process of cleaning consists in closing the inlet and outlet of the filter from its connection with the operating portion of the system and in forcing filtered water into the effluent pipe, through the drains, and up through the sand layer, at a high velocity, which stirs up the sand layer, loosens the mud and causes it to overflow through troughs placed at a higher elevation than that to which this velocity will raise the sand of which the filtering material is composed. It takes less than ten minutes to go through the entire operation of washing a filter, and only about one-half to one per cent of the water filtered is required for filter washing.

The entire cost of treating and filtering the water and pumping it into the distribution system is not over two cents per 1,000 gallons, and the cost of water delivered to domestic consumers through meters by the city is now usually less than one-fourth of what these same consumers had to pay for raw river water pumped direct from the river before the city constructed and operated its own waterworks plant.

**The Weeks Island Salt Mine**—Weeks Island, La., is 125 miles west of New Orleans, situated on Vermilion Bay, an arm of the Gulf of Mexico, and rises 204 feet above sea level. It has an area of 2500 acres and the salt underlies practically the entire island.

This wonderful deposit of pure rock salt was discovered by Gen. F. F. Myles in 1898. It analyzes 99.84 pure chloride of sodium. The deposit obtains in a solid mass and is found at a depth of 93 feet from the surface. It is several thousand feet thick. This company acquired the entire salt deposit, sank a shaft 650 feet into the salt and erected a plant, completed in 1903, with a capacity of 1500 tons daily, thoroughly equipped with every modern device for the economical production of all the commercial grades of rock salt. These are shipped to all parts of the United States, England, Australia, Central and South America, Cuba and the Philippines.

The mine chambers are opened from 80 to 100 feet wide and 85 feet high with the overlying mass of salt, supported by pillars of salt 80 × 85 feet. The interior is lighted by electricity and, being all translucent, clear, crystal salt, has the appearance of an enchanted palace, whose domes are studded with saline diamonds. The mine is, of course, perfectly dry and is different from most mines in that no artificial scaffolding is used, the strength of the pillars of salt being more than sufficient for the support of the roof.

Rock salt is mined in very much the same manner as are all the baser minerals. The first operation is the drilling of the holes for the insertion of the dynamic charges, rock salt having a resisting power of 5000 lbs. to the sq. in. This is accomplished by eleven-foot drills. The salt is cut out in tunnel form, arched columns being left to prevent a collapse. These tunnels are 750 to 1000 ft. long and 80 to 100 ft. wide, and of about the same height. The blasting is generally done at night, as well to prevent accident as to allow the atmosphere to clear in time for the following day's work. As blasted, the salt is loaded on regular narrow gauge mule trains, which carry it to the foot of the shaft.

The salt passes through a forty H. P. electric-motor-driven crusher, after which it is fed by gravitation into the cage and carried to the mill, where it is fed automatically into screens and separated into the various commercial grades. If shipped in bulk it is deposited by gravity into the cars; if not, it is automatically fed into sacks.

In the twelve years of the mine's operation, 1,000,000 tons of salt have been removed, and there remains 5,000 times that

much on the level now being worked. Drillings to a depth of 250 ft. below the present level showed a continuation of the salt deposit.

The excursion to the mine was made over the Southern Pacific line by special train, 102 persons making the trip. A box lunch was furnished on the train before arrival at the mines. Delicious refreshments were served by Mr. Myles, owner of the mine; ice cream and cooling drinks were plentiful on the return trip. As the route passed through sugar plantations and truck farms, the journey gave a good idea of the importance and extent of agriculture in Louisiana.

## INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION AMERICAN CHEMICAL SOCIETY

### MINUTES OF NEW ORLEANS MEETING

The first meeting of the Division was devoted to the Public Symposium held at Tulane University and was presided over by *Vice-chairman* H. E. Howe. The program of papers is given on page 442.

The regular divisional meeting was held at the Grunewald Hotel, New Orleans, La., April 2, 1915, with *Vice-chairman* H. E. Howe presiding.

The Secretary reported for the Chairman and the Executive Committee the appointment of the following committees:

STANDARD SPECIFICATIONS AND METHODS OF ANALYSIS—A. M. Comey, J. O. Handy, Robert Job, F. G. Stantial.

NON-FERROUS METALS AND ALLOYS, a Sub-committee of preceding Committee—Wm. Price, *Chairman;* Allen Merrill, Geo. L. Heath, Gilbert Rigg, Bruno Woichiechowski.

SOAP PRODUCTS—Archibald Campbell, *Chairman;* C. P. Long, J. R. Powell, Percy H. Walker.

GLYCERINE, a Sub-Commitee of preceding Committee—A. C. Langmuir, *Chairman;* W. H. Low, S. S. Emery, R. E. Devine, J. W. Loveland, A. M. Comey.

NAVAL STORES—J. E. Teeple, *Chairman;* other members not yet selected.

ALUM—W. M. Booth, *Chairman;* Chas. P. Hoover, Wm. C. Carnell.

PLATINUM—W. F. Hillebrand, *Chairman;* Percy H. Walker, H. T. Allen.

The Secretary reported on the financial condition of the Division as follows:

| | | | |
|---|---|---|---|
| Balance on hand April 6, 1914 | $68.02 | Expenditures for printing postage, etc | $25.55 |
| Received | 1.00 | | |
| TOTAL FUNDS | $69.02 | | |
| BALANCE ON HAND April 1, 1915 | | | $43.47 |

No Committee reports were received.

The reading of the papers was then continued in accordance with the program as given above.

The various methods for the analysis of alum which were offered by Wm. M. Booth, Chairman of the Committee on Alum, for discussion by the Division, were laid on the table as the time was too short for their attention.

Under new business the matter of the relation of the various committees to each other was brought up and it was moved by W. F. Hillebrand and seconded by A. H. Sabin that this matter be referred to the Executive Committee for settlement. The motion was carried.

LEHIGH UNIVERSITY
SO. BETHLEHEM, PA.

S. H. SALISBURY, JR., *Secretary*

## FERTILIZER DIVISION AMERICAN CHEMICAL SOCIETY

### MINUTES OF NEW ORLEANS MEETING

The Meeting was called to order, Friday morning, April 2nd, in accordance with the official program, by Chairman Breckenridge. About thirty members attended.

PAUL RUDNICK, Chairman of the Committee on Research and Methods of Analysis, presented a report in which tentative standard methods for the sampling and analysis of phosphate rock were proposed. The degree of fineness of the coarse moisture sample was discussed. It was generally agreed that 4 mesh (Bureau of Standards specification), rather than 20 mesh, as proposed, would be fine enough. There was a lively discussion as to whether all silica should be made insoluble before determining sulfuric acid. The motion that the analysis be so conducted that all silica be made insoluble was finally carried. The motion to otherwise adopt the Committee's report was carried.

F. B. CARPENTER, Chairman of Committee on Fertilizer Legislation, presented a report regarding some fertilizer laws now in force.

After the Committee Reports the papers listed in the above program on page 442 were read.

The paper by H. C. Moore was referred to the Committee of Research and Methods of Analysis.

H. C. MOORE, *Secretary, pro-tem.*

#### REPORT OF COMMITTEE ON FERTILIZER LEGISLATION

During the past year, there have been no changes in the laws of the several states, which materially affect the fertilizer industry. There have been several bills presented in different states, which failed to pass and there is some legislation pending, but only a few minor changes have been noted, during the past twelve months.

There seems to be a growing tendency for the states to change from the brand tax to a tonnage tax. In some cases, this change has evidently been effected for the purpose of increasing the revenue, while in other instances, the reason assigned is to obtain statistical information, relative to the fertilizer business, which some companies now refuse to give. There seems to be no reason why any reputable company should be unwilling to furnish this information; on the contrary, the industry should be greatly benefited by having a reliable statistical bureau, through which it might be possible to ascertain the total tonnage of fertilizers sold in each state and the amount of plant food in these fertilizers. If such statistics were available, it is our opinion that they would become an important factor in increasing the sales of fertilizers.

In many of the states, the fertilizer laws have not been revised to meet present conditions, or when revision has been made, old forms have been copied. For instance, an expression commonly used is as follows: "It shall be unlawful to offer for sale any fertilizer or fertilizer material containing any hoof meal, horn, hair, leather, or any other substance in which the ammonia is largely unavailable." By this statement, it assumes that the ammonia in these articles is largely unavailable; while, as a matter of fact, from various tests, we find that hoof meal shows a satisfactory availability, and by modern practice, the ammonia in hair, leather, etc., can be made available by proper treatment.

When any of the state laws are undergoing revision, we should see that this form of expression is modified to read: "Any hoof meal, horn, hair, leather, or any other substance that has not been so treated as to render it largely available." This would allow the manufacturer to use materials which would cheapen the cost of fertilizers without in any way reducing their value.

Organic ammoniates, available for fertilizer purposes, are becoming scarcer each year, and if the manufacturer is restricted to such materials as Blood, Tankage, Cottonseed Meal, etc., the prices of ammoniated fertilizers will be largely increased in the future.

There seems to be little hope of getting a uniform law which will be applicable in the different states, but the fertilizer manufacturers should have the hearty co-operation of the agricultural departments in having only such laws enacted as will amply protect both the producer and consumer, without imposing unnecessary hardships on the manufacturer.

All unnecessary restrictions tend to increase the expense of production and must necessarily result in higher prices for the consumer.

J. E. BRECKENRIDGE, PAUL RUDNICK, H. A. HUSTON, H. J. WHEELER, F. B. CARPENTER, *Chairman* — COMMITTEE ON FERTILIZER LEGISLATION

## REPORT OF THE COMMITTEE ON RESEARCH AND ANALYTICAL METHODS—PHOSPHATE ROCK

The following tentative standard methods for sampling and determination of moisture, phosphoric acid and iron and alumina in phosphate rock are recommended to the Division.

### METHODS OF SAMPLING AND DETERMINATION OF MOISTURE

I. GROSS SAMPLE—*A*: CAR SHIPMENTS—100 lb. sample per car.

1—SAMPLING FROM THE CAR: In sampling car shipments in the car at least ten scoopshovelsful, aggregating 100 lbs., shall be taken from each car at approximately equal distances from each other so as to average the car. Care shall be taken to see that each scoopful shall cover the entire face of the pile from floor to top.

2—SAMPLING FROM THE CART OR BARROW: A small hand scoopful of 1 to 2 lbs. shall be taken from each cart or barrow either as it is being loaded or as it leaves the car.

*B*: CARGO SHIPMENTS—100 lb. minimum sample per vessel.

1—SAMPLING IN HOISTING TUB: In sampling cargoes generally running from 1000 tons upward a small hand scoopful shall be taken from approximately every tenth tub before it is hoisted from the hold.

2—SAMPLING FROM CONVEYOR: If unloading is being done with automatic bucket and conveyor, periodical sections of the entire discharge of the conveyor shall be taken of such intervals and quantity as to give a sample equivalent to approximately one lb. per each ten tons of cargo.

3—SAMPLING FROM CONVEYING VEHICLE: Samples shall be taken with a hand scoop from various cars at such regular intervals and in such quantities as to give approximately one lb. for each ten tons of cargo.

II. LABORATORY SAMPLE—The resulting gross sample obtained by any one of the methods outlined shall be crushed to pass a four mesh screen, thoroughly mixed on a clean, hard surface and quartered down to a 10-lb. average sample.

*A*. CRUSHING—This 10-lb. sample shall all be crushed to pass an eight mesh screen.

*B*. MIXING AND QUARTERING—This eight mesh sample shall be carefully mixed and quartered down to two 2-lb. samples.

*C*. GRINDING—1—MOISTURE SAMPLE: One of these 2-lb. samples shall be held in an air-tight container. This sample is to be used for the determination of moisture.

2—ANALYTICAL SAMPLE: The other 2-lb. sample shall be further mixed and quartered down to a 2- or 4-oz. sample which is then to be ground to pass a 60 mesh screen or preferably a 65 mesh screen. This sample is to be used for the analytical determination.

NOTE: It is essential that the taking of the gross sample be done with small hand scoops and that the practice of taking the sample in the hand be absolutely prohibited, for it has been found that there is considerable selective action in the finer materials sifting through the fingers while a scoop retains the entire sample.

The dimensions of the screens referred to above are to be as follows:

| No. of Mesh | Size of Opening Inches | Diameter of Wire Inches |
|---|---|---|
| 4 | 0.185 | 0.065 |
| 8 | 0.093 | 0.032 |
| 65 | 0.0082 | 0.0072 |

III. DETERMINATION OF MOISTURE—Moisture is to be determined on both the moisture sample and analytical sample. Of the moisture sample not less than 100 grams are to be weighed out for each determination. Of the analytical sample approximately 2 grams are to be weighed out for each determination. Both are to be dried to constant weight at a temperature of 105° C. in a well ventilated oven, preferably with a current of dry air passing through the oven. The containers in which moisture is determined should be provided with well fitting covers so that the samples may be cooled and weighed in the well covered container.

IV. CALCULATION OF RESULTS—The percentages of phosphoric acid and iron and alumina as determined on the analytical sample are to be calculated to a moisture-free basis and subsequently to the basis of the original sample as shown by the moisture content of the moisture sample.

### DETERMINATION OF PHOSPHORIC ACID

REAGENTS—To be prepared as in Official Methods, A. O. A. C. Bureau of Chemistry, *Bulletin* **107** (Rev.), 1910, p. 2. Preparation of Reagents (*c*), (*d*), (*e*) and (*f*), except that the ammonium nitrate solution in (*d*) is changed to 5 per cent instead of 10 per cent.

METHOD OF SOLUTION—To 5 grams of the sample add 30 cc. of concentrated hydrochloric acid (sp. gr. 1.20) and 10 cc. of concentrated nitric acid (sp. gr. 1.42) and boil down to a syrupy consistency. The residue, which should be nearly solid after cooling, is taken up with 5 cc. of concentrated nitric acid and 50 cc. of water. Heat to boiling, cool, filter and make up to 500 cc. through the filter. This procedure eliminates practically all of the silica and it is necessary to filter as quickly as possible after digestion so as to avoid redissolving the silica.

DETERMINATION—Draw off an aliquot portion of 50 cc., corresponding to 0.5 gram, neutralize with ammonia, then add nitric acid until the solution is just clear. Add 15 grams of ammonium nitrate (free from phosphates), heat the solution to 50° C. and add 150 cc. of molybdate solution. Digest at 50° C. for 15 minutes with frequent stirring. Filter off the supernatant liquid and test the filtrate with molybdate solution to see if precipitation has been complete. (If not, add more molybdate to the filtrate and digest for 15 minutes longer.) Wash with 5 per cent ammonium nitrate solution by decantation, retaining as much of the precipitate as possible in the beaker. Dissolve the precipitate in the beaker in the least possible quantity of ammonium hydroxide (specific gravity 0.90) and dilute this solution with several times its volume of hot water. Dissolve the remainder of the precipitate on the filter with this solution, washing beaker and filter with hot water and keeping the volume of the filtrate between 75 and 100 cc. Neutralize with hydrochloric acid, cool to room temperature and add 25 cc. of magnesia mixture from a burette, drop by drop, stirring vigorously with a rubber tipped rod, then add 15 cc. of ammonium hydroxide (sp. gr. 0.90) and allow to stand for four hours or over night at room temperature. The time of standing may be reduced to two hours if kept in a refrigerator or still better in an ice water bath. Filter through a platinum or porcelain Gooch crucible, fitted with a platinum or asbestos mat carefully made and ignited to constant weight. Wash with 2.5 per cent ammonium hydroxide until practically free from chlorides; dry, ignite, cool and weigh as magnesium pyrophosphate. If desired, filtration may be made through an ashless filter paper, igniting in the usual manner. Calculate to $P_2O_5$ by multiplying by 0.6378 (log 80468).

### DETERMINATION OF IRON AND ALUMINUM TOGETHER AS PHOSPHATES

I. SOLUTIONS REQUIRED: 1—Hydrochloric acid (1 : 1); prepared by mixing 1 part by volume of concentrated HCl (sp. gr. 1.19) with 1 part of distilled water.

2—A saturated solution of ammonium chloride, which should be filtered before use.

3—A 25 per cent solution of ammonium acetate, faintly acid to litmus paper.

4—A solution of ammonium phosphate (10 per cent), prepared by dissolving 20 grams of $(NH_4)_2HPO_4$ in 180 cc. of distilled water and filtering. (This should be prepared frequently in small quantity as it attacks glass containers on standing.)

5—A standard solution of ferrous ammonium sulfate, con-

taining iron equivalent to about 0.0100 gram of $Fe_2O_3$ in 10 cc. and 50 cc. of conc. HCl per liter.

6—A solution of calcium and magnesium phosphates for blank determinations, prepared as follows: Dissolve 4 grams of MgO and 35 grams of $CaCO_3$ (both free of iron and aluminum) in 100 cc. of conc. HCl, add an aqueous solution of 30 grams of $(NH_4)_2HPO_4$, make up to 2 liters and filter.

7—A solution of ammonium nitrate (5 per cent) for washing precipitates. About 400 cc. are required for each determination.

All reagents used should be as pure as practicable and all solutions should be free of suspended matter.

II. PREPARATION OF ROCK SOLUTION—Place 2.5 grams of pulverized rock with 50 cc. of 1 : 1 HCl in a graduated 250 cc. flask, the glass of which contains less than 1 per cent of iron and aluminum oxides.[1] Boil gently with occasional shaking for 1 hour in such a manner as to avoid concentrating the solution to less than half of its original volume,[2] dilute, cool to room temperature, make up to volume and mix; filter immediately through a dry filter into a dry flask, discarding the first few cc. of the filtered solution.

Pipette a 50 cc. aliquot, representing 0.5 gram of rock, into a platinum dish and evaporate nearly to dryness.[3] Cool, take up with a few cc. of water and when the salts are loosened from the dish, add 5 cc. of 1 : 1 sulfuric acid and evaporate to fumes. Increase the temperature and evaporate nearly to dryness.[4] Cool, dilute with about 50 cc. of distilled water, add 10 cc. of conc. HCl and heat, with occasional stirring, until sulfates are dissolved. Filter into a 600 cc. Jena glass beaker through a 9 cm. paper (S & S No. 597), washing the paper thoroughly with dilute HCl and hot water.

III. FIRST PRECIPITATION WITH AMMONIUM ACETATE—To the solution in the beaker, add 25 cc. of the standard iron solution when the amount of combined iron and aluminum oxides in the rock does not exceed 5 per cent and 50 cc. of the standard iron solution when the combined oxides exceed 5 per cent.[5] Oxidize with about 3 cc. of bromine water and boil in covered beaker for about 15 minutes to expel the excess of bromine. Rinse cover and sides of beaker with distilled water and cool to room temperature.

(Run a blank determination containing 10 cc. of 1 : 1 HCl, 25 cc. of the calcium and magnesium phosphate solution, and the same quantity of standard iron solution as is added to the rock solution.)

Add 100 cc. of saturated ammonium chloride solution,[6] 3 cc. of 10 per cent ammonium phosphate solution, 2 drops of methyl orange indicator and conc. ammonium hydrate (free of spangles and dissolved mineral matter) to alkaline reaction. Then add dilute HCl (about 1 : 20) drop by drop, with constant stirring, until the solution becomes faintly acid and the pink color of the methyl orange is just restored.[1] Dilute to 450 cc.[2] with distilled water, heat to boiling, and add 25 cc. of 25 per cent ammonium acetate solution. Continue heating for about 5 minutes, after adding ammonium acetate, filter on a 12.5 cm. ashless filter paper (S & S No. 589 "White Ribbon" is suitable), in a 3 inch rapid filtering funnel, keeping the contents of the beaker and funnel hot.[3] Wash 3 times with hot 5 per cent ammonium nitrate solution, each time cutting the precipitate loose from the filter and stirring it thoroughly with the stream from the wash bottle and filling to within about $^1/_4$ inch of its upper edge. About 30 cc. are required for each washing. Return the precipitate to the precipitating beaker by washing it out of the filter with a stream of hot water. Dissolve the precipitate with dilute HCl (1 : 6), pouring about 50 cc. through the filter in successive washings and using about 25 cc. to wash down inside the beaker. Finish filter paper with distilled water.

IV. SECOND PRECIPITATION WITH AMMONIUM ACETATE—Cool the solution to room temperature, add 50 cc. saturated ammonium chloride solution, 4 cc. of 10 per cent ammonium phosphate solution, 2 drops of methyl orange, and adjust acidity as before. Dilute to 300 cc. with distilled water. Heat to boiling, add 15 cc. of 25 per cent ammonium acetate solution and continue heating for about 5 minutes. Filter on the same paper as used for the first filtration, scrubbing the inside of the beaker with a rubber-tipped stirring rod and rinsing with hot 5 per cent ammonium nitrate solution. Wash the precipitate 10 times with hot 5 per cent ammonium nitrate solution, each time cutting the precipitate loose, stirring it thoroughly as before and breaking up all lumps that it may contain. About 300 cc. of wash solution are required.

As a precautionary measure, boil the filtrate and washings from both the first and second precipitates, and recover any additional precipitate.

V. IGNITION OF PRECIPITATE—Transfer filter with precipitate to a weighed deep-form porcelain crucible (40 mm. in diameter is a good size) and heat gently over a low flame until the contents are dry, increase the temperature a little and continue heating until the paper is charred, increase the temperature again and continue heating until the paper is entirely burned. Ignite the *uncovered*[4] porcelain crucible for one-hour periods over blast lamp or No. 4 Meker burner to constant weight, each time cooling to room temperature in desiccator before weighing. Deduct the weight of blank from each determination, and after subtracting the weight of $FePO_4$ equivalent to the amount of iron found in 0.5 gram of rock by titration, calculate the remainder to $Al_2O_3$. $AlPO_4 \times 0.4184 = Al_2O_3$.

DETERMINATION OF IRON

I. SOLUTIONS REQUIRED—1—*Standard Potassium Permanganate, N/40*, containing 0.79015 gram of $KMnO_4$ per liter, and having a value of 0.001996 (or practically 0.002) gram of $Fe_2O_3$ per cc. Standardize with pure sodium oxalate (Bureau of Standards standard sample No. 40.)

2—*Stannous Chloride.* Dissolve 50 grams of the crystallized salt in 100 cc. of hot conc. HCl and make up to 1 liter with distilled water.

[1] Experiments have shown that the solution cannot be made in flasks made of glass containing a higher percentage of alumina, because the fluorine in the rock partially dissolves the glass and adds alumina to the solution. Neither "Nonsol," "Jena" nor "Weber's" resistant glass "R" is suitable. Flasks made of glass containing little alumina, such as "Kavalier," "F Z resistant glass" or other Bohemian glass of lower alumina content have proven satisfactory. See "Chemical Glassware," P. H. Walker, *J. Am. Chem. Soc.*, **27**, 865.

[2] This may be accomplished by heating the flask over a low Bunsen flame or on a hot plate which is just hot enough to keep the solution boiling. A glass tube about 12 inches long by $^3/_8$ of an inch in diameter with a bulb in the middle makes a very satisfactory condenser when placed in the neck of the flask.

[3] It is advisable to remove as much of the HCl as possible before adding sulfuric acid so as to minimize the chances of loss by effervescence or bumping. The evaporation may be conducted in glass beakers of low alumina content. Kavalier glass has been used satisfactorily. In no case should the evaporation be conducted in porcelain.

[4] It is best to remove as much sulfuric acid as possible so that the calcium sulfate which might hold iron will dissolve readily in HCl.

[5] It has been found that when iron oxide is present in considerable excess over aluminum oxide the precipitation of the phosphates is more complete, the combined phosphates are more readily ignited to constant weight, and the precipitate does not become red on ignition.

[6] Ammonium chloride in large quantity increases the solubility of calcium and magnesium phosphates and decreases the solubility of iron and aluminum phosphates.

[1] This method of adjusting acidity was suggested by F. B. Carpenter and was found to give satisfactory results.

[2] All our work has confirmed Brown's statement (see Wiley's "Principles and Practice of Agricultural Analysis," 2nd edition, **1908**, Vol. II, p. 245) that the separation from calcium under the conditions of the method depends upon sufficient dilution.

[3] The contents of the funnel will remain hot if the solution in the beaker is kept hot over a low flame and filtration is fairly rapid.

[4] Heat over Bunsen to redness before placing over blast in order to prevent loss of precipitate by blowing out of crucible.

3—*Mercuric Chloride.* Prepare a cold saturated solution.

4—*Manganese Solution.* (Preventive solution): (*a*)—Dissolve 200 grams of crystallized manganese sulfate in 1000 cc. of water. (*b*)—Pour slowly, with constant stirring, 400 cc. of conc. sulfuric acid into 600 cc. of water and add 1000 cc. of phosphoric acid of 1.3 sp. gr. Mix solutions (*a*) and (*b*).

II. ANALYTICAL PROCEDURE—Determine iron according to Jones' and Jeffrey's modification of the Zimmermann-Reinhardt method[1] as follows: Place in a 250 cc. beaker an aliquot of the rock solution, containing not more than 5 cc. of conc. HCl, boil and reduce with the smallest possible excess of stannous chloride, added drop by drop while agitating the solution. Wash sides of beaker with distilled water and cool rapidly. Add 10 cc. of mercuric chloride solution and stir vigorously for about 30 seconds.[2] Pour the mixture into a large porcelain casserole or dish containing 20 cc. of the manganese solution in about 500 cc. of water which has just been tinted with the permanganate solution.

Titrate with $N/40$ permanganate solution to original tint and correct result by the volume of $KMnO_4$ required for a blank containing the same quantity of HCl (diluted), adding 2 or 3 drops of stannous chloride to the hot solution, cooling, adding 10 cc. of mercuric chloride and titrating similarly.

When the rock solution contains carbonaceous matter it is necessary first to oxidize this with a little potassium chlorate, evaporate to dryness to eliminate chlorine, and redissolve with 5 cc. conc. HCl and about 10 cc. of water.

Calculate the $Fe_2O_3$ found to $FePO_4$, using the factor 1.8898, and after deducting from the weight of combined phosphates found, calculate the difference ($AlPO_4$) to $Al_2O_3$.

F. K. CAMERON, A. J. PATTEN, J. E. BRECKENRIDGE, C. H. JONES, PAUL RUDNICK, *Chairman* } COMMITTEE ON RESEARCH AND ANALYTICAL METHODS

[1] *Analyst*, **34** (1909), 306.

[2] Barneby has shown that only a short interval of time is necessary between the addition of mercuric chloride and manganese sulfate, if the solution is thoroughly agitated. *J. Am. Chem. Soc.*, **36** (1914), 143.

## AMERICAN ELECTROCHEMICAL SOCIETY TWENTY-SEVENTH GENERAL MEETING ATLANTIC CITY AND PHILADELPHIA, APRIL 22-4, 1915

The Twenty-seventh General Meeting of the American Electrochemical Society was held at Atlantic City, N. J., and Philadelphia, Pa., April 22–4, 1915. The meeting opened in Atlantic City with headquarters at the Hotel Chalfonte. Sessions on the 24th were held in the Harrison Laboratory, of the University of Pennsylvania, Philadelphia.

### PROGRAM OF PAPERS

**The American Electrochemical Society in Its External Relation. Presidential Address.** F. A. LIDBURY.

**Some Mechanical Analogies in Electricity. Experimental Lecture.** W. S. FRANKLIN.

**Efficiency of Light Production.** H. E. IVES.

**Experimental Lecture in the Harrison Laboratories, University of Pennsylvania.** E. F. SMITH.

1. **Depolarization in LeClanché Cells.** M. DE KAY THOMPSON AND E. G. CROCKER.
2. **The Thermal Conductivity of Refractories.** BOYD DUDLEY, JR.
3. **Chemistry in the Development and Operation of Flaming Arc Carbons.** W. C. MOORE
4. **The Formation of Magnesium Suboxide in the Electrolytic Preparation of Magnesium.** F. C. FRARY AND H. C. BERMAN.
5. **Electrodeposition of Smooth Lead from Lead Nitrate Solutions.** F. C. MATHERS AND ASA MCKINNEY.
6. **The Coagulation of Albumin by Electrolytes.** W. D. BANCROFT.
7. **Neutralization of Absorbed Ions.** W. D. BANCROFT.
8. **Fibrox.** E. WEINTRAUB.
9. **Thermo-Electromotive Force of Certain Iron Alloys.** T. E. FULLER.
10. **Calorizing Metals.** W. E. RUDER.
11. **Commercial Nitrogen Fixation.** S. PEACOCK.
12. **Electroplating with Cobalt.** H. T. KALMUS, C. H. HARPER AND W. L. SAVELL.
13. **The Cyanamide Process.** F. S. WASHBURN.
14. **Fixation of Atmospheric Nitrogen.** L. L. SUMMERS.
15. **Cleaning and Plating in the Same Solution.** O. P. WATTS.
16. **Some Problems in Copper Leaching.** (General Discussion.)
17. **On the Temperature of Reaction between Acheson Graphite and Magnesia.** O. L. KOWALKE AND D. S. GRENFELL
18. **Lighting of Electrolytic Tank Rooms.** R. E. HARRINGTON.

The annual business meeting of the Society and the announcement of the election of officers for the coming year were held at the opening of the Thursday (22nd) afternoon session. Following the lecture by Prof. Franklin, Thursday evening, an informal social meeting was enjoyed in the Café Alamac.

The morning session on the 24th was a joint session with the Illuminating Engineering Society, while that in the afternoon was held with the American Electroplaters' Society. The laboratories and museums of the University of Pennsylvania were visited by the members and guests.

## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS TENTATIVE ITINERARY TO SAN FRANCISCO

| LEAVE | AUG. | | ARRIVE | AUG. | |
|---|---|---|---|---|---|
| New York | 6 | 5.04 P.M. | Chicago | 7 | 2.00 P.M. |
| Chicago | 7 | 6.00 P.M. | Colo. Springs | 9 | 7.00 A.M. |
| Colo. Springs | 10 | 6.45 P.M. | Grand Canyon | 12 | 1.50 A.M. |
| Grand Canyon | 12 | 8.00 P.M. | San Diego | 13 | 6.00 P.M. |
| San Diego | 15 | 11.59 P.M. | Los Angeles | 16 | 3.30 A.M. |
| Los Angeles | 19 | 7.30 A.M. | Santa Barbara | 19 | 11.00 A.M. |
| Santa Barbara | 19 | 11.20 P.M. | Del Monte | 20 | 7.20 A.M. |
| Del Monte | 20 | 1.43 P.M. | San Francisco | 20 | 4.00 P.M. |
| San Francisco | 21 | 9.40 P.M. | Yosemite | 22 | 10.45 A.M. |
| | | | San Francisco | 25 | 8.28 A.M. |

*Monday*, Aug. 16 to *Thursday*, Aug. 19—Excursions, sightseeing trips and joint session with the Southern California Section of the American Chemical Society.

*Saturday*, Aug. 21 to *Wednesday*, Aug. 24—Members may visit the Fair for three days or take the trip to the Yosemite Valley.

*Wednesday*, Aug. 25 to *Saturday*, Aug. 28—Excursions and sessions of the Institute at the University of California and Leland Stanford University.

Members have the option of leaving San Francisco on Saturday, Aug. 28 at 10.30 A.M. by steamer for Astoria, reaching Portland on Sunday, Aug. 29, at 5 P.M., remaining in Portland one day and reaching Seattle on Tuesday, Aug. 31 at 6.50 A.M., in time for the meeting of the American Chemical Society.

Members may also go by rail from San Francisco to Portland by the Southern Pacific Shasta route, a very beautiful scenic trip, but must decide at time of purchase of ticket from starting point, or take the following schedule:

| LEAVE | | | ARRIVE | SEPT. | |
|---|---|---|---|---|---|
| San Francisco | Aug. 31 | 10.30 A.M. | Portland | 1 | 5.00 P.M. |
| Portland | Sept. 1 | 11.30 P.M. | Seattle | 2 | 6.50 A.M. |
| Seattle | Sept. 2 | 7.10 P.M. | Butte | 3 | 9.28 P.M. |
| Butte | Sept. 5 | 9.30 A.M. | Anaconda | 5 | 10.30 A.M. |
| Anaconda | Sept. 5 | 6.35 P.M. | | | |

TRIP TO THE YELLOWSTONE PARK

| | | |
|---|---|---|
| Arrive Gardiner | Mon., Sept. 6 | 10.15 A.M. |
| Leave Gardiner | Sat., Sept. 11 | 7.15 P.M. |
| Arrive Duluth | Mon., Sept. 13 | 2.05 P.M. |

FOUR-DAY LAKE TRIP

| LEAVE | SEPT. | | ARRIVE | SEPT. | |
|---|---|---|---|---|---|
| Duluth | 14 | 8.00 P.M. | Buffalo | 18 | 12.30 P.M. |
| Buffalo | 18 | 7.30 P.M. | New York | 19 | 7.57 A.M. |

Members may omit the trip to the Yellowstone Park, arriving at Chicago, *Tuesday*, Sept. 7, 9.00 P.M.

# GIBBS MEDAL AWARD

The Willard Gibbs Medal, for the year 1915, was conferred upon Dr. Arthur A. Noyes, the celebrated physical chemist, at the April meeting of the Chicago Section of the American Chemical Society, held April 16, 1915.

After an introductory address by Chairman Otto Eisenschiml, of the Chicago Section, the medal was presented by Professor Julius Stieglitz, of Chicago University. Following the presentation and acceptance of the medal, informal addresses were made by President W. E. Stone, of Purdue University; Prof. James H. Tufts, representing the City Club; and by President Kenneth Lockett, of the Chicago Tech. Club. The presentation address, and a short abstract of Dr. Noyes' Willard Gibbs Address on "A System of Qualitative Analysis, Including Nearly All the Metallic Elements," are given below. It is expected that the papers dealing with this subject will be published later in the *Journal of the American Chemical Society*.

ARTHUR AMOS NOYES—WILLARD GIBBS MEDALIST, 1915

The Willard Gibbs Medal was founded in 1910 by William A. Converse. After serving for seven years as secretary and one year as Chairman of the Chicago Section, Mr. Converse was compelled by growing business responsibilities to retire from active connection with the Section. In token of his continued interest in its welfare, he donated a sum sufficient to enable the Section to bestow annually a gold medal in recognition and encouragement of eminent research in theoretical or applied chemistry—the recipient to be selected by a competent jury and to be obligated only to the extent of delivering an address before the Section on some topic in his field of research. The medal was called after J. Willard Gibbs, by permission of his nearest surviving relatives. The medal has now been conferred upon five great chemists:

| | |
|---|---|
| Svante August Arrhenius | 1911 |
| William Theodore Richards | 1912 |
| Leo H. Baekeland | 1913 |
| Ira Remsen | 1914 |
| Arthur Amos Noyes | 1915 |

Arthur Amos Noyes was born in Newburyport, Mass., Sept. 13, 1866. He was graduated from the Massachusetts Institute of Technology in 1886 and obtained the Master's degree from the same institution the following year. After a year spent as assistant in analytical and organic chemistry, he went to the University of Leipzig where after two years of study with Professor Wilhelm Ostwald he obtained the doctor's degree. Returning to the Institute he served four years as assistant and associate professor of organic chemistry and in 1899 was made professor of theoretical chemistry; in 1903 he became director of the Research Laboratory of Physical Chemistry. From 1907 to 1909 Professor Noyes was acting president of the Massachusetts Institute of Technology. He is a member of the National Academy of Sciences, and of numerous other scientific societies. During 1904 he was president of the American Chemical Society and served for many years as a member of its board of editors. He is the author of several books in the fields of physical, organic and analytical chemistry, and is especially well known for his many important contributions to the ionic theory and its applications. He is also a member of the editorial board of the *Zeitschrift für physikalische Chemie*.—[W. D. Harkins.]

## PRESENTATION ADDRESS

By Julius Stieglitz

Mr. Chairman, Dr. Noyes, Ladies and Gentlemen:

Illustr ous men, leaders of thought in our science, have added, by the dignity of their names, to the significance of the award of the Willard Gibbs Medal by the Chicago Section of the American Chemical Society: Svante A. Arrhenius, founder of the theory of ionization; Theodore Richards, genial leader of one of the earliest onslaughts on the secrets of the subatomic world; Leo H. Baekeland, inventor of Velox and Bakelite and through them and their followers dispenser of the pleasures of picture making and of music to millions of art lovers; Ira Remsen, sturdy sponsor for American chemical research in the days when it stood in sorest need of protection—we look with pride on the high purpose which these names show to be underlying the foundation and award of our medal. And tonight we are adding to the luster of the medal by bestowing it on another of those brilliant Americans, whose genius is fast making American chemical research in quality the peer of any in the world. Many of us will recall that when Arrhenius was here and told us his own picturesque story of the history of his theory, he remarked that the very finest work in developing his theory in the way of rigorous measurements was being done in this country in the research laboratory of the Massachusetts Institute of Technology under the direction of Arthur Amos Noyes. With accuracy as its goal and scientific honesty as its talisman, the laboratory of Dr. Noyes has produced classic after classic on the conductivity relations forming the basis of the theory of ionization. Every

theory, however brilliant its success may be in its first qualitative and roughly quantitative garb, must, in order to survive and prove its permanent justification, conform ultimately to the test of minutely accurate quantitative measurement. This necessary and vital service to the theory of ionization was undertaken by Dr. Noyes and his associates and has been brilliantly carried out. Last year, in his Faraday address in London, Arrhenius again and again referred gratefully to the value of this work. It is interesting to note that this insistence on the utmost limits of accuracy is becoming the most striking characteristic of the genius of our best American scientists: to mention only a few names familiar to all of us. We saw it in Gibbs in his far-going mathematical analysis of chemical and physical changes; we find it in Michelson, in Richards, in Morley, in Millikan—and again, tonight, in our medalist. This insistence on accuracy is evident in all of the contributions of Dr. Noyes to chemistry: van't Hoff developed a method for determining the order of a given chemical reaction, but van't Hoff's formula was, after all, not a rigorous one and sometimes left one in doubt as to the result: a more reliable formula, based on rigorous analysis, was developed by Dr. Noyes and is displacing van't Hoff's. Accuracy again characterized the searching work of Dr. Noyes on the sensitiveness of indicators, on the correct use and understanding of which the reliability of so much of our technical and scientific research and practice depends.

Undoubtedly it was this same pressing need of accuracy that led Dr. Noyes into the monumental work on which we shall hear him speak tonight: his work on the revision of the methods of qualitative analysis. Bringing to this labor the ardor for exactness combined with a masterly knowledge of the laws of physical chemistry—an advantage not held by his greatest predecessor in this field, Fresenius—Dr. Noyes could be content with nothing less than methods which approach quantitative analysis in accuracy, content with nothing less than a system broad enough to include ultimately the rare as well as the common elements in its scope. He thus escaped the chance for error inherent in older methods, which results from the setting of limitations not recognized by nature.

I cannot close this short review of some of the contributions of our medalist to our science without a grateful recognition of two other important forms of service other than original investigation: Dr. Noyes has been uniquely successful in associating with himself a group of great chemists: Lewis, Whitney, Washburn, Kraus, Bray, Tolman, Harkins are carrying the traditions of accuracy and thoroughness of his laboratory into all parts of our country, in technical as well as scientific fields, in work fertilized by their own brilliant ideas, characterized by the standards of the research laboratory of the Massachusetts Institute of Technology. In the second place, Dr. Noyes has been and is a great teacher of the young, the undergraduate chemist-to-be: like A. W. Hofmann, in his day the greatest teacher of chemistry in the world, Dr. Noyes has insisted on presenting to the beginners in chemistry the new physico-chemical theories in lucid, transparent terms, and, in pursuance of this ideal, he has invented a long series of beautiful lecture experiments on physico-chemical relations—the best we have, which, like Hofmann's, are now incorporated, more or less consciously or unconsciously, into our best elementary courses. These lecture experiments, like the work on the theory of ionization, like the work on qualitative analysis, have already become classics of American chemical endeavor.

To Dr. Noyes:

In consideration of these great contributions to chemistry by you, Dr. Arthur Amos Noyes, as an investigator and as a teacher, the Chicago Section of the American Chemical Society decided to bestow upon you its highest honor, the Willard Gibbs Medal, founded by our service-loving fellow member, Mr. William A. Converse. In the name of the Section, I have the honor to present to you this, the Fifth Willard Gibbs Medal, with the best wishes for, and confidence in, further great productive work on your part on behalf of our common science and country.

## ADDRESS OF ACCEPTANCE[1]

By Arthur Amos Noyes

In replying to the address of presentation, Dr. Noyes expressed his deep appreciation of the honor conferred upon him, particularly in being placed in a group with the four great chemists to whom the award has been given on previous occasions, and most of all in being presented with a medal given in the name of America's greatest chemist, Willard Gibbs. He also wished the Section to know how much more he valued such an honor on account of the fact that it came as a token of appreciation from his fellow chemists, of work done in the past.

On account of the fact that the work which he described in his address is still incomplete, even although it is finished in all its essential parts, Dr. Noyes has decided that it will be best at this time to publish only a short abstract written by one of the members of the Section. The work when completed will be published in full.

The driving force which kept him at work during fifteen years of investigation was his feeling of the great need of chemists for a systematic scheme of qualitative analysis to include all of the elements. The lack of such a scheme was most vividly impressed upon his mind when twenty years ago he received from Colorado an ore said to contain uranium. Even by making use of the best methods then available it took three weeks to determine that the rare element present was not uranium but vanadium. This incident he cited to illustrate the difficulties which then lay in the path of chemists when they started out to make analyses for the rare elements by using the isolated statements which were all that could be found in the literature at that time.

Now many of the so called rare elements have been found in such large quantities that they are no longer rare. The reason for the omission of these elements from the ordinary scheme for a qualitative analysis is twofold: (1) the historical development of analytical chemistry; (2) the fact that they are more difficult to detect than most of the common elements. On the other hand, many of these so-called rare elements have come to play an enormously important part in science and industry, and some of them, for example titanium, have been found to be much more abundant in nature than some of the members of the group of the 22 common elements. In steel, tungsten, vanadium, and uranium have found an extensive use; thorium and cerium have come to be enormously important in the making of mantles for gas lighting, while tantalum, and to a greater extent tungsten, have rendered the same service in connection with lighting by electricity.

In papers already published in the *Journal of the American Chemical Society* a revision of the usual scheme of analysis for the common elements has been described, and in this a few of the rare elements have been included. In the present scheme the aim has been to provide for the detection of nearly all of the rare elements as well as the common ones, and at the same time to develop such detailed and explicit instructions that the results of an analysis may be certain if carried out by a chemist of ordinary skill. The aim has been to provide a method which will detect the presence of 1 mg. of any element in a mixture with 500 mg. of any common element or elements, or with 100 mg. of any rare element. It is often stated that a qualitative analysis is unnecessary if a quantitative analysis is to be made, and that the former is only a waste of time. That this is not in general true is proved by the fact that many quantitative analyses are made inexact by a failure to realize the presence of an ele-

[1] Abstracted, by consent of the author, by Professor William D. Harkins, of Chicago University.

ment which would have been detected easily by the use of the proper methods of qualitative analysis, while on the other hand a qualitative analysis can be so conducted as to enable the proportions of the various elements to be estimated roughly, thus making in many cases a quantitative analysis superfluous.

A former president of the society, Mr. Dudley, spoke on the dignity of analytical chemistry, and now it is necessary that the dignity ofqualitative analysis in particular should be upheld. Why is qualitative analysis so much discredited? This is due to the slack methods usually used in teaching the subject. Thus the manipulation is not given such painstaking attention as is considered necessary in the teaching of quantitative analysis.

In general, in making a qualitative analysis according to the system advocated, 1 g. of the sample is used, since in this case 1 mg. is equal to 1 per cent. However, the strict adherence to the rule that 1 mg. should be detected, is somewhat irrational, since the results of a test depend upon the number of atomic weights of an element present, rather than upon its weight in grams.

The idea of the present presentation of the subject is not to give a method for making a qualitative analysis, but to show rather the character of the research. The systematic treatment of the analytical schemes must be left for the final papers.

A great deal of attention has been paid to an investigation of the methods for the preparation of the solution. Nitric acid is used for the solution of the substance rather than hydrochloric since the latter gives the volatile chlorides or arsenic, germanium, and selenium, and also mercuric chloride, which is somewhat volatile. For the solution of the insoluble residue, hydrofluoric acid is used rather than fusion with carbonates, since the former method not only introduces less foreign substance, but at the same time it removes silicon. This residue is treated with hydrofluoric acid, and then evaporated with nitric acid. After this nitric acid treatment, tin, antimony, tantalum, columbium, titanium, and tungsten are left in the form of insoluble compounds, and the platinum metals and certain iron alloys are found to remain largely undissolved. The residue is heated with hydrofluoric acid, and after filtration the residue of metal is fused with sodium peroxide, which may now be obtained pure, and osmium is distilled off as $OsO_4$.

The solution is evaporated, concentrated hydrobromic acid is added, and arsenic, selenium, and germanium are distilled off as bromides. This process of distillation is, contrary to the usual opinion, somewhat quicker than the application of methods of filtration. Silver is left in the form of bromide.

Some of the most marked deviations from the usual method of procedure may be mentioned. Thus for the precipitation with hydrogen sulfide the solution is first saturated with the gas in a bottle, a cork is inserted tightly, and the corked bottle is heated for $^1/_2$ to 1 hour in boiling water. Arsenic, antimony, and tin have been removed before this; the platinum metals cannot be completely removed by ammonium sulfide, so the treatment with this latter substance is not used.

In a later part of the analysis, $TiO_2$ is removed from a residue containing $Ta_2O_5$, and $Cb_2O_5$, by boiling with potassium salicylate. The work has now proceeded so far that fairly good separations have been devised for almost every group, and considerable success has been attained in separations of certain of the rare earth elements. Those who have worked on the rare earths have neglected too much methods of separation which depend upon the fact that a number of these elements are capable of existence in several stages of oxidation.

# NOTES AND CORRESPONDENCE

## NOTE ON REVIEW OF DR. THOMPSON'S "OCCUPATIONAL DISEASES"

*Editor of the Journal of Industrial and Engineering Chemistry:*

My attention has been called to a review,[1] by W. A. Hamor, of Dr. W. Gilman Thompson's recent work on "Occupational Diseases, etc."

In this review the statement is made that " 'Brass Founders' Ague' is more likely due to the inhalation of zinc oxide and not zinc fume." This statement is based on visits made to brass foundries, but zinc works, where this metal is handled in large quantities, were not visited, and those connected with such works, whose opinions and experiences would have been of value, were not consulted. For the past seven years I have been surgeon to one of the largest zinc plants in the country, and have just finished making a thorough physical examination of all of the employees. With this experience I have no hesitation in saying that I have never seen a case of illness which could be directly attributed to zinc.

Sir Thomas Oliver[2] states that zinc is non-toxic and described symptoms seen among brass founders which resemble those which he has seen in workers in copper, especially gastro-intestinal symptoms. Though he states that copper workers seem to be "as healthy as persons following other occupations elsewhere," he distinctly states that copper gives rise to acute attacks of illness, and also states "that animals exposed to oxide of zinc in the form of dust or who receive it in their food over a length of time" show no signs of poisoning. In his visits to the large smelting works at Bleiberg, Belgium, he could not find any evidence of ill-health among the workmen traceable to the zinc itself.

Rambousek, Professor of Factory Hygiene and Chief State Health Officer at Prague,[1] states that "Industrial poisoning, from zinc is unknown. The chronic zinc poisoning among spelter workers described by Schlockow, with nervous symptoms, is undoubtedly to be attributed to lead."

Armit[2] claims having seen a similar syndrome in the case of the inhalation of nickel-carbonyl, iron-carbonyl and cobalt fumes. It is generally conceded that copper has a toxicity, though according to Lehman (quoted by Rambousek) "opinions are divided on this point."

The experience of C. A. Hansen, of the General Electric Company, is worth giving in extenso:

"We have just had an experience here that seems to warrant the publication of this warning to any one who contemplates working with copper, in the electric arc furnace.

"We melted 5000 lbs. of electrolytic copper scrap—uncontaminated except for a small amount of admixed iron—in a three-phase arc furnace of the ordinary steel furnace type, the experiment lasting some five hours. A few hours after pouring off, all of the ten men in the furnace building suffered inconvenience in breathing. For the 24 ensuing hours severe nausea was experienced in each case and a soreness throughout the entire system similar to that of acute grippe.

"Since in all other respects the run resembled an ordinary steel run, I attribute the trouble we experienced to copper which was shown to be present in the furnace fumes. The temperature of the copper bath as a whole at no time exceeded 1300° C., so that probably the copper was volatilized only at points directly beneath the electrodes.

[1] THIS JOURNAL, **6**, (1914), 871-2. [2] "Diseases of Occupation," 1907.

[1] Rambousek, "Industrial Poisoning," 1913, translated by Sir Thomas Legge, p. 151.

[2] "Toxicology of Nickel Carbonyl," *Journal of Hygiene*, **7** (1911), 525–551; *Ibid.*, pp. 565–600.

"From the severity of the attack, coupled with the short time we were exposed to the fumes, and that in a building which was well ventilated, I am of the opinion that very serious results might obtain under less favorable conditions.

"I also attach more importance to the above from the fact that in five years of continuous research work on a large scale with furnace processes which involved, among others, tellurium, tellurides, arsenic, arsenides, zinc and sulfide ores, the only physical inconvenience suffered has been an occasional carbon monoxide headache."

The hypothesis that zinc is the cause of "Brass Founders' Ague" is to a large extent based upon the fact that the boiling point of zinc is 915° C., while that of copper is 2200°, and consequently that zinc, and zinc alone, forms the vapor that arises from the brass pot. That this is incorrect is shown by analyses of brass furnace flue dust, which shows as much as 10 parts of copper to 100 of zinc. The microscope also shows that copper is present as a true fume and not as splashes of metal.

The volatility of metals at temperatures well below their boiling points is well established. For example, in the case of common spelter: while lead has a boiling point of 1500° C. spelter made at a temperature of 1200° will contain about 1 per cent of lead. Hoffman, in his "Metallurgy of Copper" (McGraw Hill Book Co., 1914), states that in the case of copper, volatilization is noticeable *in vacuo* at 700°, and decided near the melting point.

(1) The symptoms of this disease are very characteristic and pronounced, and the fact that it is known as "Brass Founders' Ague" shows its close connection with brass. On the other hand, there is no name for this trouble among zinc smelters, and many of them have never heard of its existence.

(2) Hansen's communication is of peculiar interest in that symptoms of a very serious type developed where copper alone was being melted with the same equipment that had been used for zinc without any trouble whatever.

(3) Evidence collected by investigators of world-wide repute is negative as far as the toxicity of the zinc fume met with in spelter works is concerned.

(4) Our own experience in connection both with the manufacture of spelter and the manufacture of zinc oxide, has failed to show any symptoms whatever resembling those of the "spelter shakes." Under these circumstances it seems to me that the connection between zinc oxide or zinc fume and "Brass Founders' Ague" is not proven, and that the balance of evidence is in favor of the trouble being due to the vapor of copper.

THE PALMERTON HOSPITAL
PALMERTON, PA., April 15, 1915

J. W. LUTHER

## NOTE ON ANALYSIS OF CHROME YELLOWS AND GREENS

*Editor of the Journal of Industrial and Engineering Chemistry:*

The April number of THIS JOURNAL, page 324, contains methods of analysis of chrome yellows and chrome greens which, it is believed, do not satisfy the requirements of commercial accuracy, especially in the case of chrome greens.

The method for greens in its essential features was employed for a time in our laboratory, but it was abandoned upon finding that the determination of blue in chrome greens, precipitated in whole or in part on china clay, gave results entirely too high when estimated by difference. The objection to the method of analysis named appears to lie in the presence of combined water in china clay. W. G. Scott, in "White Paints and Painting Materials," page 168, records the observation that when china clay is treated with hot, dilute hydrochloric acid, there is a decided loss in weight of the substance with no appreciable gain in the filtrate, which the observer attributes to combined water. The loss of weight by ignition of china clay has been noted by several chemists, the latest analyses that have come to the writer's notice being those of the Bureau of Standards and Bureau of Chemistry (*Proceedings of the American Society for Testing Materials*, **13**, 409) which show a loss on ignition of from 12 to 13 per cent. It is obvious that no little error in the determination of blue would be involved with material of this character, if estimated by difference.

Furthermore, in our experience, the determination of lead as chromate in nitric acid solution is found unreliable in comparison with precipitation in acetic acid.

The quantitative estimation of Prussian blue from the percentage of iron, in all ordinary kinds of chrome greens, has proved fairly satisfactory, in all events more accurate than by the method of difference.

DAYTON, OHIO
April 16, 1915

THE LOWE BROTHERS COMPANY
*Per* L. H. MCFADDEN

## ARREST OF PLATINUM THIEF

Upon a description furnished by the Bridgeport Testing Laboratory, a suspected platinum thief was arrested March 6th at the laboratory of Arthur D. Little, Inc., Boston, and was later identified by Mr. F. C. Barrows, of Bridgeport, Conn., as the man who had visited the Bridgeport Hydraulic Laboratory and the Bridgeport Testing Laboratory immediately prior to their discovery of the loss of a considerable amount of platinum.

When the man was searched, a flattened platinum crucible, from which the number had been cut, was found tucked between the slide and cover of a box of safety matches. The man was found to have a criminal record and to have served a State Prison term. He was held for the Grand Jury which, however, for lack of evidence failed to bring a bill against him.

The man was about 35 years old, with prominent nose, peculiar eyes, reddish hair, and freckles. He speaks with a down-East accent. His height is about 5 ft. 9 in., and his weight about 175 pounds. He gave the name of Rubin.

A few days ago an assay balance was stolen from the laboratory of Henry Carmichael at 15 Exchange Street, Boston.

The description published in THIS JOURNAL, **7** (1915), 358, in a note from the Hahnemann Medical College, leaves little doubt that the man is the same who was reported as operating in Philadelphia.

# PERSONAL NOTES

Dr. Ira Remsen, president emeritus of Johns Hopkins University, will deliver the principal address at the formal opening of the new chemistry building of the University of Minnesota, on May 24th.

The address to the graduating class of the Michigan College of Mines was given this year by Prof. James F. Kemp, of Columbia University, on April 16th.

A pamphlet, prepared under the direction of the Chemists' Committee of the United States Steel Corporation, on the Sampling and Analysis of Alloy Steels is now being distributed to its various chemical laboratories. This makes the fifth pamphlet so distributed, the purpose of which is to unify and simplify methods of analyses. The first four pamphlets covered the Sampling and Analysis of Iron Ores, Pig Iron, Plain Steel and Gases. To curtail the requests for copies of these pamphlets a charge of one dollar each is now being made, to persons and firms outside the Corporation. Mr. J. M. Camp, Carnegie Building, Pittsburgh, Pa., is chairman of the committee.

Mr. Watson Smith, retiring Editor of the *Journal of the Society of Chemical Industry*, was entertained at dinner, on February 23rd, by members of the Council and Publication Committee. Opportunity was taken to present to him, as a souvenir of his 33 years' service as Editor of the Journal, an album containing a short address signed by the President and all available Past Presidents, the Members of the Council and Publication Committee, and the Abstractors. At the request of the President, the presentation was made by the Dean of the Chemical Press, Sir William Crookes, O.M., F.R.S.

The Southern California Section of the American Chemical Society through its President, Edgar Baruch, 804 Wright and Calendar Bldg., and its Secretary, H. L. Payne, 223 W. 1st St., Los Angeles, extends its welcome and hospitality to all members of the Society visiting the Expositions and Los Angeles this year.

At the annual meeting of the London Chemical Society, held on March 25th, the new officers elected were: *President*, Dr. Alexander Scott; *Vice-President*, Prof. F. R. Japp and Prof. R. Threlfall; *Treasurer*, Dr. M. O. Forster; *Ordinary Members of Council*, Mr. D. L. Chapman, Prof. F. G. Donnan, Mr. W. Macnab and Dr. J. F. Thorpe.

At the regular meeting of the Cincinnati Section of the A. C. S. on April 21st, the following papers were presented: "General and Historical Discussion of the Soap Industry," by Howard Dock; "The Manufacture of Laundry Soaps and Soap Powders," by A. Campbell; "The Manufacture of Glycerine," by C. P. Long.

Prof. Richard S. McCaffery presented a paper on "Some Defects in Steel Ingots," before the Wisconsin Section of the A. C. S. on April 21st.

Emil E. Lungwitz, chemical and industrial engineer located in New York City, announces a change of address from 80 Maiden Lane to 30 Church Street, to take effect May 1, 1915.

The second delivery of radium from the plant of the National Institute, being operated by the Bureau of Mines in Denver, has been made to the officers of the Institute. It consisted of 300 mg. of radium bromide having a market value of approximately $19,000. This delivery of radium bromide is a small fraction of the radium extracted from the first 240 tons of ore treated in the experimental plant first erected. The crystallization of the radium itself has not kept pace with the extraction from the ore, owing to the impossibility to obtain from abroad certain special apparatus not manufactured in this country. Deliveries will gradually increase until they are equal to the capacity of the combined plants which is approximately three tons of ore per day.

Notice has been given by the Society of Chemical Industry that the Annual General Meeting will be held in Manchester, England, on Wednesday, July 14th.

President Butler, of Columbia University, has announced an anonymous gift of $30,000 to be used in the reconstruction and new equipment of the laboratories of quantitative, organic and engineering chemistry in Havemeyer Hall.

Dr. Julius Stieglitz, professor of chemistry and director of analytical chemistry in the University of Chicago, has accepted an invitation to give courses in chemistry at the University of California during the summer term that begins June 21st and closes on August 1st. Prof. Stieglitz will give a seminar on special topics in organic chemistry and also a college course in organic chemistry.

Dr. Frederick Winslow Taylor, of Philadelphia, past president of the Society of Mechanical Engineers, known for his inauguration of methods of "scientific management," died on March 21st at the age of sixty-nine years.

Franklin C. Gurley, a graduate assistant in chemistry at the Massachusetts Agricultural College, has accepted a position as chemist with the Benzol Products Company of Philadelphia.

Dr. Augustus H. Gill, professor of technical analysis at the Massachusetts Institute of Technology, addressed the Detroit Engineering Society on March 19th, on "Lubricating Oils: Essentials and Characteristics."

Mr. George A. Rankin, of the Geophysical Laboratory, Washington, D. C., spent the week of April 12th in the Lehigh Cement District, making measurements of the actual working temperatures in the clinkering zones of Portland cement kilns.

The following members were present at the meeting of the Council at the New Orleans Meeting of the A. C. S., March 31st to April 3rd: Charles Baskerville, B. C. Hesse, E. J. Crane, Charles E. Coates, H. E. Howe, J. H. Long, Frank N. Smalley, Edward Bartow, D. K. French, W. A. Noyes, William Brady, W. D. Richardson, W. D. Bigelow, B. B. Ross, Floyd W. Robison, Charles A. Catlin, J. S. Goldbaum, F. E. Tuttle (substitute), C. G. Derick (substitute), L. F. Nickell, E. H. S. Bailey, Frank R. Eldred, Harry McCormack, L. H. Baekeland, George N. Prentiss (substitute), A. D. Little and Frank R. Cameron.

Prof. H. P. Talbot, of the Massachusetts Institute of Technology, lectured on "The Noble Gases," on March 25th before the Phi Lambda Upsilon of Columbia University.

The Pittsburgh Section of the A. C. S. is planning Saturday afternoon excursions to some of the manufacturing plants around Pittsburgh.

The Dorr Cyanide Machinery Co. announce that after May 1st, 1915, the address of their New York office will be Room 2843, Whitehall Bldg., New York City.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### BUREAU OF FISHERIES

**Report on Alaskan Investigations in 1914.** E. Lester Jones. 155 pp. Paper, 50 cents. The investigations reported on relate principally to the fisheries but some attention is given to fur-bearing animals. The salmon industry is covered at length with discussion of modes of catching, canning and shipping.

### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Canned-Tomato Industry in Italy.** J. Alexis Shriver. Special Agents Series 93. 23 pp. Paper, 5 cents. This report gives interesting comparisons with the business as it is carried on in the United States, including a description of the varieties cultivated, modes of culture and methods of canning with suggestions of considerable interest to American packers.

**Canned-Goods Trade in the Far East.** J. Alexis Shriver. Special Agents Series 92. 78 pp. Paper, 10 cents. This report gives a detailed description of the markets for canned goods and

the nature of competition to be expected and suggestions of interest to American packers as to development of trade.

**Dyestuffs for American Textile and Other Industries.** THOMAS H. NORTON. Special Agents Series 96. 57 pp. Paper, 10 cents. This extensive review of trade conditions was prepared in response to a resolution of the United States Senate. The dyestuff situation in the United States is discussed with summaries of the consumption of dyes, an outline of the coal tar chemical industry and coal-tar dye industry in so far as these are in existence in the United States and a summary of the supply of raw materials and general chemicals required for the development of the industry. The German industries of this general group are also explained and the processes of manufacture outlined. Particular emphasis is laid upon the American attitude toward the German industry and the economic necessity for a very complicated system if the dyestuff industry is to be developed in America. A considerable amount of the material presented duplicates that given before the New York Section of the American Chemical Society, particularly the reports which have been prepared by Dr. B. C. Hesse.

### COMMERCE REPORTS—MARCH, 1915

The **corundum** industry of India is discussed. (P. 822.)

In the past most of the **vegetable-oil seeds** from India have been shipped to other countries, though some oil has been extracted in India. Among the oil-bearing materials exported are linseed, peanuts, rape seed, sesame, cottonseed, castor beans, copra, mahwa seed, poppy seed, mustard seed, and nigar seed. Efforts are being made to increase the oil production in India. (Pp. 828–31.)

The Swedish **iron industry** is almost paralyzed. (P. 857.)

The value of potatoes raised in Ireland is too high to warrant their use in the manufacture of **alcohol.** (P. 861.)

The **soy-bean** industry of Manchuria is discussed. (P. 863.)

Statistics of the **copper industry** in Austria are given. (P. 882.)

Prospects for **petroleum** in Papua are favorable. (P. 883.)

Canada has just put into effect a **white-phosphorus match** law. (P. 888.)

Norway has placed an embargo on **copper** and **brass.** (P. 897.)

A **beet-sugar** factory is proposed for Gloucestershire, England. (P. 899.)

The milling of **rape seed** and **soy beans** in Japan has increased because of the war. (P. 941.)

Statistics of the Russian **petroleum** industry are given. (P. 945.)

The embargo on **rattan** from Singapore has been removed with respect to America. (P. 945.)

Methods of mining **coal, sulfur, and petroleum** in Tuscany, Italy, are described. (P. 952.)

Owing to a shortage of vessels, the **trade of the Philippines** is practically paralyzed. The suggested use of United States colliers to relieve the situation is against existing laws. (P. 963.)

The Japanese **iron industry** is improving. (P. 971.)

Spain has placed am embargo on **potash.** (P. 977.)

France has placed an embargo on all **lenses** for optical instruments. (P. 993.)

The **Portland-cement** industry of Alberta, Canada, is described. (P. 996.)

The British **cyanide industry** produces large amounts of export, the largest factory being in Glasgow. (P. 998.)

The Standard Oil Company is equipping a new **candle factory** in Tientsin, China, with a daily capacity of 400,000 candles. (P. 1003.)

Efforts are being made to increase the output of **benzol and toluol** from by-product coke ovens in Canada. (P. 1010.)

Old abandoned **copper mines** of Cyprus are being reopened. (P. 1017.)

The **sugar industry** of the Philippines is increasing. (P. 1020.)

A **camphor-bearing plant,** "Blumes balsamfera," has been discovered growing in abundance in the Philippines, and efforts will be made to utilize it. (P. 1022.)

The German **pottery industries,** and especially the use of continuous kilns (Kanalofen), are described in some detail. (Pp. 1028–31.)

The Philippine **copra industry** is improving. (P. 1048.)

Additions to the British absolute contraband list include **tin, tin chloride, castor oil, paraffin, copper iodide, lubricants, hides, ammonia and ammonium salts, urea, and aniline.** (P. 1057.)

**Aniline oil and salts** have been placed on the British embargo list. (P. 1058.)

The Brazilian **monazite** industry is described in some detail. (Pp. 1059–62.)

The British importation and crushing of **oil seeds,** including castor, cotton, flax and rape seeds, soy beans and copra, shows an increase. (Pp. 1069 and 1220.)

The export of **senna** from Egypt has been prohibited except to the United Kingdom and France. (P. 1073.)

The nut of the tree known as "Chisochiton cuningianus" contains 45 per cent of an oil suitable for **soap making.** (P. 1088.)

The **metric system** has been adopted in the new British Pharmacopoeia. (P. 1103.)

Italy is experiencing a great shortage of **dyestuffs.** (P. 1108.)

The Scotch **shale-oil** industry is flourishing, there being a great demand for the oil, **paraffin,** and **ammonium sulfate.** (P. 1108.)

Sales of **cottonseed meal** in Canada for stock food are increasing. (P. 1141.)

The **kelp industry** of British Columbia is to be placed under government supervision. (P. 1152.)

The embargo on **graphite** from Ceylon to the United States has been removed. (P. 1153.)

RECENT DEMANDS FOR AMERICAN GOODS

SPAIN—821
Coal

ALGERIA, CANADA, CHINA, and IRELAND—838-43
Window glass
Plate glass
Mirrors
Cut glass

INDIA—850, 862
Glass
Matches

SIBERIA—893
Matches
Paints
Tanning materials

ENGLAND—901, 908
Hardware
Steel billets
Brass
Gold plate
Bronze
Glass

CANADA—990
Cottonseed meal

SOUTH AMERICA—1055
Soap

COLUMBIA—1099
Drugs
Caustic soda
Sodium silicate

IRELAND—1266
Gypsum
Metal lath
Plaster board

The mineral industries of Brazil include **iron, manganese, coal, copper, diamonds, and semiprecious stones.** (P. 1163.)

The **fiber** of the water hyacinth in French Indo-China has been used in the manufacture of rope, twine, matting, as a substitute for rattan, and as a fuel. (P. 1182.)

The condition of the **rubber industry** in England is discussed. (P. 1190.)

An embargo has been placed on **tin** from the Straits Settlements to other than British ports. (P. 1201.)

Imports of **potash salts** except carbonate and cyanide into the United States show a marked falling off. (P. 1202.)

Indications of **oil** in Chile are promising. (P. 1239.)

Efforts are being made to cultivate the Japanese **camphor** tree ("cinnamonium camphora") in the Malay States. (P. 1243.)

New fuels being used for German automobiles include mixtures of **gasoline, benzene, and alcohol;** 25,000 automobiles have been ordered to cease operating. (P. 1271.)

STATISTICS AND OTHER INFORMATION REGARDING EXPORTS TO THE U. S.

WINNIPEG—Sup. 23*a*
Fertilizer
Glycerine
Flaxseed
Hides
Paper
Paper pulp
Pulp wood
Seneca root
Sulfur ore

NICARAGUA—Sup. 34*a*
Dyewoods
Gold
Hides
Rubber
Silver
Sugar

ARGENTINE—Sup. 38*a*
Hides
Linseed
Quebracho
Sugar
Tallow
Copper
Fertilizer
Bones

SHEFFIELD—Sup. 19*a*
Pipe clay
Chemicals
Cutlery
Electroplate (silver, etc.)
Glass
Glue
Grindstones
Platinum
Steel

BRAZIL—968, 1156
Ipecacuanha
Hides

OTTAWA—Sup. 23*b*
Gold
Hides
Mica
Paper
Pulp wood
Wood pulp
Corundum

BRITISH COLUMBIA—Supplement 23*c*
Brewers' grits
Bullion
Explosives
Fertilizer
Glycerine
Hides
Copper
Gold
Tin
Silver
Coal
Whale oil

CARDIFF—Sup. 19*a*
Glue
Cardboard
Paper
Steel plates

HUDDERSFIELD, ENGLAND—Sup. 19*b*
Chemicals
Copper
Dyes
Explosives
Iron and steel
Hides
Soluble starch

DUBLIN—Sup. 19*d*
Hides
Liquors

NOTTINGHAM, ENGLAND—Sup. 19*c*
Artificial silk
Cement
Glue
Leather
Hides
Sod oil
Stoneware
Oxide of iron
Rotten stone
Umber

SWEDEN—Sup. 16*a*
Ammunition
Hides
Iron and steel
Ferro-manganese
Ferro-silicon
Matches
Paper
Caustic soda and potash
Wood pulp
Cocoa butter
Enameled ware
Milk powder
Pine tar

BOLIVIA—1252
Hides
Peruvian bark
Rubber

DENMARK—Sup. 4*a*
Casein
Cinematograph films
Flint pebbles
Glycerine
Hides
Safety matches
Rennet
Soya bean oil

The **tin industry** of the Malay States has fallen off greatly. (P. 1290.)

**Special supplements** issued in March include the following:

CANADA
Prairie Provinces—23*a*
Ottawa—23*b*
British Columbia—23*c*
Nicaragua—34*a*
Malaysia—56*b*
Sweden—16*a*
Denmark—4*a*

UNITED KINGDOM
Huddersfield—19*b*
Nottingham—19*c*
Ireland—19*d*
Cardiff and Sheffield—19*a*
Turkey—Harput—18*a*
Argentina—38*a*

## BUREAU OF STANDARDS

**Electric Wire and Cable Terminology.** ANONYMOUS. Circular 37, 2nd edition. 13 pp. A revision with minor changes.

**Temperature Coefficient of Magnetic Permeability within the Working Range.** RAYMOND L. SANFORD. Scientific Paper 245. 10 pp. It is shown that errors of large magnitude may be introduced by neglecting the temperature coefficient of magnetic permeability.

## GENERAL SUPPLY COMMITTEE

**Specifications and Proposals for Supplies for Executive Departments and Other Government Establishments for the Fiscal Year 1916.** These specifications and forms for proposals to supply materials are of interest in some cases to the chemical industry. The various classes which contain items of chemical interest are as follows: Class 1, stationary and drafting supplies. Class 2, hardware, metals, leather and saddlery. Class 5, laboratory apparatus, hospital appliances and surgical instruments. Class 6, electrical, engineering, and plumbing supplies. Class 8, brushes, glass, lubricants, painters' supplies, and paints. Class 9, furniture and floor coverings. Class 12, photographic supplies, meteorological instruments, etc. Class 13, engraving, printing, and lithographic supplies.

These specifications can be secured on application to the General Supply Committee by those interested in offering bids. Some of the contracts have already been closed and others are still open. Full information can be had from the General Supply Committee, Washington, D. C.

## TREASURY DEPARTMENT

**Lubricant-Standard Specifications.** Department Circular 42. 1 p. This circular calls attention to the regulations regarding sampling of all deliveries of lubricants. Each delivery whether accepted or not must be sampled and the sample forwarded to the Bureau of Standards for test, with a statement of use for which the oil was intended and whether or not it was satisfactory with statements as to the cause of rejection if delivery is not accepted. Persons contemplating delivery of lubricants to any Federal official should take account of this regulation.

## PUBLIC HEALTH SERVICE

**Efforts to Curb the Misuse of Narcotic Drugs.** MARTIN I. WILBERT. Public Health Reports, **30,** 893–924. This is a comparative analysis of the Federal and State laws designed to restrict or to regulate the distribution and use of opium, coca, and other narcotic or habit-forming drugs. There is included a detailed review of each of the laws now in force. The part of particular interest to chemical dealers is the summary of the drugs which are included under the provisions of each of these regulations. In this connection see also an article entitled:

**"Harrison Anti-Narcotic Law—The Effect of Its Enforcement on the Drug Addict."** MURRAY GALT MOTTER. Public Health Reports, **30,** 979–81.

**Foot and Mouth Disease.** ANONYMOUS. Public Health Reports, **30,** 892–93. A brief discussion of the relation of this disease to public health with particular emphasis of the possibilities of the conveyance of the disease in milk and a discussion of the efficiency of pasteurization for preventing the transmission.

**Quinine To Be Sold at Cost in Venezuela.** ANONYMOUS. Public Health Reports, **30,** 981. A note to the effect that the Venezuelan government is contemplating distribution and sale of quinine at cost in order to extend the use of this drug and to ensure a good quality.

## DEPARTMENT OF AGRICULTURE

**Net Energy Values of Feeding Stuffs for Cattle.** HENRY PRENTISS ARMSBY AND J. AUGUST FRIES. Journal of Agricultural Research, **3,** 435–92. This is an extended summary of the result of 76 experiments with the respiration calorimeter upon 9 steers in which the balance of matter and of energy was determined.

**Commercial Fertilizers, Their Composition and Use.** EDWARD B. VOORHEES. Farmers' Bulletin 44. A new edition reprinted without changes. Paper, 5 cents.

**The Eastern Hemlock.** E. H. FROTHINGHAM. Department Bulletin 152. 43 pp. Paper, 10 cents. This Bulletin describes the more important characteristics of the hemlock, presents tables of its volume and rate of growth and gives important facts regarding the range, commercial value, utilization, and amount of standing, with many statistics of this valuable forest product.

**Para-Dichlorobenzene as an Insect Fumigant.** A. B. DUCKETT. Department Bulletin 167, from the Bureau of Entomology. 7 pp. Paper, 5 cents. This report gives directions for the use of *p*-dichlorobenzene both as an insecticide and as a fumigant with a discussion of costs.

**Injury by Disinfectants to Seeds and Roots in Sandy Soils.** CARL HARTLEY. Department Bulletin 169, from the Bureau of Plant Industry. 35 pp. Paper, 5 cents. This is a report on preliminary tests of disinfectants in controlling damping-off in various nursery soils.

**The Production and Consumption of Dairy Products.** EUGENE MERRITT. Department Bulletin 177, from the Bureau of Crop Estimates. 19 pp. Paper, 5 cents. This bulletin outlines the changes in geographic distribution of the dairy industry and gives information concerning the consumption of dairy products on farms and in cities. It includes a statistical review of the subject, with comments on the influencing factors. It is of interest to those engaged in any phase of dairying or the distribution of dairy products.

**Agricultural Alcohol: Studies of Its Manufacture in Germany.** EDWARD KREMERS. Department Bulletin 182, from the Bureau of Plant Industry. 35 pp. Paper, 5 cents. This report discusses the problems of manufacture, the economic situation.

capacity, taxes, marketing sources, etc., with statistics. The report brings out the fact that "the success of agricultural alcohol in Germany is the result of long-continued experiments, backed by a determination on the part of those high in authority that the project should succeed."

**Ammonification and Nitrification in Hawaiian Soils.** W. P. KELLEY. Bulletin 37. Hawaii Agricultural Experiment Station. 52 pp. Paper, 10 cents.

GEOLOGICAL SURVEY

**The Inorganic Constituents of Echinoderms.** F. W. CLARKE AND W. C. WHEELER. Professional Paper 90–L. 9 pp.

**Springs of California.** G. A. WARING. Water Supply Paper 338. 410 pp. "As a basis for the discussion of springs and spring waters of California this paper opens with a brief outline of the physical features of the State, together with a few notes on the character of the rocks and their structure, then proceeds to explain the usual or possible composition and properties of most natural waters as well as the source of their constituent substances, and concludes with discussions of the springs of California classified under the following groups: hot, carbonated, sulfur, saline, magnesic, iron, artesian, large cold, and minor perennial springs. Accompanying the discussions of many of the springs are analyses of their waters, and at the end of the book are two tables, one of which gives an alphabetic list, by counties, of the best-known springs of the State, with name of owner, location, temperature, and yield, and the other a list of California spring resorts."

**Underground Waters of the Coastal Plain of Georgia.** L. W. STEPHENSON AND J. O. VEATH, with a Discussion of the Quality of the Waters, by R. B. DOLE. Water Supply Paper 341. 539 pp. "Gives the results of investigations made to determine the composition, structure, and stratigraphic relations of the formations of the Coastal Plain of Georgia and the geologic position, quality, quantity, and economic adaptability of the waters they contain." It is concluded that "all the underground waters of this province may be used advantageously for domestic and industrial purposes, although those from the later formations may require a little softening. The surface waters of this section are even better for industrial use than the ground waters, because they are lower in mineral content."

NAVY DEPARTMENT

**Description of Navy Standard Boiler Water-Testing Outfit and Instructions for Use.** Revised edition. 12 pp. A brief and simple description of methods and apparatus for alkalinity test and chlorine test of boiler water is given.

BUREAU OF MINES

**Probable Effect of the War in Europe on the Ceramic Industries of the United States.** A. S. WATTS. Technical Paper 99. 15 pp. Paper, 5 cents. This report discusses the sources of china clay, ball clay, cornwall stone, chert pebbles for grinding, and indicates the probable effect of the war on the mining and transportation of these supplies. The white-clay resources of the United States are also discussed with suggestions as to the possibility of substituting domestic product for those formerly imported. The value of imports and extent of domestic trade are indicated.

WAR DEPARTMENT

**Report on Fuel Tests and Issue of Fuel, 1914.** FRANK T. HINES AND OTHERS. War Department Document 473. 145 pp. and 18 maps. Cloth, $1.00. This report is principally of interest in connection with the question of utilization of fuel for heating of residences, apartment buildings and other buildings of similar heat requirements. There is included a set of maps giving zones of equal temperature over the United States for the various months of the year and averages for different seasons and a map showing the mean annual temperature in different parts of the Philippine Islands.

# BOOK REVIEWS

**Chemistry of Cyanogen Compounds.** By HERBERT E. WILLIAMS. Published by P. Blakiston's Son & Co., Philadelphia, Pa. No illustrations. 423 pp. Price, $3.50 net.

In the 27 chapters which make up the body of this work the author has compiled practically all the information available on the chemistry of cyanogen compounds, and has used unusual judgment in his abstracting, evidently having checked most of his information personally; there is little inserted in the book that is not of value, and much has been left out that is found in the usual dictionary or similar compilation that should never have appeared in print in permanent form because of inaccuracy.

The chapters on Simple Cyanides and the Iron Cyanogen Compounds forming Part I are particularly interesting because these seem to be the special field in which the author did most of his laboratory work, and we have, therefore, a catalogue here of these compounds, more complete than anything heretofore published, and as far as the reviewer can check the same, very much more authoritative. The book is worth its purchase price alone for this extremely valuable listing and description of the general properties of the cyanogen compounds.

There have been a number of treatises which have recently appeared on the manufacture and application of cyanogen compounds, and the 100 pages of Mr. Williams' book devoted to this portion do not balance up well with some of the very recent publications nor with the rest of his own book; he has not exercised the same care in choosing his processes of manufacture that he has in cataloguing the properties of his compounds. While the information given in Part II on Manufacture is carefully chosen from the standpoint of accuracy, it does not always present the most modern and standard practice.

In Part III of the work, covering the detection and estimation of cyanogen compounds, the methods of determination have again been very carefully chosen and compare in this respect with the catalogue of compounds in Part I. Many of the methods here described are in use in the reviewer's laboratory and are giving excellent results.

The arrangement of the work is excellent, and leads to very ready reference to the subject matter contained. Such quick reference is particularly assisted by the extremely liberal use of heavy font type for designating the various compounds discussed, and the chapter headings and special divisions stand out most prominently in this heavy type.

The literary style is excellent, and the author is to be complimented upon the clearness with which he has presented certain of the complicated chemistry of this field.

One of the most valuable features of the book is the care which has been taken to reproduce reference to the original sources of the information, a task which has too often been shirked in cases of preparing a mere catalogue of chemical compounds.

On the whole, the work certainly demands a place in every working library concerned with cyanogen compounds, for it is so complete in itself that it will largely supplant reference to the unwieldy periodicals, and is far superior, from the purely chemical standpoint, to anything which has heretofore appeared on cyanogen compounds, but it must not be misunderstood as replacing several of these recent works which concern themselves solely with the industrial phase.

W. S. LANDIS

**The Iron Ores of Lake Superior.** Second Edition by CROWELL & MURRAY, Chemists and Metallurgists, Cleveland, Ohio. Pp. 258 + v. The Penton Publishing Co., Publishers, Cleveland, O. Price, $3.50.

The authors, in the second edition, have corrected and redrawn the maps, rewritten much of the general matter, secured the latest descriptions of the mines on the different ranges and added data concerning their locations.

The book contains facts of interest relating to the mining and shipping of iron ores and is a very useful reference volume.

WILLIAM BRADY

**Dyestuffs: Lehrbuch der Farbenchemie.** By DR. HANS TH. BUCHERER, Direktor der Chemischen Fabrik auf Actien in Berlin. Published by Otto Spamer, Leipzig, 1914. 557 pp. Price, 22 Marks.

This book is a greatly enlarged edition of Dr. Bucherer's smaller handbook on the same subject which appeared several years ago. The subject matter is divided in the general method of all such books, into three parts: the first dealing with the raw materials including a good deal of matter relating to distillation of various kinds of tars, the second relating to the intermediate products derived from the previous raw materials, and the third dealing with the synthetic methods for the preparation of various classes of dyestuffs. The chemistry relating to methods of preparation of the intermediate products in this book is given in a very complete manner and takes up over 160 pp. The subject is dealt with, however, in a rather general manner and the manufacturer or works chemist would refer to this volume in vain for definite methods of manufacturing specific products. The same is also true of the third and main section relating to the dyestuffs themselves. The matters are gone into with the usual German thoroughness regarding theoretical considerations and relations, such, for instance, as the relation between color and constitution, to which subject alone thirty-three pages are devoted. There is, however, a distinct lack of definiteness in describing the methods for the preparation of the dyestuffs, and very little concerning factory practice is given. Indeed, this side of the subject, which is really the most valuable from the practical point of view, is entirely neglected. In fact, this book of Bucherer's is rather an extensive discussion of the general chemistry of dyestuffs and the methods of sulfonation, nitration, halogenation, etc. In this sense it cannot but be of considerable help to any chemist interested in the manufacture of dyes as the matter is put before the reader in a rather concise and simple manner and the author even goes so far as to give the synthetic methods, by various simplified diagrams, of how one product is derived from another. Also a very large number of structural formulas are given including the more important dyestuffs and the reactions which are usually given in terms of their structural formulas throughout, so that the reader can easily follow the synthesis of the product in question. This helps a great deal in the understanding of these complicated organic reactions as the reader is enabled to more or less visualize the bodies entering into the reaction and can thus follow more intelligently the up-building of the synthetic product than if the formulas of the different substances were merely given in their empiric form.

On the whole, this book is rather complete in its presentation of the subject if we consider that subject limited to the pure chemistry of the dyestuffs, and this, of course, limits the usefulness of the book to the technical chemist. It is a book primarily to be employed as a text-book for the student rather than as a technical handbook for the works chemist. It also requires that the reader should be well drilled in rather advanced organic chemistry; but in the hands of such a student it will have a distinct value in developing his knowledge of this special field.

J. MERRITT MATTHEWS

# NEW PUBLICATIONS

By JOHN F. NORTON, Massachusetts Institute of Technology, Boston

**Agriculture: The Chemistry of Agriculture: for Students and Farmers.** By C. W. STODDART. 8vo. 364 pp. Price, $2.00. Lea and F., Philadelphia.

**Bio-chemistry: Chimie Biologique médicale.** By J. VILE AND E. DERRIEN. 8vo. 400 pp. Price, $1.25. Paris.

**Blowpipe Analysis: Lötrohrprobierkunde, Anleitung zur qualitativen u. quantitativen Untersuchung mit Hilfe des Lötrohres.** By H. KRUG. 8vo. 88 pp. Price, $1.00. Berlin.

**Chemistry: A Manual of Chemistry, Theoretical and Practical, Inorganic and Organic.** By A. P. LUFF AND H. C. H. CANDY. 2nd Ed. 12mo. 680 pp. Price, $2.25. Cassell, London.

**Distilling: Brennerei Lexikon, Herausgegeben unter Mitwirkung von W. Behrend, E. Duntze, F. Kohrmann, u. a.** By M. DELBRÜCK. 8vo. 787 pp. Price, $7.00. Berlin.

**Food: Das Lebensmittelgewerbe, Handbuch für Nahrungsmittelchemiker u. s. w. Band I.** By K. v. BUCHKA. 8vo. 906 pp. Price, $9.50. Leipzig.

**Food: Food Industries: an Elementary Text-book on the Production and Manufacture of Staple Foods.** By H. T. VULTE AND S. B. VANDERBILT. 8vo. 309 pp. Price, $1.75. Chemical Publishing Co., Easton, Pa.

**Food: Nahrungsmittelchemie, mit besonderer Berücksichtigung der modernen physikalisch-chemischen Lehren.** By T. PAUL. 8vo. 77 pp. Price, $1.00. Leipzig.

**General Chemistry: Jahrbuch der Chemie. Bericht über die wichtigsten Fortschritte der reinen und angewandte Chemie.** By R. MEYER. Ed. Jahrgang 28. 8vo. 642 pp. Price, $5.00. Braunschweig.

**Iron: The Cementation of Iron and Steel.** Translated from the Italian by J. W. Richards and C. A. Rouiller. By F. GIOLOTTI. 8vo 407 pp. Price, $4.00. McGraw-Hill Book Co., New York.

**Irrigation: Practical Irrigation and Pumping.** By BURTON P. FLEMING. 8vo. 226 pp. Price, $2.00. John Wiley & Sons, New York.

**Masonry: A Short Text-book on Masonry Construction, Including Descriptions of the Materials Used, Etc.** By M. A. HOWE. 8vo. 160 pp. Price, $1.50. John Wiley & Sons, New York.

**Microscopy: Praktikum der klinischen chemisch-mikroskopischen und bakteriologischen Untersuchungsmethoden.** By M. KLOPSTOCK AND A. KOWARSEY. 3rd Ed. 8vo. Price, $2.00. Wien.

**Minerals: Die Lagerstätten der nutzbaren Mineralien und Gesteine, nach Form, Inhalt und Entstehung dargestellt. Bd. I.** By F. BEYSCHLAG, P. KRUSCH, U. J. H. L. VOGT. 2nd Ed. 8vo. 578 pp. Price, $4.50. Stuttgart.

**Minerals: Die nutzbaren Mineralien, mit Ausnahme der Erze, Kaliumsalze, Kohlen u. des Petroleums. Bd. II.** By B. DAMMER AND O. TIETZE. 8vo. 539 pp. Price, $4.00. Stuttgart.

**Paints: A Manual of Oils, Resins and Paints. Vol. I.** By H. INGLE. 8vo. 138 pp. Price, $1.00. C. Griffin, London.

**Poisons: Inorganic Plant Poisons and Stimulants.** By W. E. BRENCHLEY. 8vo. 110 pp. Price, $1.25. Cambridge University Press, London.

**Radioactivity: Acquired Radioactivity.** By SIR WILLIAM CROOKES. 4to. 14 pp. Price, $0.50. Dulau, London.

**Sanitation: Practical Tropical Sanitation: a Manual for Sanitary Inspectors and Others.** By W. ALEX. MUIRHEAD. 8vo. 288 pp Price, $3.50. E. P. Dutton, New York.

**Sewage: Sewage Purification and Disposal.** By G. B. KERSHAW. 8vo. 350 pp Price, $3.00 Cambridge University Press, London.

**Steel: Steel and Its Treatment.** By E. F. HOUGHTON AND OTHERS. 2nd Ed. 12mo. 104 pp. Price, $1.00. E. F. Houghton & Co., Philadelphia.

**Varnish: Die Fabrikation der Lacke, Firnisse usw.** By E. ANDRES. 6th Ed. 8vo. 270 pp. Price, $1.00. Wien.

**Ventilation: Heating and Ventilating Buildings.** By R. C. CARPENTER. 6th Ed. 12mo. 598 pp. Price, $3.50. John Wiley & Sons, New York.

**Wastes: Utilization of Waste Products,** Translated from the German. By T. KOLLER. 2nd Ed 8vo 340 pp. Price, $2.00. London.

**Water Supply: Country Plumbing Practice: Design, Installation and Repair of Systems of Water Supply and Sewage Disposal.** By W. HUTTON. 8vo. 310 pp. Price, $2.00. D. Williams Co., New York.

## RECENT JOURNAL ARTICLES

**Absorption: Fur l'absorption des gaz par le charbon aux basses températures.** By G. Glaude. *Bulletin de la Société Chimique de France.*

**Cellulose: Recent Progress in the Analysis of Cellulose and Cellulose Derivatives.** By J. F. Briggs. *The Analyst,* Vol. 40, 1915, No. 468, pp. 107–20.

**Concrete: Basis of Current Practice in Concrete Design.** By C. A. P. Turner. *The Cement Era,* Vol. 13, 1915, No. 4, pp. 50–1.

**Copper: Hydrometallurgical Treatment of Michigan Copper Tailings.** By R. D. Leisk. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 4, pp. 233–4.

**Cyanide: Copper Cyanide Plating Solutions.** By M. C. Weber. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 4, pp. 255–6.

**Electrolysis: Electrolysis and Its Mitigation.** By E. B. Rosa. *Journal of the New England Water Works Association.* Vol. 29, 1915, No. 1, pp. 49–72.

**Gas: Burning Blast Furnace Gas.** Anonymous. *The Iron Age,* Vol. 95, 1915, No. 11, pp. 612–3.

**Ice: The Economical Ice Plant of Today.** By Thomas Shipley. *Ice and Refrigeration,* Vol. 48, 1915, No. 4, pp. 204–9.

**Ice: Suggestions for the Improvement of Refrigerating and Ice-Making Plants.** By Robert P. Kehoe. *Refrigerating World,* Vol. 49, 1915, No. 2, pp. 27–9.

**Inorganic Chemistry: Experimentelle anorganische Chemie und Elektrochemie im Jahre 1914.** By A. Gutbier. *Zeitschrift fur angewandte Chemie,* Vol. 28, 1915, No. 20, pp. 93–111.

**Lighting: Street Lighting Practice with Incandescent Lamps.** By G. H. Stickney. *Municipal Engineering,* Vol. 48, 1915, No. 2, pp. 80–8.

**Minerals: General Principles Governing the Complete Analysis of Minerals and Ores.** By W. R. Schoeller. *The Analyst,* Vol. 40, 1915, No. 468, pp. 90–106.

**Nitrogen: The Fixation of Atmospheric Nitrogen.** By W. S. Landis. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 4, pp. 213–20.

**Organic Compounds: The Electrochemical Production of Organic Compounds.** Anonymous. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 4, pp. 211–13.

**Ozone: The Use of Ozone as a Sterilizing Agent for Water Purification.** By S T. Powell. *Journal of the New England Water Works Association,* Vol. 29, 1915, No. 1, pp. 87–93.

**Paving Material: Misuse of a Good Paving Material Is Detrimental to Florida Road Development.** By Charles E. Foote. *Engineering Record,* Vol. 71, 1915, No. 15, pp. 452–3.

**Roads: Frost Action on Roads.** By Andrew M. Lovis. *The Cement Era,* Vol. 13, 1915, No. 3, pp. 49–50.

**Refractories: Refractories of the Rocky Mountain Region and Some of Their Products.** By J. C. Bailar. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 4, pp. 257–8.

**Sanitation: The Federal Meat Inspection Service and Sanitation of Packing Houses under Its Supervision.** By George H. Shaw. *American Journal of Public Health,* Vol. 5, 1915, No. 3, pp. 236–45.

**Sewage: Sewage Aeration at Lawrence and Manchester Compared.** By H. W. Clark. *Engineering Record,* Vol. 71, 1915, No. 12, pp. 367–8.

**Sewage: The West End Sewage Treatment Works, Hamilton, Ont.** By Bernard E. T. Ellis *Engineering News,* Vol 73, 1915, No. 9, pp. 424–8.

**Steel: Acid Open-Hearth Steel for Castings.** By Edwin F. Cone. *The Iron Age,* Vol. 95, 1915, No. 10, pp. 551–3.

**Steel: "Areagrams" of Open-Hearth Furnace Flues.** By A. R. Mitchell. *The Iron Age,* Vol. 95, 1915, No. 11, pp. 607–8.

**Steel: Heat Energy from the Bessemer Process.** By G. Butz. *The Iron Age,* Vol. 95, 1915, No. 11, pp. 618–9.

**Steel: Hysteresis Loss in Medium-Carbon Steel.** By F. C. Langenberg and R G. Webber. *The Iron Age,* Vol. 95, 1915, No. 9, pp 506–8.

**Sulfates: The Formation and Decomposition of Sulfates during Roasting.** By Boyd Dudley, Jr. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 4, pp. 221–6.

**Sulfuric Acid: Neuerungenbetreffend Bleikammern, Turmsysteme und andere Vorrichtungen zur Herstellung von Schwefelsäure.** By Oskar Kausch. *Chemische Apparatur,* Vol. 2, 1915, No. 4, pp. 53–5.

**Turbines: Turbine Efficiency Test by Chemical Methods.** Anonymous. *Engineering Record,* Vol. 71, 1915, No. 12, pp. 358–60.

**Valence: A Criticism of the Electron Conception of Valence.** By Roger F. Brunel. *Journal of the American Chemical Society,* Vol. 37, 1915, No. 4, pp. 709–22.

**Water: Philadelphia Water-Filter Operations in 1914.** Anonymous. *Engineering News,* Vol. 73, 1915, No. 12, pp. 576–7.

**Wood: Die Imprägnierung des Holzes nach dem Verfahren des Dr. Boucherie.** By Friedrich Moll. *Chemische Apparatur,* Vol. 2, 1915, No. 4, pp. 49–53.

**Zinc: Die Bestimmung des Zinks als Zinkammoniumphosphat und ihre Anwendung bei Trennungen.** By P. Artmann *Zeitschrift für analytische Chemie,* Vol. 54, 1915, No. 2, pp. 89–102.

**Zinc: Leaching a Zinc-Lime Ore with Acids.** By O. C. Ralston and A. E. Gartside. *Metallurgical and Chemical Engineering,* Vol. 13, 1915, No. 3, pp. 151–5.

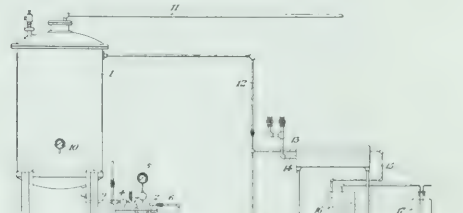
# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. Parker

Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Manufacturing Mixed Hydrogen and Nitrogen. G. P. Scholl, Jan. 5, 1915. U. S. Pat. 1,123,394.** A mixture of nitrogen and hydrogen having definite proportions is produced by vaporizing ammonia, holding it under a given pressure, which



may be from 20 to 30 lbs. per sq. in., mixing with air and dissociating the ammonia at a predetermined pressure, which may be 10 lbs. per sq. in., by passing the mixed gases over copper turnings heated to approximately 720° C.

**Preventing Accumulation of Moisture of Condensation upon Glass or Other Protected Surfaces. H. M. Pickering, Jan. 5, 1915. U. S. Pat. 1,123,367.** The composition consists of 20 parts of glycerin, 2 parts of oil of turpentine, and 1 part of oil of eucalyptus.

**Fixing Atmospheric Nitrogen. S. Peacock, Jan. 5, 1915. U. S. Pat. 1,123,584.** A compound of sulfur, carbon and nitrogen is produced by bringing a mixture containing nitrogen and an oxid of sulfur into contact with carbon at a temperature of 800° C.

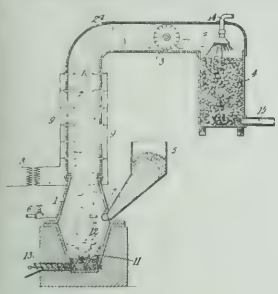
**Precipitant for Recovering Metals from Solutions. G. H. Clevenger, Jan. 5, 1915. U. S. Pat. 1,123,685.** The precipitant consists of a powder made from a brittle alloy composed of zinc and not more than 3 per cent sodium, the sodium being added to impart brittleness to the alloy.

**Marine Protective Coating. D. F. Comstock, Jan. 5, 1915. U. S. Pat. 1,123,687.** The composition consists of a water-resisting copper paint and a small amount of a radioactive substance, preferably pulverulent carnotite.

**Pigments. C. D. Holley, Jan. 5, 1915. U. S. Pat. 1,123,743.** Metallic lead is moistened with water containing a relatively small amount of nitric acid and the mass is allowed to undergo progressive spontaneous oxidation in the presence of air to form oxids of lead.

**Alkali-Metal Compounds. H E. Brown, Jan. 5, 1915. U. S. Pat. 1,123,841.** Potash is obtained from feldspar by fusing, in a non-reducing atmosphere, a mixture of feldspar with a sufficient quantity of potassium chloride to furnish combinable chlorine for all the potassium and a sufficient quantity of calcium carbonate to bring the calcium oxide content of the resulting fused material up to between 40 and 55 per cent.

**Alkali-Silico-Aluminate. A. H. Cowles, Jan. 5, 1915. U. S. Pat. 1,123,693.** Alkali-silico-aluminate and hydrochloric acid are produced by subjecting clay to the action of vapors of salt and water at a high temperature. A mixture of the salt and clay is fed into the furnace from the hopper 5, steam being introduced through the pipe 6. The suction of a fan, 3, draws the whirling charge up into the dust chamber 2 where it is electrified by the passage of electricity between the highly charged points 10, whereby, according to the process set forth by Cottrell and others, the dust particles attract each other into small masses and fall back into the furnace, the hydrochloric acid passing over into the acid-condensing systems where it is condensed.



## BRITISH PATENTS

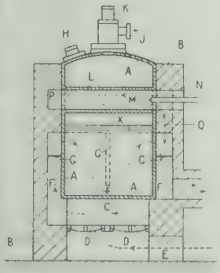
By D. Geddes Anderson
Chemical Engineer and Patent Chemist, Glasgow, Scotland

The following abstracts are taken from the latest published British specifications. The date at the end of the abstract is the date of acceptance.

**Process for Converting Unsaturated Fatty Acids into Saturated Compounds. W. J. Mellersch-Jackson, Sept. 23, 1913. Brit. Pat. 21,477.** A basic heavy metal salt of a fatty acid of high molecular weight is dissolved in, or intimately mixed with, the substance to be treated, and the material hydrogenated between 100 and 180° C. Basic oleates of nickel and copper are mentioned.—Feb. 2, 1915.

**Improvements in the Manufacture of Tungsten. C. Gladitz, Oct. 23, 1913. Brit. Pat. 24,028.** This invention relates to a new form of spool on which cold drawn tungsten wire is received, previous to undergoing heat treatment. By means of an auxiliary rotable pin the periphery of the spool is increased for the winding operation and decreased for the heat treatment. In this way any tension in the wire, caused by the differences in coefficients of expansion of the metal of the spool, and of the wire, during the heat treatment, is eliminated.—Feb. 4, 1915.

**Submarine Varnishes. G. Paterno and C. Mannelli. Dec. 22, 1913. Brit. Pat. 29,524.** Fluorides or fluosilicates of aluminum, zinc, or lead are used as ingredients in antifouling compositions.—Feb. 18, 1915.



**Apparatus for Distilling Liquids. Crossley, Wheeler and Smith, Jan. 10, 1914. Brit. Pat. 707.** A new type of apparatus for distilling liquids such as oil or tar, which are liable to froth. A superheater, L, passes through the center of the still, and is heated by means of the burner M. The superheater breaks up the froth and in addition is stated to increase the yield of distillate.—Feb. 10, 1915.

**Preparation of Vegetable Textile Fibers for Bleaching. Jardine and Nelson, Jan. 12, 1914. Brit. Pat. 802.** The process consists in treating the fibrous material in a digester with a solution of a magnesium or sodium bisulfite. The gases liberated in the course of the cooking are continuously removed.—Feb. 12, 1915.

**Coagulation of Rubber Latex. N. W. Barritt and A. Street, Feb. 12, 1914. Brit. Pat. 3,632.** Rubber latex is subjected to partial evaporation under reduced pressure, and exposed to the action of hot, dry vapors of acetic acid and formalin. The exposure is effected on a revolving drum.—Feb. 12, 1915.

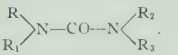
**Accelerating the Vulcanization of Caoutchouc. S. J. Peachey, Feb. 19, 1914. Brit. Pat. 4,263.** A small quantity of para-nitrosodimethylaniline, or of one of its homologues is added before vulcanization. It is stated that the isomeric nitrosamines produce no acceleration.—Feb. 18, 1915.

**Nitrogen Compounds from Pulverized Carbides. T. Fujiyama, April 14, 1914. Brit. Pat. 9,259.** Process does away with the application of external heat. A small quantity of pulverized carbide is ignited in an unheated chamber in presence of air. When the temperature has risen sufficiently nitrogen is introduced, and fresh carbide fed in, in such a manner that a heat insulating layer of the carbide is formed over the carbide undergoing reaction.—Feb. 11, 1915.

**Treatment of Iron or Steel for the Prevention of Rust. Rudge-Whitworth, Ltd. and H. L. Heathcote, April 22, 1914. Brit. Pat. 9,926.** Relates to iron and steel articles already coated with rust-resisting phosphates of iron. The phosphate coating is treated with linseed oil and stoved, or with celluloid varnish and subsequent stoving.—Feb. 18, 1915.

**Rubber Composition for Outer Covers of Pneumatic Tires. C. Pacchetti, June 6, 1914. Brit. Pat. 13,779.** Rubber when in a plastic state is mixed with lengths of horse hair or hog's hair and the mixture subsequently vulcanized. Said to give non-skid properties.—Feb. 18, 1915.

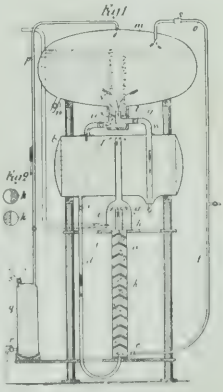
**New Substituted Ureas. Fabriques De Produits De Chimie Organique De Laire, July 23, 1914. Brit. Pat. 17,501.** Relates to tetra-substituted ureas of the general form



$R$ and $R_2$ represent alkyl radicles; $R_1$ and $R_3$, aryl radicles.

The chloride of an aryl-alkyl urea is first formed and then caused to react with an aromatic base having different radicles from those of the aryl-alkyl urea.

They are viscous liquids or solids of low melting point, and claim is made for their use in stabilizing nitro-derivatives of organic compounds.—Feb. 11, 1915.



**Impregnating Liquids with Carbonic Acid or Other Gases. A. A. Pindstofte, Sept. 14, 1914. Brit. Pat. 19,769.** The gas and liquid passing through the pipes *f* and *d*, respectively, are forced up the impregnating chamber *a*. The gas-charged liquid flows through the pipe *i* to the bottling chamber, and the superfluous carbonic acid and expelled air flow through *j* into the liquid reservoir *b* and fill the space caused by the displaced liquid: *m* is a supply reservoir connected with an air-discharge controller, *q*. The partitions of the impregnating chamber are perforated and are shown in plan in Fig. 2.— Feb. 11, 1915.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF APRIL, 1915

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid | Lb. | 1.25 | @ | 1.40 |
| Acetic Acid (28 per cent) | C. | 2.00 | @ | 2.25 |
| Acetone (drums) | Lb. | 21 | @ | 25 |
| Alcohol, denatured (180 proof) | Gal. | 33 | @ | 35 |
| Alcohol, grain (188 proof) | Gal. | 2.50 | @ | 2.54 |
| Alcohol, wood (95 per cent) | Gal. | 45 | @ | 47 |
| Amyl Acetate | Gal. | 2.70 | @ | |
| Aniline Oil | Lb. | 1.00 | @ | 1.10 |
| Benzoic Acid | Lb. | — | @ | — |
| Benzol (90 per cent) | Gal. | 1.20 | @ | 1.40 |
| Camphor (refined in bulk) | Lb. | 41½ | @ | — |
| Carbolic Acid (drums) | Lb. | 1.10 | @ | 1.15 |
| Carbon Bisulfide | Lb. | 6½ | @ | 7½ |
| Carbon Tetrachloride (drums) | Lb. | 16 | @ | 17 |
| Chloroform | Lb. | 30 | @ | 35 |
| Citric Acid (domestic), crystals | Lb. | 55 | @ | 57 |
| Dextrine (corn) (carloads, bags) | C. | 3.00 | @ | — |
| Dextrine (imported potato) | Lb. | — | @ | — |
| Ether (U. S. P., 1900) | Lb. | 15 | @ | 20 |
| Formaldehyde | Lb. | 8½ | @ | 9½ |
| Glycerine (dynamite) | Lb. | 18½ | @ | 20 |
| Oxalic Acid | Lb. | 19 | @ | 20 |
| Pyrogallic Acid (bulk) | Lb. | 1.40 | @ | 1.50 |
| Salicylic Acid | Lb. | 1.40 | @ | 1.50 |
| Starch (cassava) | Lb. | 3¼ | @ | 4 |
| Starch (corn) (carloads, bags) | C. | 2.25 | @ | — |
| Starch (potato) | Lb. | — | @ | — |
| Starch (rice) | Lb. | — | @ | — |
| Starch (sago) | Lb. | 3¾ | @ | 4 |
| Starch (wheat) | Lb. | 7 | @ | 7½ |
| Tannic Acid (commercial) | Lb. | 60 | @ | 66 |
| Tartaric Acid, crystals | Lb. | 38 | @ | 39 |

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lead (brown, broken) | Lb. | 7¼ | @ | 7½ |
| Acetate of Lime (gray) | C. | 2.50 | @ | 2.55 |
| Alum (lump) | C. | 2.50 | @ | 3.00 |
| Aluminum Sulfate (high-grade) | C. | 1.50 | @ | 1.75 |
| Ammonium Carbonate, (domestic) | Lb. | 8¼ | @ | 9 |
| Ammonium Chloride, (gray) | Lb. | 5½ | @ | 6½ |
| Aqua Ammonia (drums) 16° | Lb. | 2¼ | @ | 2½ |
| Arsenic (white) | Lb. | 4 | @ | 5 |
| Barium Chloride | Ton | 60.00 | @ | 65.00 |
| Barium Nitrate | Lb. | 16 | @ | 20 |
| Barytes (prime white, foreign) | Ton | — | @ | — |
| Bleaching Powder (35 per cent) | C. | 1.40 | @ | 1.50 |
| Blue Vitriol | Lb. | 6¼ | @ | 6¾ |
| Borax, crystals (bags) | Lb. | 4¾ | @ | 5¼ |
| Boric Acid, crystals (powd.) | Lb. | 8½ | @ | 10 |
| Brimstone (crude, domestic) | Long Ton | 22.00 | @ | 22.50 |
| Bromine (bulk) | Lb. | 40 | @ | 50 |
| Calcium Chloride (lump) | Ton | 11.70 | @ | 12.00 |
| Chalk (light precipitated) | Lb. | 4½ | @ | 5½ |
| China Clay (imported) | Ton | 14.00 | @ | 18.00 |
| Feldspar | Ton | 8.00 | @ | 14.00 |
| Fuller's Earth (powdered, foreign) | C. | 80 | @ | 90 |
| Green Vitriol (bulk) | C. | 60 | @ | 70 |
| Hydrochloric Acid (18°) | C. | 1.15 | @ | 1.65 |
| Iodine (resublimed) | Lb. | 3.80 | @ | 4.25 |
| Lead Nitrate | Lb. | 8 | @ | — |
| Litharge (American) | Lb. | 5¼ | @ | 5½ |
| Lithium Carbonate | Lb. | 1.00 | @ | 1.10 |
| Magnesium Carbonate | Lb. | 4½ | @ | 4¾ |
| Magnesite "Calcined" | Ton | nominal | | |
| Nitric Acid (36°) | Lb. | 7½ | @ | 8 |
| Phosphoric Acid (sp. gr. 1.75) | Lb. | 27½ | @ | 28 |
| Phosphorus | Lb. | 35 | @ | 95 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate | Lb. | 15 | @ | 16 |
| Potassium Bromide | Lb. | 80 | @ | 81 |
| Potassium Carbonate (calcined), 80 @ 85% | C. | 14 | @ | 14½ |
| Potassium Chlorate, crystals spot | Lb. | 35 | @ | 36 |
| Potassium Cyanide (bulk), 98–99% | Lb. | 18 | @ | 25 |
| Potassium Hydroxide | Lb. | 21 | @ | 25 |
| Potassium Iodide (bulk) | Lb. | 3.15 | @ | 3.25 |
| Potassium Nitrate (crude) | Lb. | — | @ | — |
| Potassium Permanganate (bulk) | Lb. | 60 | @ | 75 |
| Quicksilver, Flask (75 lbs.) | | 65.00 | @ | — |
| Red Lead (American) | Lb. | 6 | @ | 6½ |
| Salt Cake (glass makers') | C. | 55 | @ | 65 |
| Silver Nitrate | Oz. | 32 | @ | 34 |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash (48 per cent) | C. | 67½ | @ | 72½ |
| Sodium Acetate | Lb. | 4 | @ | 4½ |
| Sodium Bicarbonate (domestic) | C. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate (English) | Lb. | 3½ | @ | 4 |
| Sodium Bichromate | Lb. | 5 | @ | 5½ |
| Sodium Carbonate (dry) | C. | 60 | @ | 80 |
| Sodium Chlorate | Lb. | 16 | @ | 18 |
| Sodium Hydroxide (60 per cent) | C. | 1.70 | @ | 1.80 |
| Sodium Hyposulfite | C. | 1.60 | @ | 1.90 |
| Sodium Nitrate (95 per cent, spot) | C. | 2.27½ | @ | — |
| Sodium Silicate (liquid) | C. | 85 | @ | 1.15 |
| Strontium Nitrate | Lb. | 17½ | @ | 18 |
| Sulfur, Flowers (sublimed) | C. | 2.20 | @ | 2.60 |
| Sulfur, Roll | C. | 1.85 | @ | 2.15 |
| Sulfuric Acid (60° B) | C. | 85 | @ | 1.00 |
| Talc (American) | Ton | 15.00 | @ | 20.00 |
| Terra Alba (American), No. 1 | C. | 75 | @ | 80 |
| Tin Bichloride (50°) | Lb. | 14¼ | @ | 14½ |
| Tin Oxide | Lb. | 55 | @ | 57 |
| White Lead (American, dry) | Lb. | 5¼ | @ | 5½ |
| Zinc Carbonate | Lb. | 8½ | @ | 9 |
| Zinc Chloride (granulated) | Lb. | 6¼ | @ | 6½ |
| Zinc Oxide (American process) | Lb. | 5⅜ | @ | 6⅜ |
| Zinc Sulfate | C. | 2.50 | @ | — |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax (pure white) | Lb. | 40 | @ | 42 |
| Black Mineral Oil, 29 gravity | Gal. | 12½ | @ | 13 |
| Castor Oil (No. 3) | Lb. | 9¾ | @ | 10¼ |
| Ceresin (yellow) | Lb. | 10 | @ | 25 |
| Corn Oil | C. | 6.26 | @ | 6.31 |
| Cottonseed Oil (crude), f. o. b. mill | C. | 5.47 | @ | 5.55 |
| Cottonseed Oil (p. s. y.) | Lb. | 6½ | @ | 6⅝ |
| Cylinder Oil (light, filtered) | Gal. | 20 | @ | 25 |
| Japan Wax | Lb. | 13 | @ | 15 |
| Lard Oil (prime winter) | Gal. | 90 | @ | 92 |
| Linseed Oil (raw) | Gal. | 60 | @ | — |
| Menhaden Oil (crude) | Gal. | 37 | @ | 39 |
| Naphtha, 68 @ 72° | drums | — | @ | 12 |
| Neatsfoot Oil (20°) | Gal. | 93 | @ | 95 |
| Paraffine (crude, 120 & 122 m. p.) | Lb. | 2½ | @ | 3 |
| Paraffine Oil (high viscosity) | Gal. | 22 | @ | 23 |
| Rosin ("F" grade) (280 lbs.) | Bbl. | 3.95 | @ | 4.00 |
| Rosin Oil (first run) | Gal. | 25 | @ | — |
| Shellac, T. N. | Lb. | 14 | @ | 14½ |
| Spermaceti (cake) | Lb. | 25 | @ | 27 |
| Sperm Oil (bleached winter), 38° | Gal. | 70 | @ | 71 |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid (double-pressed) | Lb. | 12 | @ | 12½ |
| Tallow (acidless) | Gal. | 62 | @ | 63 |
| Tar Oil (distilled) | Gal. | 30 | @ | 31 |
| Turpentine (spirits of) | Gal. | 48½ | @ | — |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum (No. 1 ingots) | Lb. | 19 | @ | 19½ |
| Antimony (Hallet's) | Lb. | 28 | @ | 30 |
| Bismuth (New York) | Lb. | 2.80 | @ | 2.90 |
| Bronze powder | Lb. | — | @ | — |
| Copper (electrolytic) | Lb. | 17¼ | @ | 17½ |
| Copper (lake) | Lb. | 18 | @ | 18½ |
| Lead, N. Y. | C. | 4.17½ | @ | — |
| Nickel | Lb. | 42 | @ | 45 |
| Platinum (refined) | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | 50⅜ | @ | — |
| Tin | C. | 50.00 | @ | — |
| Zinc | Lb. | 11 | @ | — |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | C. | 3.15 | @ | 3.20 |
| Blood (dried) | Unit | 2.70 | @ | — |
| Bone, 4½ and 50 (ground, raw) | Ton | 30.00 | @ | — |
| Calcium Cyanamid | Unit of Ammonia | 2.20 | @ | — |
| Calcium Nitrate (Norwegian) | C. | — | @ | — |
| Castor meal | Unit | — | @ | — |
| Fish Scrap (domestic, dried) | Unit | — | @ | — |
| Phosphate, acid (16 per cent bulk) | Ton | 7.50 | @ | — |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble (68 per cent) | Ton | 2.25 | @ | 2.50 |
| Tennessee (70–80 per cent) | Ton | 5.00 | @ | 5.50 |
| Potassium, "muriate," basis 80 per cent | Ton | 1.15 | @ | 1.25 |
| Pyrites (furnace size, imported) | Unit | 12½ | @ | — |
| Tankage (high grade) | Unit | 2.70 | @ | 10 |

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# EDITORIALS

## MECHANICAL REFRIGERATION IN MANUFACTURES

Mechanical refrigeration, first used only for ice making by men still active, and next applied to brewery cellars and beer wort, soon was extended to all kinds of cold storage purposes and became the foundation of the modern fresh food distribution system. These uses of mechanical refrigeration are today so common and well known as to obscure a more recent and valuable extension of mechanical cooling as a part of manufacturing processes. While these are constantly increasing in number and variety there are even more instances where this type of machinery could be economically used and where, for some reason, its application has not been undertaken. Wherever the general process includes such steps as gas, liquid or solid cooling, condensation, crystallization, fermentation, mechanical refrigeration must be carefully considered as a possible means of improving the product, increasing rate of production or permitting recovery of new products.

Solidification of various hot molten materials is most commonly carried out with water from any natural source of available temperature, but is better controlled by mechanically cooled water or brine, as, for example, in the manufacture of candles, wherever the speed of cooling and the constancy of the rate contributes to cost reduction or to improvement of quality of product.

The output of moulds or moulding machines used for these purposes if cooled with city or surface water, which is subject to temperature changes during the several seasons of the year, decreases as the temperature of the water increases, making it necessary to carry more moulds, to instal more machines than the average sales of the product warrant, to lose profitable business during the summer months, or to keep goods stored for a longer time, all of which cost items may be balanced against the mechanical refrigeration costs.

Promotion of separation by cooling is another typical case. Water cooled to between 36° to 40° F. is used to separate the lime-treated beet sugar solution from its molasses. By this means the solution is maintained at from 45° to 50° F., the proper temperature for best results. Separation of lard, paraffine and like products, from the liquor, whether held in suspension or in solution, is promoted by cooling or partial freezing. This process is standard with some products but is not used at all with others to which it might well be applied. A few examples include: lard recovery from rendered fats by solidifying on refrigerated drums rotating in the liquid; paraffine from the mineral oils, by cooling to 18° or 20° F., and filtering in filter presses; sulfuric acid concentration by crystallization after cooling to low temperatures; acid sulfate of soda separation into sulfate of soda and sulfuric acid; similarly, gas purification or separation, by cooling it to temperatures at which one or more of the mixed vapors will liquefy with or without the assistance of pressure control. Substitution of mechanical for free water cooling may be equally advantageous in all processes of making solutions having exothermic heats of reaction or absorption, or in cooling baths which may become heated otherwise, either from the air or from hot dips. Such cooling of bleaching baths to temperatures lower than can be maintained by the use of the existing water supplies has been found advantageous, and the same is true of some of the baths used in making mercerized silk.

Mechanical refrigeration might be used to a much greater extent than is at present customary for concentrating aqueous solutions by blasting air or freezing the solutions. It is in direct competition with heated vacuum systems for concentrating liquors and is in some cases less expensive.

Air cooling and drying, whether the object be temperature or humidity control, has passed through the stages of free water contact which in most important cases has been abandoned in favor of mechanical refrigeration. Numerous systems are in use where this cooling and drying has been performed by surface, city or well water, and because the results have not been uniformly satisfactory either in obtaining the desired temperature or in reducing the humidity in the air to the proper degree for all seasons and weather conditions, they have been replaced by refrigerating equipment. All uncertainties and variations are removed by the substitution of mechanical refrigeration and yet its use is far from being as universal as it should and could be. In some classes of factory operation it has been found that the amount of labor performed by the workmen, especially during the summer months, was increased so much by mechanically cooled breathing air that the expense of this cooling is more than offset by the greater output of the operators. For humidity control, by far the largest example of air-cooling by mechanical refrigeration is the Gayley process equipment for steel furnaces, the success of which is beyond question, and yet the application of similar equipment to other industries where humidity control is necessary or desirable is painfully slow.

Numerous as are the special instances where moisture contact of air must be minimized, there is an equally large number where low temperature of air or other gas is required directly, such, for example, as concentrating solutions for crystallization of citric acid by dry air contact at low temperatures, or drying products like gelatine, to which high temperatures or moist air are unsuitable. A similar dry, cool air requirement is imposed on storage rooms, carrying hygroscopic or high vapor pressure products or organic matter such as camphor, calcium chloride and hides and these are increasing in number. In the organic field the most interesting development is in the control of germination whether in storage or in process, of seeds, silkworms, tobacco curing and fermentation, in addition to the retardation of decay growth of all foodstuffs.

Originally designed to freeze water just below 32° F.,

mechanical refrigeration processes and equipment are now available at all temperatures, ranging from a few degrees above absolute zero to a few degrees below atmospheric temperature, in great variety of plants and ranges of first and operating costs. The tendency of the day is to produce greater and greater variety of appliances, each better adapted to a special application and to correspondingly increase the number of applications. The initiative must, however, come from the user, and the user of the future is the chemical manufacturer who must meet the refrigerating machine producer half way, so that by joint effort the industries may receive maximum benefit.

C. E. LUCKE

## THE THEORY OF THE PERFECT SHEET ASPHALT SURFACE

The theory of a perfect sheet asphalt surface is based upon a study of the behavior of surfaces and films. The most modern conception of the chemistry of colloids is likewise based on the relation of surfaces and films. Colloid chemistry is, therefore, of great value in interpreting the behavior of such surfaces and in guiding to their rational construction.

As long ago as 1905 the writer called attention in "The Modern Asphalt Pavement," published in that year, to the fact that the more or less satisfactory or unsatisfactory nature of a sheet asphalt pavement depends on the surface area of the particles composing the mineral aggregate of sand and filler entering into its construction, the amount of bitumen which may be used in such a mixture, without being present in excess, being dependent on the extent of the subdivision of the aggregate and its available surface area to which bitumen may adhere. At that time he went no further into the consideration of any effect that this surface area might have upon the mixture. With the development of the modern conceptions of colloidal or dispersoid chemistry and of adsorption which have been formulated since then, it is apparent that the extent of surface area presented in any mineral aggregate, especially in connection with the presence of colloid material, is of much greater importance than had previously been appreciated. In order to understand this, one must have some comprehension of the principles of physical chemistry and, especially, of the modern conceptions of colloid material.

Colloidal chemistry originated in the investigations of Graham in the sixties of the last century. It then lay dormant for forty years and has only recently been developed to an extent commensurate with the importance which it is now recognized as having. The original idea of Graham was that substances could be classified as crystalline and colloidal, with a sharp line of division between the two, according to whether or not they would, in solution, diffuse through an animal or semi-permeable membrane.

It is now recognized that colloids are merely a state of matter, one in a highly dispersed or subdivided condition. By appropriate means, in a suitable medium or phase with which the substance does not form a molecular solution, crystalline substances can be obtained in such a degree of subdivision or dispersion that they exist in a colloid state, *i. e.*, they will remain suspended in a medium indefinitely. The chemistry of colloid matter then differs from the chemistry of matter in its ordinary form, merely by the degree of its subdivision or dispersion. In order to be dispersed in colloid form a substance must exist in a system of at least two phases: an interior or disperse one which may be solid or liquid, and an exterior or continuous phase in which it is dispersed. The main characteristic of the disperse phase is its state of subdivision or degree of dispersion. Bancroft has characterized this as follows:[1]

"If we drop a stone into water, it sinks very rapidly; if we grind the stone into coarse particles these sink less rapidly; if we grind the stone into fine particles, these sink slowly; if we grind the stone into very fine particles we should expect them to sink very slowly, the rate being a function of the diameter of the particles. This is not the case, however. Very fine particles do not follow Stokes' equation and do not settle at all, because of the Brownian movements which are negligible for coarse particles. We, therefore, conclude that any substance can be brought into a state of colloidal solution provided we make the particles of that phase so small that the Brownian movements will keep the particles suspended, and provided we prevent agglomeration of the particles by a suitable surface film."

The Brownian motion to which Bancroft refers is one which can be discerned under an instrument known as the ultra-microscope which makes visible particles which are invisible in the ordinary instrument. It serves as a means of detecting matter in a colloid state which has been unavailable except within the last decade.

The size of particles, when in a colloid state, is ordinarily as small or smaller than 0.0001 mm. in diameter, and in the case of some solids no larger than 0.000006 mm.

A realization of the enormous surface area possessed by disperse solid colloids of this size may be arrived at from the fact that if an amount of material represented by a cube, one side of which has a dimension of one centimeter, is reduced by decimal subdivision only to the coarsest colloidal size, a 10 thousandth of a millimeter in dimension, the number of cubes produced would be 10 to the 15th power, while the surface area would be increased to 60 square meters, or 100,000 times that of the original cube. The great increase in surface area of the finer material over that exhibited by the surface area of a single cube is at once made evident, and the importance of having such a material present in a sheet asphalt surface mixture is apparent, if a large surface area is a necessary feature of the mineral aggregate of a perfect surface, which, in the light of actual experience, appears to be the case.

It is also of great importance because of the surface energy developed thereby, in addition to the fact that the large surface [illegible] permit the use of a greater

[1] *J. Phys. Chem.*, 18, 549

amount of bitumen as a cementing material. Surface energy is well demonstrated by the fact that if two plates of glass, which are ground perfectly parallel, be brought together with or without water, it is difficult to separate them, owing to the surface energy of the film of air or water which is imposed between them, energy far greater than can be attributed, as has been asserted, to the pressure of the atmosphere. This same phenomena is exhibited in cementing together with bitumen the particles of a mineral aggregate of a sheet asphalt pavement, having a great surface area.

Sheet asphalt pavements consisting of a mineral aggregate which contains a large amount of filler have proved more satisfactory, and are more durable when constructed with a bitumen containing highly dispersed colloidal matter. Asphalts containing disperse colloids have given more satisfactory results than those in which the finest particles consist only of a dust or filler, not in a colloidal state, such as ground limestone or Portland cement, added by the hand of man, although the addition of such fillers in large amount will improve the character of a surface over one which contains little filler and a coarse sand. It has been recognized for some years that certain surfaces, which have been constantly exposed to heavy travel, such as that laid on Fifth Avenue, New York, in 1896–97, and on the Victoria Embankment in London, have been extremely durable under trying conditions. From a study of the subject, from the point of view of the chemistry of colloids, it can now be appreciated why this has been the case, and it opens up a new line for the rational construction of such surfaces in the future. An explanation of this now seems possible.

Adsorption is the power a solid or liquid surface has of holding thereon a thin film of solids, liquids or gases, an example of which is the film of air or water which is found under ordinary conditions on the surface of glass. Colloids possess this property to a high degree, owing to the large surface area they present. Adsorption is well illustrated by the manner in which a dye or coloring matter is removed from its solutions by a substance like charcoal or kaolin: this is known as selective adsorption. Selective adsorption is of importance in connection with the sheet asphalt paving industry because of the fact that the surface of the mineral aggregate may adsorb selectively and hold with great power certain bitumens or portions thereof which are used as binding materials. In one native asphalt in particular there is a considerable amount of mineral matter naturally present in a disperse solid colloid form, which shows great capacity for adsorption, selecting the denser portions of the bitumen and forming a substance which gives great body and density to this binding material. The bitumen in this case has been shown, however, to have a further influence in that it serves as a protective colloid or film to the highly dispersed particles. Various bitumens seem to differ in the degree in which they exercise protective properties and apparently in accordance with their viscosity or density. Their relative value in the production of a successful sheet asphalt surface seems to be closely associated with this property as well as with surface area.

The large surface area provided by a material in a colloidal state has an important bearing upon the stability of a sheet asphalt surface. As long ago as 1905 the writer called attention in "The Modern Asphalt Pavement" published in that year to the fact that the surface area of the particles composing the mineral aggregate, consisting of sand and filler, influenced or regulated the amount of bitumen which may be used in such a mixture without being present in excess.

For example the figures in the accompanying table show the area of the particles calculated in square feet occurring in a coarse and a fine mineral aggregate of the types in use in New York in the nineties. The

NUMBER OF PARTICLES AND THEIR SURFACE, PER POUND, IN MINERAL AGGREGATES OF THE TYPE IN USE IN NEW YORK IN THE NINETIES

| | Coarse Sand and Dust | | | Fine Sand and Dust | | | Dust or Filler | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Mesh of sieve | Per cent | No. of particles | Surface Sq. ft. | Per cent | No. of particles | Surface Sq. ft. | Size of particles Millimeters | Per cent | No. of particles | Surface Sq. ft. |
| 10 | 13 | 12,592 | .958 | 4 | 3,674 | 0.295 | 0.08 | 18.8 | 120,035,300 | 25.976 |
| 20 | 12 | 66,186 | 1.579 | 7 | 38,808 | 0.921 | 0.05 | 17.17 | 452,300,200 | 38.231 |
| 30 | 10 | 167,547 | 1.901 | 9 | 150,796 | 1.715 | 0.025 | 51.3 | 10,732,900,000 | 226.825 |
| 40 | 13 | 664,250 | 3.593 | 11 | 561,866 | 3.033 | 0.0075 | 5.0 | 30,775,730,000 | 58.590 |
| 50 | 27 | 5,021,870 | 11.479 | 26 | 4,835,870 | 11.054 | 0.0025 | 7.2 | 150,634,400,000 | 178.199 |
| 80 | 10 | 4,086,220 | 5.527 | 15 | 6,127,910 | 8.099 | | 100.0 | 192,715,475,500 | 527.821 |
| 100 | 7 | 10,415,700 | 5.952 | 15 | 22,319,400 | 12.754 | Or, if all the dust is of 0.025 mm. in diameter | | 20,922,050,000 | 442.157 |
| 200 | 5 | 31,924,300 | 6.909 | 7 | 44,694,000 | 9.672 | | | | |
| 0.005 mm. | 3 | 76,671,400 | 6.480 | 6 | 153,343,000 | 12.960 | | | | |
| | 100 | 129,030,065 | 44.378 | 100 | 232,075,324 | 60.503 | | | | |

contrast is striking. Another calculation shows the number of square feet of surface in a pound of dust or filler in use at that time which may be compared with the figures for the entire mineral aggregate.

From the data given it appears that the finer aggregate presents a surface area of 60.5 square feet to the pound and the coarser one but 44.4, a difference of 32.6 per cent in favor of the finer material. The enormous increase in area, the finer the material grows, is demonstrated by the figures given in the last section of the table.

In 1905 the writer went no farther into the consideration of the effect to which the extent of surface area might have upon the mixture other than in providing for an increased amount of bitumen, but with the development of our modern conceptions of the colloidal state and of adsorption, it is apparent that the extent of surface area presented in any mineral aggregate is of much greater importance than had been previously appreciated. We now understand the fact that an extended surface area in addition to providing for the use of a larger amount of bitumen exercises a still more important function, due to the greater surface energy developed by the large surface area of a fine mixture over that of a coarse one and that, aside from the greater surface presented by a fine sand as compared to a coarse one, the presence of highly dispersed

colloids with their extensive surface is necessary for the production of the most satisfactory surface.

There is one other consideration of a physical nature in connection with the relation of surface area to the films of bitumen and this is, the thickness of the film of the melted bitumen which will adhere to or be adsorbed by the surface with which it is brought in contact, dependent in one direction on the nature of the surface and in the other on the character of the bitumen. It is known that the thickness of adsorbed aqueous films on various surfaces is quite different.

The same differences have been observed as regards the behavior of surfaces with different bitumens. The more viscous the bitumen and the larger the amount of colloid material which it contains, the thicker the film and, consequently, the greater the cementing power of the bitumens which forms the thicker film.

The writer's premise, at the beginning of this paper, that the basis for the construction of a perfect asphalt surface lies in a consideration of the chemistry of surfaces and films seems, therefore, to be confirmed and to offer a solution of the rational construction of such surfaces.

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## THE EFFECT OF THE WAR ON ABSTRACTS

The reduction in the bulk of current chemical literature due to the war in Europe is reflected in the size of the recent numbers of *Chemical Abstracts*. Since a little more than two-thirds of the chemical research work reported during the past ten years was done in the countries now at war, a considerable effect was to be expected. The extent of this reduction is shown by the following figures: The first six numbers of the 1914 volume of *Chemical Abstracts* contain 5286 abstracts of journal articles; the corresponding numbers of the present year contain but 3437 such abstracts. This shows a decrease of about 35 per cent. The effect on the patent literature has not been so great; there has been a decrease of about 20 per cent, the number of patent abstracts appearing in *Chemical Abstracts* in the first six numbers of Volume 8 being 2201 and in the corresponding numbers of Volume 9, 1757. The numbers of pages in *Chemical Abstracts* for the two periods are, respectively, 1220 and 872; the decrease has been 28.5 per cent. The two periods are only approximately comparable because, since the beginning of the war, irregularities in the receipt of foreign journals in the United States have caused delays in the publication of abstracts in some cases; however, the first three months of 1915 is a more suitable period for this comparison than the months of 1914 following the outbreak of the war. Although there have been delays the field has been covered very nearly, if not, as completely as under normal conditions. Practically all of the foreign journals that are being published are now being abstracted in good time. The decrease in the number of abstracts is due to the decreased size of the journals of the warring countries, the doubling up of numbers and the fact that the publication of some journals has been discontinued, at least temporarily.

The chemical journals that have been discontinued since the outbreak of the war are few in number. The papers being published in the warring countries are in some cases below the normal standard of quality; nevertheless a considerable number of important papers is appearing. Surprise has been expressed that the reduction in number has not been greater. There has been no interruption in the receipt in this country of English chemical journals. With the exception of the abstract sections of the *Journal of the Chemical Society of London* and the *Journal of the Society of Chemical Industry* and a slight decrease in size, the English journals show but little effect of the war. There have been delays and irregularities in the receipt of German journals but almost all of them are being published and are now reaching the United States with some degree of promptness if obtained directly from the publisher. In many cases two or more numbers of the German journals are appearing bound together as one normal-sized number. Several of the French journals have been discontinued but the more important ones chemically are appearing. The number of papers published in them during the first three months of 1915, while small, is greater than the number appearing during the last three months of 1914. The *Journal of the Russian Physical Chemical Society* is the only important Russian chemical journal. The January, 1915, number of this journal was received April 10th; every effort to obtain or locate the 1914 numbers published since the outbreak of the war met with failure until May 3rd, at which time all were received in one bundle. No decrease in size is shown. A full-sized number of *Recueil des travaux chimiques des Pays-Bas et de la Belgique* was published in January.

This is a very important period for *Chemical Abstracts*. These are troublesome days for an abstract journal which endeavors to report completely and promptly the progress of chemistry throughout the world; however, the handicap to *Chemical Abstracts* is less than that experienced by the other chemical abstract journals of the world. *Chemical Abstracts* will be the only complete record of the chemical researches reported during the war period. The January, February and March numbers of the *Journal of the Chemical Society of London*, which correspond to the period being used for comparison, do not contain a single abstract of a German paper published since the outbreak of the war. The *Journal of the Society of Chemical Industry* has published during this period abstracts for only a small number of the papers that have appeared in the German journals. The numbers of *Chemisches Zentralblatt* for the period (two not available for checking at time of writing) contain a number of references to English journals, but they are not covered completely; no references to French, Russian or Japanese journals are to be found. Unless the mails from the warring countries are interrupted, *Chemical Abstracts* can be relied on to continue to cover the field completely and in most cases as promptly as delays in the receipt of journals will permit.

E. J. CRANE

# ORIGINAL PAPERS

## THE CONSTITUENTS OF PORTLAND CEMENT CLINKER[1]

By G. A. Rankin

The question of the constitution of Portland cement clinker has long been in dispute and has called forth a large number of papers and many theories; unfortunately, however, the experimental bases of most of this work have been altogether insufficient to decide the several questions at issue. There has been in general a failure to realize the fact that a system so complicated as this can be unravelled only by proceeding systematically, using as a guide the principle known as the phase rule and establishing definite criteria for the recognition of the several substances which occur. The work recounted in the following pages forms part of a complete investigation of the whole system of mixtures of lime-alumina-silica, carried out in this systematic way; it is believed therefore that the conclusions reached can be regarded as established.

In the great bulk of the published work on the constitution of Portland cement the evidence offered in support of the statements as to the reactions which take place during the burning of cement and the several substances formed is largely unconvincing; accordingly, an extended review of the literature would be futile. The most common fault is that the criteria employed to define a compound have been indefinite or insufficient; thus in some cases it is taken for granted that a substance is necessarily a compound, if, when mixed with water, it remains "volume constant." Again the refractive index is frequently spoken of as "high;" but very many substances have a "high" refractive index, so that such a statement helps us little in identifying a compound and may actually be misleading. Such evidence, to be of any use, must be capable of quantitative statement.

Cement clinker is a mixture of substances of very similar properties, and is moreover exceedingly fine grained, as a consequence of which it is a matter of some difficulty to make quantitative determinations of the optical characteristics of the constituents; but this difficulty can be surmounted by studying separately each of the presumable constituents of the clinker and determining definite values of certain properties which serve to characterize it and to distinguish it from the other possible constituents.

According to Meade,[2] the average of a large number of analyses of commercial Portland cement is:

| | | | |
|---|---|---|---|
| CaO | 62.0 per cent | $Fe_2O_3$ | 2.5 per cent |
| $SiO_2$ | 22.0 per cent | MgO | 2.5 per cent |
| $Al_2O_3$ | 7.8 per cent | $SO_3$ | 1.5 per cent |

That is, more than 90 per cent of an average Portland cement consists of the three oxides, CaO, $Al_2O_3$, $SiO_2$; one would therefore expect that its properties are due mainly to the presence of the above 3 components and that the relatively small admixture of the other oxides exerts at most a wholly secondary influence. Indeed Clifford Richardson[3] has shown that good Portland cement can be made by using only the pure oxides lime, alumina and silica in the proper proportions. Accordingly the first problem is to isolate and determine all the possible CaO, $Al_2O_3$, $SiO_2$ compounds which we may expect to find in Portland cement clinker, to establish their relations at high temperatures, and to ascertain their optical characteristics, which constitute the most convenient and satisfactory criterion of the identity of the several substances.

These characteristic properties of the various solid substances containing CaO, $Al_2O_3$, $SiO_2$ only, which are likely to occur in Portland cement, we have determined in the course of a complete investigation of all compounds formed when any mixture of these three oxides is heated to a high temperature. In Portland cement clinker the relative proportions of these oxides vary only between comparatively narrow limits: $SiO_2$, 18.5 to 23.2; $Al_2O_3$, 6.1 to 11.9; CaO, 63.1 to 68.1;[2] in other words, in considering this special problem we have to deal with a very restricted portion of the equilibrium diagram for the whole system, $CaO–Al_2O_3–SiO_2$. This problem is therefore but a small portion of the larger problem which we undertook and its investigation was incidental to that work. We believe, however, that the results of our investigation, which were concerned with the behavior of systems made up only of the three pure oxides, establish a working basis from which those more especially interested in the study of commercial Portland cement clinker may start with confidence; work of this character has already been undertaken at the Pittsburgh laboratory of the Bureau of Standards[3] and has led to results which, as we shall see later, bear out the conclusions derived from the work here.

The experimental results utilized in the present paper are taken from the complete report[4] of the investigation of the three-component system $CaO–Al_2O_3–SiO_2$, a paper to which the reader desirous of fuller information with respect to the application of the phase rule, the experimental procedure, the course of crystallization, etc., is referred.

### THE TERNARY SYSTEM $CaO–Al_2O_3–SiO_2$

The working out of this system necessitated the investigation of about 1000 different concentrations and fully 7000 heat treatments and microscopical examinations. Each concentration was made up of especially pure CaO, $Al_2O_3$ and $SiO_2$ and was fused repeatedly in a platinum crucible with fine grinding between fusions, in order to obtain a product chemically homogeneous. Each of these products was subjected to a careful optical study to determine the crystalline

[1] Paper presented at the 30th Meeting of the American Chemical Society, New Orleans, March 31 to April [illegible]

[2] Richard K. Meade, "Portland Cement," p. 80.

[3] Clifford Richardson, [illegible] 5, [illegible]

[4] 6, 20.

The Constitution of Portland Cement [illegible] P. H. Bates [illegible] Cement Mill Section, 2 [illegible]

The Ternary System [illegible] A. V. Rankin [illegible] Study [illegible] P. Wright, [illegible] 39 [illegible]

phases present at temperatures ranging from that at which melting begins to that at which the charge is completely melted.

The data required are obtained most readily by means of the "quenching" method which was found to be invaluable. In this method a small charge of the desired composition is placed in a platinum resistance furnace and held at a constant temperature until equilibrium is attained, when the charge is "quenched" (suddenly cooled by dropping into a bath of mercury or water). In this way one is able to obtain for microscopical examination the material as it existed at the temperature in the furnace. Thus if the charge were completely melted at the temperature of the furnace, it would on quenching appear as a glass; but if the charge had been only partially melted the chilled product would contain unmelted or crystalline material embedded in glass, whereas if no melting had taken place, the chilled product would contain no glass. These differences are very easily recognized by microscopical examination; hence by holding charges of the same composition at a series of constant temperatures, one is enabled to fix, within $\pm 3^\circ$ C., the temperature at which melting begins and is complete for the particular mixture. One is able to obtain by this method not only melting temperatures up to $1625^\circ$ C. (the limit of the platinum furnace) but also to grow crystals, the optical properties of which can be readily measured, since in the quenched product they are embedded in clear glass. By proceeding systematically in this way the optical properties of all compounds which occur in melts of CaO, $Al_2O_3$ and $SiO_2$ were definitely determined.

This general description of the mode of attack in working out the ternary system will suffice for the present purpose; we shall not take up the other methods employed or a detailed discussion of the results obtained, as all this has already been published in the full report already referred to. That report presents the following data which, it is to be remembered, apply strictly only to conditions of heating or cooling such that equilibrium was continuously attained:

1—The compositions, melting or dissociation temperatures, and optical properties, of the components and of all the compounds both binary and ternary, which are found in dry melts of CaO, $Al_2O_3$, $SiO_2$.

2—The temperatures and regions within which the several components and compounds, pure or in mixtures, can exist in equilibrium in contact with melt (liquid).

3—The order in which the several solid phases crystallize from a slowly cooling melt (which is the reverse of the order of disappearance of the several crystals when a solid mixture is slowly heated).

4—The final products obtained when any melt composed only of these three oxides has completely crystallized.

The final products of crystallization are the only essential data required for the elucidation of most of the problems with which we are concerned. If equilibrium has been continuously attained, the final product will, in accordance with the requirements of the phase rule, consist always of a group of three solid phases (except the composition is exactly that of a pure compound or a binary mixture). The manner in which the constitution of these groups varies with variations in the composition of the original mixture can be determined only by experiment, the results of which can be most readily understood if they are plotted on an equilateral triangular concentration diagram such as Fig. 1.

In this diagram the pure components CaO, $Al_2O_3$, $SiO_2$ are represented by the apices of the triangle; the binary mixtures CaO-$Al_2O_3$, $Al_2O_3$-$SiO_2$ and $SiO_2$-CaO, respectively, by points on the three sides of the triangle and the ternary mixtures by points within the triangle. Each side of this equilateral triangle is divided into 100 parts; this enables one to represent the sum of the percentage amounts of the components (in either binary or ternary mixtures) by a side of the triangle. The percentages may be given either as molecular or weight percentages; in

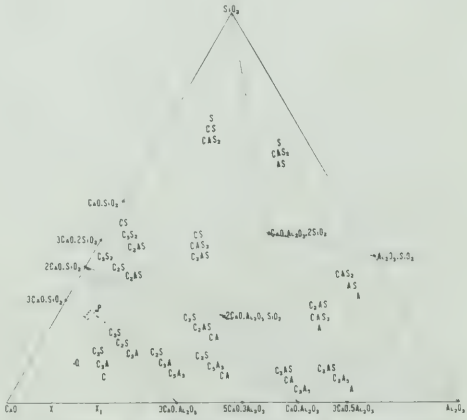


FIG. 1 DIAGRAM TO SHOW FINAL PRODUCTS OF CRYSTALLIZATION OF SOLUTIONS OF CaO, $Al_2O_3$, AND $SiO_2$

Within each small triangle symbols, C=CaO; A=$Al_2O_3$; S=$SiO_2$, are used to simplify the designation of the compounds. Thus $3CaO.SiO_2$=C$_3$S; $5CaO.3Al_2O_3$=C$_5$A$_3$; etc.

Fig. 1 all compositions are given as percentage weights of the components. As the location of points which represent compositions in a triangular diagram may be puzzling to those not familiar with its use it may be well to illustrate with examples. The apices of the triangle, of course, represent the components, each 100 per cent pure, so that it is an easy matter to determine the composition of a binary mixture represented by a point on a side of the triangle; thus consider the point $Al_2O_3.SiO_2$ on the side $Al_2O_3$–$SiO_2$ as representing an unknown composition, then, since the length of the side $Al_2O_3$–$SiO_2$ is taken as 100, the portion $SiO_2$–$Al_2O_3.SiO_2$ will give the percentage weight of $Al_2O_3$ and the portion $Al_2O_3.SiO_2$–$Al_2O_3$ the percentage weight $SiO_2$ in the composition represented by the point $Al_2O_3.SiO_2$. As an illustration of points within the triangle, consider point $Q$ as representing a ternary mixture of CaO, $Al_2O_3$, $SiO_2$ of unknown composition. If, now, one line is drawn through $Q$ parallel to the

side $SiO_2$–$Al_2O_3$ and another through $Q$ parallel to the side CaO–$SiO_2$, we find that the side CaO–$Al_2O_3$ has been divided into three parts, CaO — X = 10.0 per cent, X — $X_1$ = 10 per cent, and $X_1$ — $Al_2O_3$ = 80 per cent, which give the weight percentage of $Al_2O_3$, $SiO_2$ and CaO, respectively, in the composition represented by point $Q$. If, on the other hand, the composition of a mixture is known and one wishes to locate the corresponding position in the triangle, it is only necessary to reverse the order of procedure. A very useful property of the equilateral triangle should be noted here. Points on a straight line, joining an apex of the triangle with the opposite side will represent compositions, in which the relative proportions of two of the components remain constant. Thus in Fig. 1 for all compositions represented by points on the line joining $Al_2O_3$ and $2CaO.SiO_2$, the relative proportion of CaO and $SiO_2$ remain constant being CaO 65 per cent, $SiO_2$ 35 per cent.

Having shown how compositions of CaO, $Al_2O_3$, $SiO_2$ are represented by points within the triangular diagram, Fig. 1, we shall proceed with the discussion of the final products of crystallization obtained from melts of these three oxides as given in this diagram.

As has been said, the final product of crystallization, under conditions of equilibrium, from a melt of CaO, $Al_2O_3$, $SiO_2$ will consist of three solid phases. It is also true that the same three final solid phases will be found together at all compositions within a region which has definite boundaries. These boundaries are given in Fig. 1; it will be seen that they divide the large triangle into a large number of small triangular areas. Each of these triangles represents all possible mixtures of those three compounds whose compositions are represented by the apices of that triangle. Though a given group of three compounds can exist only in *one* triangle, yet as can be seen in the diagram, any one of these compounds may be found in a number of adjacent triangles.

In applying the data presented in Fig. 1 to any problem involving a part or all of this diagram, it must be remembered that the diagram represents equilibrium conditions; *i. e.*, this diagram represents the compounds and components as they would occur together in mixtures if time were allowed for all reactions to go to completion. Hence, it is not permissible to apply directly the data in Fig. 1 to problems involving mixtures containing only the three oxides CaO, $Al_2O_3$, $SiO_2$, unless one is sure that equilibrium conditions have been substantially attained. In the problem to which we wish to apply this diagram, we know that the reactions involved are not always completed, that equilibrium conditions are not attained. It does *not* follow, however, that this diagram is worthless in its application to such problems. On the contrary, it simply means that this diagram must be studied in order to determine the possible conditions which may exist if equilibrium is not reached.

For example, if any mixture of these three oxides is heated, the compounds present in the product would be to a large extent those given in the small triangle in which the point representing the composition of the original mixture occurs, and if any other compounds did occur (owing to the non-attainment of equilibrium) one would expect that they would be members of the groups belonging to the adjacent triangles.

### APPLICATION TO PORTLAND CEMENT CLINKER

It is a well known fact that Portland cement can be made from the pure oxides CaO, $Al_2O_3$ and $SiO_2$. According to Richardson's data[1] cement clinker can be made from mixtures of these three oxides whose compositions are represented by a group of points near the letter $P$ in Fig. 1. The points lie entirely within the triangle whose apices are $3CaO.SiO_2$–$3CaO.Al_2O_3$–$2CaO.SiO_2$. Therefore a cement clinker made from pure CaO, $Al_2O_3$ and $SiO_2$, burned at a sufficiently high temperature for a sufficiently long time, would consist of the three compounds $2CaO.SiO_2$, $3CaO.SiO_2$ and $3CaO.Al_2O_3$. If, however, equilibrium were approached but not reached we would expect to find, in addition to these three compounds, either free lime or the compound $5CaO.3Al_2O_3$ or both, CaO and the compound $5CaO.3Al_2O_3$ being the only other constituents present in the adjacent triangles.

To illustrate with a concrete example, let us consider the point $P$ which represents a mixture whose composition is CaO 68.4, $Al_2O_3$ 8.0, $SiO_2$ 23.6. Richardson[2] found that a perfectly burned clinker of this composition, when ground and made into a mortar, possessed all the properties of a desirable Portland cement. We have found that a perfectly burned clinker of this composition will consist of the compounds $3CaO.SiO_2$, $3CaO.Al_2O_3$ and $2CaO.SiO_2$. Therefore it may be definitely stated that a clinker consisting only of these three compounds can be prepared which will possess the properties of a desirable Portland cement. Furthermore, subsequent work by the Bureau of Standards has shown that these three compounds go to make up the major portion of clinkers of commercial Portland cement.

However, before taking up a discussion of the constitution of commercial Portland cement clinker, data are presented on the properties and behavior of the substances, composed solely of pure CaO, $Al_2O_3$, $SiO_2$, which are found to occur in Portland cement.

### THE CaO, $Al_2O_3$, $SiO_2$ COMPOUNDS IN PORTLAND CEMENT CLINKER

The substances composed only of CaO, $Al_2O_3$ and $SiO_2$ which have been observed in Portland cement clinker are five in number: the component CaO and the compounds $2CaO.SiO_2$, $3CaO.SiO_2$, $5CaO.3Al_2O_3$ and $3CaO.Al_2O_3$. Each of these has received careful study, the results of which we shall now consider, taking in order (1) the methods of formation and (2) their optical characteristics. In the course of this discussion frequent reference will be made to the work done at the Pittsburg laboratory of the Bureau of Standards by P. H. Bates[3] and A. A. Klein and A. J. Phillips.[4]

[1] "The Constitution of Portland Cement," Clifford Richardson, *Cement*, **5** (1904), 316.

[2] Clifford Richardson, *Cement*, **5**, 315.

[3] "The Constitution of Portland Cement," by P. H. Bates, *Concrete-Cement Age* (Cement Mill Section), **2** 1913), 5.

[4] *Orig. Comm. 8th Intern. Congr. App. Chem.*, **5**, 81.

METHODS OF FORMATION

THE COMPONENT CaO is formed by burning $CaCO_3$ to drive off $CO_2$; it is stable at its melting point which is 2570° C.[1]

THE COMPOUND $2CaO.SiO_2$ is easily formed by crystallizing a melt of the composition $2CaO.1SiO_2$ (by weight CaO 65, $SiO_2$ 35), though it will also form at temperatures much below its melting point which is 2130° C. It occurs in four forms: $\alpha$, which is stable between 2130–1420°; $\beta$, which is stable between 1420–675°; $\gamma$, which is stable below 675°; and $\beta'$, which is unstable or monotropic and is found occasionally in charges rapidly cooled from a temperature of about 1400°. The change $\beta$ to $\gamma$ at a temperature of 675° is accompanied by a volume change of about 10 per cent, which shatters the crystals; this is the phenomenon commonly known as "dusting." Of these four forms of $2CaO.SiO_2$, the high temperature forms $\alpha$ and $\beta$ are the more common in Portland cement. Bates finds that $2CaO.SiO_2$ is found in well burned commercial clinkers largely as the $\beta$ form. The $\gamma$ form is not found to any extent except in underburned clinkers which "dusted" on cooling.

THE COMPOUND $5CaO.3Al_2O_3$ (by weight CaO 47.78, $Al_2O_3$ 52.22) is the most easily fusible; it melts at 1455° and crystallizes again readily from the melt. It is also found in a second form which is monotropic and generally occurs in melts that have cooled rather rapidly, though the precise conditions under which it does form have not been ascertained. The stable form of this compound is, according to Bates, the more common in commercial cement clinker.

THE COMPOUND $3CaO.Al_2O_3$ (by weight CaO 62.22, $Al_2O_3$ 37.78) has no stable melting point; at a temperature of 1535° C. it dissociates into CaO and liquid wherefore it is exceedingly difficult to obtain free from admixture of free lime and $5CaO.3Al_2O_3$. If a well-mixed charge of the oxides in the proportion 3CaO (as $CaCO_3$) : $Al_2O_3$ is fused and examined under the microscope, it is seen to consist largely of $3CaO.Al_2O_3$, but to contain also some free CaO and $5CaO.3Al_2O_3$. If, however, the mixed oxides are not fused but are held for several hours at a temperature somewhat below 1535° (*i. e.*, the dissociation point of this compound)—say 1400°—the charge becomes homogeneous and contains only $3CaO.Al_2O_3$. This compound has been found in but one form.

THE COMPOUND $3CaO.SiO_2$ also has no melting point, dissociating at about 1900° into free CaO and $2CaO.SiO_2$, but this dissociation differs in one respect from that of $3CaO.Al_2O_3$ in that the charge remains solid because 1900° is still about 100° below the temperature at which melt (liquid) appears in this case. It can be obtained in the pure state by a procedure analogous to that for $3CaO.Al_2O_3$, namely by prolonged heating of a mixture of the oxides in the proper proportions at a temperature somewhat below 1900°. The formation of this compound pure is very difficult, owing to the high temperature required. The compound $3CaO.SiO_2$ occurs in but one form; on fusion it is transformed completely into CaO and $2CaO.SiO_2$.

[1] Kanolt, *J. Wash. Acad. Sci.*, **3** (1913) 315.

As was to be expected, it was found by Bates that the relative amounts of this compound in commercial clinker increased with the temperature of burning.

Having considered the formation of each pure compound separately, let us now take up the mode, and order of formation of the four compounds in the burning of cement clinker made up from the pure oxides CaO (as $CaCO_3$), $Al_2O_3$, $SiO_2$ in the proper proportions. When such a mixture is heated, the first change is the evolution of the $CO_2$; the lime then unites with the other components to form the compounds $5CaO.3Al_2O_3$ and $2CaO.SiO_2$ (both of which form readily, as we have shown) probably in this order, since the former melts at a lower temperature than the latter; subsequently these two compounds unite in part with more lime and the compounds $3CaO.SiO_2$ and $3CaO.Al_2O_3$ appear. This formation of the last two compounds—a process which goes on very slowly in mixtures of their own composition—is materially facilitated by the circumstance that in the ternary mixtures a portion of the charge has already melted and promotes reaction by acting as a flux or solvent. The temperature at which this flux first appears is 1335° C.,[1] the eutectic temperature for the three compounds, $2CaO.SiO_2$, $5CaO.3Al_2O_3$, $3CaO.Al_2O_3$. As the temperature of burning gradually rises above 1335° the relative amount of flux increases and the rate of formation of $3CaO.Al_2O_3$ and $3CaO.SiO_2$ increases correspondingly. At a temperature somewhat above 1335° (the exact temperature depending on the original composition) the compound $5CaO.3Al_2O_3$ will have completely melted in the flux and the formation of the compound $3CaO.Al_2O_3$ will be completed. The substances present as crystals at this stage are $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$ and free CaO. Of these the $3CaO.SiO_2$ is rapidly increasing in amount, due to combination of $2CaO.SiO_2$ with CaO, while the amount of solid $2CaO.SiO_2$, CaO and $3CaO.Al_2O_3$ are all decreasing, the $2CaO.SiO_2$ partially by combination with CaO and partially by dissolving along with $3CaO.Al_2O_3$ in the flux. At a temperature of about 1475° C., the $3CaO.Al_2O_3$ will all have dissolved in the flux and most of the CaO will have combined with $2CaO.SiO_2$ to form $3CaO.SiO_2$, so that the crystalline substances now present in the flux are $3CaO.SiO_2$, $2CaO.SiO_2$ and CaO. As the temperature is raised still further each of these crystalline compounds will gradually disappear, but it is possible to state which of these three crystalline phases will be the last to dissolve only if the original composition of the charge is known. In any case the temperature of complete melting will be about 1900° and if such a charge is cooled the final product of crystallization will consist largely of $3CaO.SiO_2$, $2CaO.SiO_2$ and $3CaO.Al_2O_3$.

In order to show the temperature required and the percentage composition of the final product obtained in a well burned clinker, let us consider, for example, a mixture (represented in the diagram) by the point *P*

[1] The temperatures, presented here, are taken from data which are given in a diagram in the complete report of the ternary system CaO, $Al_2O_3$, $SiO_2$. The explanation of this diagram requires a discussion of some length and is not presented here.

whose composition is CaO 68.4 per cent, $Al_2O_3$ 8.0 per cent, $SiO_2$ 23.6 per cent—a mixture which Richardson found on burning produced a clinker which when ground and treated with water possessed the properties of a desirable Portland cement. During the burning of this mixture the reactions which take place will proceed, up to a temperature of 1475° C. in the manner already described; that is, at 1475° we shall have the three crystalline phases $3CaO.SiO_2$, $2CaO.SiO_2$, CaO and liquid. But at a temperature somewhat above 1475° the free CaO will also have entirely disappeared as a crystalline entity, so that the clinker will then consist of $3CaO.SiO_2$, $2CaO.SiO_2$ as crystalline material in contact with a liquid (flux) saturated with respect to those compounds. As the temperature is raised still further the $3CaO.SiO_2$ and $2CaO.SiO_2$ will gradually dissolve in the flux. But it is not necessary to raise the temperature until the charge is completely melted as normal cement clinker is obtained at temperatures much below complete melting; in other words, the necessary reactions will go to completion and the final product obtained will in time reach the state of equilibrium even below the temperature required for complete melting. The rapidity with which the reactions go to completion will of course depend upon the temperature and upon the amount of the flux at that temperature, this amount increasing of course when small quantities of admixtures such as FeO, MgO, etc., are present. In normal commercial cement the temperature required for burning has been found to be about 1425° C. Clinker of the above composition, which is composed of pure CaO, $Al_2O_3$ and $SiO_2$, would require a much higher temperature, owing to the high CaO content. At a temperature of 1650° C. this clinker would be about 30 per cent melted and 70 per cent solid crystalline material, a proportion of flux which would be sufficient to admit of the necessary reactions going to completion in a reasonable time. The charge will always crystallize completely on cooling; the percentage composition (based on actual data) of the clinker thus obtained would be approximately $3CaO.SiO_2$ 45 per cent, $2CaO.SiO_2$ 35 per cent, $3CaO.Al_2O_3$ 20 per cent.

In the foregoing discussion we have followed to completion the course of the reactions which take place when cement clinker composed of pure CaO, $Al_2O_3$, $SiO_2$ is burned; in other words, we have shown the order of formation of the compounds during the burning of mixtures of these three oxides in the proper proportions for cement clinker and stated which compounds will be present in the final product if the burning is continued long enough and at sufficiently high temperatures to obtain a condition of equilibrium. If, however, equilibrium is not attained, the two constituents CaO and $5CaO.3Al_2O_3$ which are present during the earlier stages of the burning will not disappear completely and so will be found in the final product.

### OPTICAL CHARACTERISTICS

The earlier investigators did not use sufficiently definite criteria in their endeavor to identify the several substances present in Portland cement clinker; hence, their evidence is not conclusive. Definite criteria can be established only by isolating each substance in a substantially pure state, and determining the characteristic properties, whether chemical or physical, of such material; constants ascertained in this way may then be applied with confidence in the detection of a crystalline substance in a complex mixture. In the present work the optical determinations were made on pure material largely by Dr. F. E. Wright and in part by Dr. H. E. Merwin; to these gentlemen the writer is especially indebted for their valuable collaboration.

Each of the compounds found in cement clinker made only of CaO, $Al_2O_3$ and $SiO_2$ has optical properties peculiar to itself; certain of these properties may appear common to several but each has at least one or more characteristic properties which serve to distinguish it from the rest. The several optical-crystallographical properties of each compound in its various forms are given in Table I, the data in which were obtained by a study of each compound by itself. These values are constants for the individual compounds in all mixtures which are composed only of compounds of CaO, $Al_2O_3$ and $SiO_2$; *i. e.*, in such mixtures the compounds are present as individuals of

TABLE I.—OPTICAL CRYSTALLOGRAPHICAL PROPERTIES OF THE COMPOUNDS PRESENT IN PORTLAND CEMENT CLINKER[1]

| Composition | Crystal system | Crystal habit | Cleavage | Hardness | Elongation | Optical orientation | $\alpha$ | $\beta$ | $\gamma$ | Optical character | Optic axial angle | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CaO | isometric | unmodified cubes | perfect (100) | 3-4 | | | | | 1.83 | | | Crystals often show optical anomalies. |
| $\gamma$-$2CaO.SiO_2$ | probably monoclinic | prismatic | g (001)<br>g (100) | | $\gamma$<br>$a$ | $b = \beta$<br>$c : \gamma = 37°(?)$ | 1.642 | 1.645 | 1.654 | — | $2E = 52°$ | Obtainable only as fine powder. Plane of optic axes normal to cleavage direction. |
| $\beta$-$2CaO.SiO_2$ | orthorhombic or monoclinic | irreg. grains prisms | poor | 5-6 | | ..... | 1.717 | | 1.735 | + | large | Plane of optic axes parallel to elongation. |
| $\alpha$-$2CaO.SiO_2$ | monoclinic or triclinic | irregular grains | | 5-6 | | $c : a' = 18°$ | 1.715 | 1.720 | 1.737 | + | large | Intricate polysynthetic twinning is characteristic of this form. |
| $\beta'$-$2CaO.SiO_2$ | | equant gr | | | | | | | 1.715 | + | small or uniaxial (+) | Birefringence very weak. |
| $3CaO.SiO_2$ | monoclinic (?) | equant grains | | | | $\gamma = \gamma$ | | | 1.715 | - | small or uniaxial | Birefringence very weak. Twinning lamellae not uncommon. |
| $3CaO.Al_2O_3$ | isometric | equant grains | p (111), or p (110) | 6 | | ..... | | | 1.710 | | .... | Occasionally gray interference colors appear as result of strain |
| $5CaO.3Al_2O_3$ (stable) | isometric | equant grains | | 5 | | ... | | | 1.608 | | | Stable form |
| $5CaO.3Al_2O_3$ (unstable) | probably orthorhombic | fibers prisms | p prismatic | 5 | $a$ | | 1.687 | | 1.692 | (+) | large | Plane of optic axes parallel with fiber elongation. |

[1] This table is a portion of that giving optical properties of all compounds of CaO, $Al_2O_3$ and $SiO_2$ as determined by F. E. Wright and published in *Am. Jour. Sci.*, [4] **39** (1915), 75-76.

constant optical properties and not as solid solutions. Consequently the data of Table I serve as certain criteria for the identification of the several substances present in such mixtures.

We do not discuss at length the distinguishing optical properties of all the forms as given in Table I, but merely take up those which characterize the several constituents of Portland cement clinker; namely, the two minor constituents CaO and $5CaO.3Al_2O_3$ (stable form) and the three major constituents $\beta$-$2CaO.SiO_2$, $3CaO.SiO_2$ and $3CaO.Al_2O_3$, which, as Bates has shown, go to make up the major portion of commercial clinker.

CaO is easily recognized as it occurs in colorless isotropic rounded grains; its refractive index is 1.83, which is much higher than the refractive indices of any of the CaO, $Al_2O_3$, $SiO_2$ compounds.

The compound $5CaO.3Al_2O_3$ (stable form) is also isotropic but is easily recognized by its brown color and low refractive index, 1.608.

The three major constituents $\beta$-$2CaO.SiO_2$, $3CaO.SiO_2$ and $3CaO.Al_2O_3$, however, are not so easily differentiated, owing to a similarity of certain optical characteristics. This similarity probably accounts for the fact that certain investigators who have studied these compounds only in mixtures or who have at least not given accurate quantitative values to the optical characteristics of each, have concluded that Portland cement clinker is in the main either a solid solution or a single definite ternary compound. That the conclusions of these investigators are erroneous is evident to one who makes a careful study of these three compounds even as they occur in fine-grained mixtures.

It will be noticed by reference to Table I that the refractive indices of these three compounds are more or less similar, especially those for $3CaO.SiO_2$ and $3CaO.Al_2O_3$ which are respectively 1.715 and 1.710. But $3CaO.SiO_2$ is birefracting, though its birefringence is weak, often shows twinning lamellae, and is optically negative, while $3CaO.Al_2O_3$, on the other hand, is isotropic. Both appear as colorless grains. The $\beta$-$2CaO.SiO_2$ is more easily identified by its somewhat higher refractive indices $\alpha$1.717, $\gamma$1.735, its stronger birefringence and optical character, which is positive.

It may be noted that these conclusions relative to the formation and occurrence of the above compounds in cement clinker made from pure materials and to the optical properties of these compounds have been corroborated by subsequent work under the auspices of the Bureau of Standards.

Hitherto we have considered the constituents of clinkers composed of the three pure oxides only; let us now inquire into the effect of the presence of $Fe_2O_3$ and MgO, small quantities of which are always present in commercial clinker, on the optical characteristics of CaO-$Al_2O_3$-$SiO_2$ compounds. We have done little direct work on this question here, so we shall rely mainly on the results obtained by Bates, Klein and Phillips.

They found that both the compounds $\beta$-$2CaO.SiO_2$ and $5CaO.3Al_2O_3$ are colored by the iron oxide but that otherwise the optical properties are not materially affected. The iron oxide apparently does not color either $3CaO.SiO_2$ or $3CaO.Al_2O_3$. In so far as we have studied the effect of iron oxides on the optical properties of these compounds our results corroborate the statements just made.

The question as to the effect of MgO on the optical properties of compounds in Portland cement clinker is the subject of a special investigation by Klein and Phillips.[1] They found in certain Portland cement clinkers of high MgO content that the $\beta$-$2CaO.SiO_2$ and $3CaO.Al_2O_3$ agree very closely with those described in the published work of this laboratory, in all obtainable properties except the index of refraction which was lower in both instances and furthermore not constant. This led them to an investigation of the possibility of the replacement of CaO by MgO in these compounds, from which they concluded, that in all compositions in which MgO replaces up to 10 per cent of the CaO in the compound $3CaO.Al_2O_3$, the product obtained on burning is homogeneous, with a refractive index which ranges from 1.71 (that of pure $3CaO.Al_2O_3$) to 1.67 when 10 per cent of the CaO has been replaced by MgO.

However, on repeating their experiments we found that in no case was the final product homogeneous; on the contrary, it is a mixture of free MgO, the compound $5CaO.3Al_2O_3$ and the compound $3CaO.Al_2O_3$. Furthermore, the refractive index of the compound $3CaO.Al_2O_3$ in these mixtures is constant, being 1.71; indeed, the refractive index of this compound remains constant for all compositions of CaO, $Al_2O_3$, MgO in which it occurs as we have found in the course of an extended investigation of the ternary system of these three oxides.[2]

There are, then, two similar series of experiments performed with the same oxides in the same proportions resulting in apparently widely different products; but this discrepancy can, we believe, be explained readily. The products we obtained are composed of MgO, $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ all of which are isotropic with refractive indices 1.734, 1.710 and 1.608, respectively. Taken as individuals, the refractive index of each of these compounds is easily determined but in fine-grained mixtures of all of them, the product might appear homogeneous with a refractive index equal to that of the aggregate unless great care is exercised in the microscopical analysis. That Klein and Phillips may have mistaken this aggregate effect for homogeneity appears probable if we consider the value of the average refractive index of MgO, $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ in the proportions such that the total composition of the mixture can be represented as $3CaO.Al_2O_3$ in which a portion of the CaO is replaced by MgO. From our study of the percentage of each of these compounds present in such a case, we know that as the MgO, replacing the CaO, increases from 0 to 10 per cent, the $3CaO.Al_2O_3$ decreases from 100 to about 50 per cent while $5CaO.$-

[1] *Orig. Comm. 8th International Congr. App. Chem.*, **5**, 81.

[2] The results of an investigation by G. A. Rankin and H. E. Merwin of this system will be published in the near future.

$3Al_2O_3$ increases from 0 to about 40 per cent; that is, the $5CaO.3Al_2O_3$ of low refractive index increases in amount relatively faster than the MgO of high refractive index, while $3CaO.Al_2O_3$ decreases in amount; consequently, the average refractive index will decrease with increase of MgO. If now we calculate the average refractive index for the aggregate containing 10 per cent MgO, 50 per cent $3CaO.Al_2O_3$, 40 per cent $5CaO.3Al_2O_3$ we obtain the value 1.672—a value which corresponds very closely with 1.67 obtained by Klein and Phillips as the refractive index of their so-called homogeneous compound in which 10 per cent of the CaO in the 3–1 aluminate is replaced by MgO. Further increase in the percentage of MgO does not materially change the aggregate refractive index; moreover, as Klein and Phillips found, the identification of free MgO is then more readily made, though they were apparently not able to distinguish $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ in these mixtures.

In the foregoing discussion we have presented an explanation for the apparent partial replacement of CaO by MgO in the compound $3CaO.Al_2O_3$, which Klein and Phillips believe to take place but which our investigation would tend to disprove. We have found, moreover, that pure MgO does not form solid solution with pure $3CaO.Al_2O_3$. It may be, however, that in presence of iron oxide or some other minor constituent of Portland cement clinker, MgO does form solid solution with $3CaO.Al_2O_3$. This is a matter which we have not investigated and so for the present, at least, we accept the statements of Klein and Phillips to the effect that Portland cement clinker may contain 7.5 per cent MgO without its being present as free MgO or $MgO.Al_2O_3$, and that MgO replaces CaO in $\beta$-$2CaO.SiO_2$ up to 6 per cent. However, as the average percentage of MgO in Portland cement is only about 2.5 per cent, its effect on the optical properties of the CaO, $Al_2O_3$, $SiO_2$ compounds is necessarily slight; in other words, as Klein and Phillips have found, the effect of the MgO, no matter in what form it may be present, is not such as to materially change the optical characteristics of the CaO, $Al_2O_3$, $SiO_2$ compounds in Portland cement.

## CONCLUSIONS

From the work which has been done in this laboratory on clinkers composed only of the pure oxides CaO, $Al_2O_3$, $SiO_2$, and the supplementary work by the Bureau of Standards on commercial cements, it would seem that certain conclusions may be drawn as to the nature of the constituents of Portland cement clinker.

I—Well-burned cement clinker made up from the pure oxides CaO, $Al_2O_3$, $SiO_2$, in the proper proportions, will consist largely of the compounds $3CaO.SiO_2$, $2CaO.Al_2O_3$, $2CaO.SiO_2$, with small quantities of free lime and of the compound $5CaO.3Al_2O_3$. These are present as individuals of constant optical properties and not as solid solutions.

II—The work at the Bureau of Standards has shown that the constituents of commercial Portland cement clinker are essentially the same as those which we found in clinker made up only of CaO, $Al_2O_3$, $SiO_2$. This fact is best illustrated with data such as are presented in Table II.

The examples given in Table II to prove this point are based on the averages for a large number of analyses of each of three types of Portland cement clinker, *viz.*, pure cement, made only of CaO, $Al_2O_3$, $SiO_2$; commercial white cement; and the more common gray variety of commercial Portland cement.

If the raw material for pure cement is perfectly burned at a temperature of 1650°, the clinker obtained will consist of the three compounds—orthosilicate of lime, tricalcic silicate, and tricalcic aluminate. The example of a pure cement, given in Table II, has the chemical composition 68.4 per cent lime, 8.0 per cent alumina, 23.6 per cent silica.

TABLE II—COMPOSITIONS AND BURNING TEMPERATURES OF VARIOUS PORTLAND CEMENTS[1]

| Portland Cements | Percentage Composition of Clinker: Actual Constituents | | Relative to content of $CaO-Al_2O_3-SiO_2$ | | Burning temperature °C | Constituents of Resulting Cements | |
|---|---|---|---|---|---|---|---|
| Pure (P) | CaO 68.4<br>$Al_2O_3$ 8.0<br>$SiO_2$ 23.6 | 100.0 | CaO 68.4<br>$Al_2O_3$ 8.0<br>$SiO_2$ 23.6 | | 1650 | 2 $CaO.SiO_2$<br>3 $CaO.SiO_2$<br>3 $CaO.Al_2O_3$ | |
| White (A) | CaO 66.2<br>$Al_2O_3$ 6.4<br>$SiO_2$ 25.0 | 97.6 | CaO 67.9<br>$Al_2O_3$ 6.5<br>$SiO_2$ 25.6 | | 1525 | 2 $CaO.SiO_2$<br>3 $CaO.SiO_2$<br>3 $CaO.Al_2O_3$ | Small amount of CaO |
| | MgO, $Fe_2O_3$, $Na_2O$ and $K_2O$ | 2.4 | | | | | |
| Gray (B) | CaO 63.2<br>$Al_2O_3$ 7.7<br>$SiO_2$ 22.4 | 93.3 | CaO 66.7<br>$Al_2O_3$ 9.0<br>$SiO_2$ 24.3 | | 1425 | 2 $CaO.SiO_2$<br>3 $CaO.SiO_2$<br>3 $CaO.Al_2O_3$ | Small amounts of 5 $CaO.3Al_2O_3$, CaO and ferrites |
| | MgO, $Fe_2O_3$, $Na_2O$, $K_2O$ and $SO_3$ | 6.7 | | | | | |

[1] The data given in this table are based largely on the work of this laboratory. The analyses of commercial clinkers are from publications from the Bureau of Standards and from "Portland Cement" by R. K. Meade. The temperatures of burning and the constituents given are based both on our work and that of the Bureau of Standards.

The raw material for white commercial cement, when burned at a temperature of 1525°, will produce a clinker which consists largely of the same three compounds found in pure clinker except for a small amount of free lime. The average chemical composition of this type of cement as given in the table is 66.2 per cent lime, 6.4 per cent alumina, 25 per cent silica, and 2.4 per cent magnesia, iron oxide and alkali.

The clinker obtained on burning the raw material for commercial gray cement at 1425° will consist largely of the same three compounds found in the other two types of clinker, except for small amounts of free lime, the compound $5CaO.3Al_2O_3$, and iron oxide as ferrites. The composition of this clinker is 63.2 per cent lime, 7.7 per cent alumina, 22.4 per cent silica, 6.7 per cent MgO, $Fe_2O_3$, alkali and $SO_3$.

The similarity of these three types of cement clinkers is not surprising if we consider their chemical compositions. The lime, alumina, silica content of each type is over 90 per cent, while the composition relative only to these three oxides approaches a constant, the maximum difference being 2.5 per cent in the case of alumina, since there is 6.5 per cent in white cement and 9.0 per cent in gray cement. We should expect,

therefore, and it has been found experimentally to be true, that these three types of cement clinker are made up largely of the same constituents; these are, as we have shown, tricalcic silicate, dicalcium silicate, and tricalcic aluminate, all compounds of the three major components of cement, namely, lime, alumina, silica.

Microscopical examinations of cement clinkers have shown that these three compounds have definite optical characteristics. These definite optical characteristics persist even when these compounds are formed in the presence of magnesia, iron oxides, etc., in the proportions in which these minor components occur in Portland cement during the burning of the clinker. Of these minor components, the iron oxide combines with CaO to form a ferrite, and is at times found in clinker as magnetite. The MgO and alkalies are apparently taken up in solid solution by tricalcium aluminate and dicalcium silicate. The percentage of MgO with the alkali is, however, so small (not over 3.0 per cent) that the optical identity of these two compounds, $3CaO.Al_2O_3$, $2CaO.SiO_2$, is not in the least obscured.

During the burning of cement clinker, however, these minor constituents play an important part, since their presence makes possible the formation of a flux at a low temperature, and this materially assists the combination of CaO with $Al_2O_3$ and $SiO_2$. This fact is well illustrated by the data in Table II. Pure cement requires a temperature of 1650° for burning; white cement (with 2.4 per cent MgO, $Fe_2O_3$, etc.) requires a temperature of only 1525°, while gray cement with 6.7 per cent of the minor constituents, requires a temperature no higher than 1425° for producing a clinker which makes a sound cement. The importance of these minor components is evident, therefore, since an average gray commercial clinker can be burned at a temperature 225° lower than that required for a pure clinker.

These minor components ($Fe_2O_3$, MgO, alkali, etc.), then, may be considered as catalyzers; *i. e.*, they assist in the formation of the CaO, $Al_2O_3$, $SiO_2$ compounds which make up the larger part of the clinker but they do not materially affect the identity of those compounds. Consequently, the constitution of cement clinker depends largely on the composition of the clinker relative *only* to its CaO, $Al_2O_3$, $SiO_2$ content.

The average commercial composition relative *only* to these three oxides, for the three types of clinker, approaches a constant, as is shown by data in Table II. In Fig. 2 (an enlarged portion of Fig. 1) these average compositions of the three types of clinker are represented by the points: P, pure cement; A, white cement; and B, gray cement. The other dots, crosses, and circles in this figure represent several compositions for each of these three types of cements. It will be seen that the three groups of dots lie within a rather limited area of composition, and that this composition area is all included within the triangle in which dicalcium silicate, tricalcium silicate, and tricalcium aluminate are the only compounds present under conditions of equilibrium. For pure cement, made only of CaO, $Al_2O_3$ and $SiO_2$ we have shown that it is possible to attain this condition of equilibrium, and that the clinker obtained will consist of only these three compounds, which, when ground and made into a mortar, will produce a sound cement.

Commercial cements, A and B, have a lime, alumina, silica content of over 90 per cent. The remainder, less than 10 per cent MgO, iron oxide, alkali, etc., as a flux assists the combination of the CaO with alumina and $SiO_2$ but does not materially enter into these combinations. In other words, the CaO, $Al_2O_3$, $SiO_2$ in commercial clinker combine to form the same compounds which are found in pure cement clinker.

In actual practice, however, commercial clinker is not always perfectly burned, so that one often finds small amounts of free lime and the compound $5CaO.Al_2O_3$, the two constituents other than the three already mentioned, which occur if pure cement is not perfectly burned (equilibrium has not been attained). This is to be expected since CaO and the compound $5CaO.3Al_2O_3$ are the two constituents, other than the three major constituents, found in the adjacent triangles of Fig. 2.

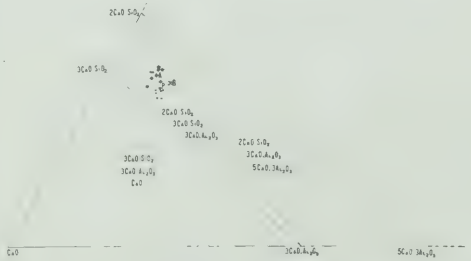

FIG. 2—AN ENLARGED PORTION OF FIG. 1

This shows several compositions relative only to the CaO, $Al_2O_3$, $SiO_2$ content for each of three types of cement clinker. The dots represent these compositions of pure clinker, the crosses white commercial clinkers, and the circles gray commercial clinkers.

That the free lime and the compound $5CaO.Al_2O_3$ nearly always occur only in *small* amounts clearly indicates, however, that most commercial cement clinker approaches a condition of equilibrium, *i. e.*, most commercial clinker has been almost perfectly burned.

It is true that we do not as yet know how close an approach to equilibrium is desirable in commercial clinker. We do know, however, that there are three factors which can be controlled and which influence during burning the clinker obtained from a given raw mix. These factors are: F, fineness of raw material; T, temperature of kiln; and S, speed of material through the kiln.

For a practical working formula, Mr. Richard K. Meade has expressed the relation of these three factors in the form of an equation: FTS = C, C being a constant. If we increase F sufficiently, it is possible to reduce T and S, and similarly, if T is sufficiently high F and S may be decreased. While this is but a rough attempt to explain in simple terms the three factors influencing the burning of clinker, still it should be possible to establish, from a given raw mix, a rela-

tion between F, T and S, which would be the most economical for producing a desirable clinker.

SUMMARY

In attacking a problem such as the question of the constituents of Portland cement clinker one must proceed in a systematic manner. After ascertaining which are the essential components, one must determine by experiment just how these components combine under the particular conditions, and the nature and mutual relations of the several compounds formed; this involves the investigation of the composition, the number and relation of the various crystalline forms of the several compounds, and their optical characteristics, as well as the study of the state of equilibrium reached by mixtures of all compositions throughout the range of temperatures. One is then able to state precisely what will happen when any mixture of the above three oxides is heated or cooled slowly (so that equilibrium is continuously attained) and to indicate the course and final products of reaction when equilibrium is approached but not completely attained.

The essential chemical components of Portland cement clinker are lime, alumina, and silica, from a mixture of which in the proper proportions a clinker, possessing all the properties of a desirable Portland cement, can be made by proper burning. Such a clinker will consist of the three compounds, $3CaO.SiO_2$, $2CaO.SiO_2$ and $3CaO.Al_2O_3$; if, during the burning, complete equilibrium has not been reached—as happens in actual practice—there will be, in addition to the above three major constituents, two minor ones, *viz.*, CaO and $5CaO.3Al_2O_3$.

It has been argued by some that not even an approximation of equilibrium conditions obtains in the actual manufacture of Portland cement, and hence that conclusions derived from a study of the equilibrium diagram of this system would have little or no bearing on the question of the constituents of commercial clinker. It may be contended that equilibrium conditions are not attained in the burning of commercial clinker, but the work on actual clinkers already published from the laboratory of the Bureau of Standards, which was based upon the equilibrium diagram of the system $CaO–Al_2O_3–SiO_2$, has disproved this contention. Indeed, one must conclude that the nearer the approach to equilibrium the better the resultant cement, judging from the great stress which is now laid on fine grinding of the raw materials and from the lengthening out of the cement kilns—factors which, by securing more intimate contact of the components and by increasing the period of heating, obviously make for a nearer approach to equilibrium. As to how close an approach to equilibrium (perfect burning) is desirable or economically possible, it is not as yet possible to say from the data available; these data can be obtained, for a given raw mix, only by investigation. Such an investigation would necessitate careful research to determine the relation between time, temperature of burning, and fineness of grinding, of given raw materials, in order to produce good clinker at the lowest possible cost to the manufacturer.

Actual cement clinker contains small quantities of MgO and iron oxide, which are advantageous in that their presence during burning promotes the attainment of equilibrium by lowering the temperature at which liquid appears (fluxing) and by increasing the amount of such liquid; but they would seem—to judge from the available reliable evidence—to have little influence on the final main constituents of the clinker. This latter statement, be it noted, refers only to the clinker, and implies nothing as to whether such admixtures have or have not a beneficial influence on the cementing qualities of the product when mixed with water.

Now that the constitution of the clinker has been definitely established, it is practicable to attack the problem of the hydration of Portland cement; indeed the results of an investigation along this line have already been published from the Pittsburg laboratory of the Bureau of Standards.[1] By ascertaining precisely what happens on the hydration of each possible constituent of the clinker separately and in all the possible permutations and combinations, it should finally prove possible to determine the proportions of the various constituents which should be present in the clinker in order to produce a cement which on setting will possess the most desirable qualities, *e. g.*, the greatest strength; and from a study of the equilibrium diagram one can learn just how to proceed in order to produce a clinker of this optimum composition. In conclusion, it may be remarked that the effect of admixture of other materials can be definitely ascertained only by the systematic, and somewhat laborious procedure described above; such a procedure, nevertheless, will lead sooner to the discovery of the optimum composition in various cases and for various purposes than the empirical or cut and try method which hitherto has been the only method tried.

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## THE FUSIBILITY OF COAL ASH IN VARIOUS ATMOSPHERES[2]

BY A. C. FIELDNER AND A. E HALL

*(Concluded from May issue)*

### E—MOLYBDENUM FURNACES 1 AND 2

In order to study the fusibility of ash in an atmosphere of hydrogen, a molybdenum-wire resistance furnace[3] was built as shown in Fig. 9. The maximum safe working temperature of this furnace was ample for softening any ash. At 1750° the alundum tube carrying the molybdenum wire began to soften perceptibly. The furnace was operated with alternating current from a transformer having a number of leads from the secondary connected to a switchboard, so that by a suitable manipulation of switches the voltage

[1] "Hydration of Portland Cement," by A. A. Klein and A. J. Phillips. No. 43, of the Technologic Papers of the Bureau of Standards.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Winne, R., and Dantsizen, C., "Small Electric Furnace with Heating Element of Ductile Tungsten or Ductile Molybdenum," THIS JOURNAL, 3 (1911), 770–771.

on the furnace could be varied from 2 to 90 volts in steps of 2 volts. A field rheostat in series with the furnace was used for closer regulation: 2 to 2.5 K. V. A. were required to heat the furnace to 1600° C. The front of the furnace was water-jacketed to prevent overheating the rubber gaskets and insulation surrounding the electrodes. Hydrogen[1] was admitted from a tank through a reducing valve and a wash bottle of concentrated sulfuric acid, to the interior of the furnace at two points. During operation, the rate of flow was just sufficient to sustain a small flame at the upper exit at the rear of the furnace. Any water collecting in the furnace was drawn off at the bottom of the exit tube.

The heating space ($1^1/_4$ in. diameter × 12 in. long) afforded a very uniformly heated portion approximately 4 in. long. Back of the center the tube was closed by 4 thin disks of alundum. The ash cone was placed in a No. 5811 alundum extraction thimble ($1^1/_8$ in. diameter × 3 in. long) which was then pushed back to a distance of $^1/_2$ in. from the first alundum disk as shown in Fig. 9. It was necessary so to adjust the distance of the cone from the back of the capsule that a slight difference of temperature existed between them, otherwise the cone became invisible.

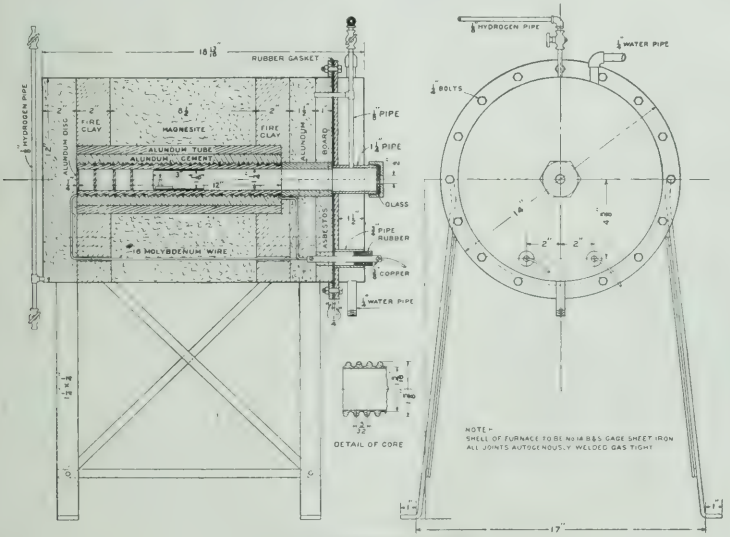


FIG. 9—MOLYBDENUM FURNACE

The temperature measurements were made with a Wanner optical pyrometer. The correction for the glass used in the observation window was determined at various temperatures between 1000 and 1500° C. This was done by observing the apparent temperature of an alundum disk in a platinum resistance furnace, with and without interposing the glass, the temperature of the disk being kept constant during the two readings as indicated by a thermo-element embedded in it. The following corrections were observed:

APPARENT TEMPERATURE (CENTIGRADE) BY WANNER PYROMETER

| | | | | | |
|---|---|---|---|---|---|
| Without glass | 1080 | 1185 | 1287 | 1380 | 1486 |
| With glass | 1068 | 1170 | 1267 | 1360 | 1462 |
| Difference | —12 | —15 | —20 | —20 | —24 |

All results given are corrected for glass according to the above table. The order of accuracy of the temperature readings is shown by the following apparent melting points obtained on thin strips of Kahlbaum's pure copper and nickel, which were mounted in the same position as the ash cones:

| COPPER (M. P. = 1083° C.) | | NICKEL (M. P. = 1450° C.) | |
|---|---|---|---|
| Date | Apparent melting point | Date | Apparent melting point |
| 5/ 5/13 | 1084 | 10/ 1/13 | 1455 |
| 9/23/13 | 1088 | 11/ 6/13 | 1448 |
| 11/ 6/13 | 1084 | 12/ 1/13 | 1445 |
| 12/ 1/13 | 1082 | 1/ 5/14 | 1448 |
| 1/12/14 | 1080 | 2/12/14 | 1440 |
| 5/ 5/14 | 1088 | 3/18/14 | 1448 |
| 6/ 9/14 | 1096 | 4/ 9/14 | 1451 |
| 10/ 6/14 | 1088 | 6/ 4/14 | 1440 |
| 11/ 3/14 | 1080 | 11/ 3/14 | 1448 |

In operating the molybdenum furnace, a rapid current of hydrogen was admitted until on ignition at the exit tube it burned with a steady flame. The hydrogen current was then reduced to 3 bubbles per sec. through the sulfuric acid bottle and the heating current turned on. A temperature of 900° was reached in approximately 1 hr.; the temperature was then increased at the rate of 10° per minute to a point not less than 200° below the probable softening point, and thence at a predetermined rate of 2, 5, or 10° per min. as desired, until the cone was down.

SERIES 1, comprising all the softening points determined in molybdenum furnace No. 1, is given in Table VIII. Since the heating space was only $1^1/_4$ in. high, the $^1/_4$ in. × $1^1/_2$ in. cone could not be used in this furnace without cutting off $^1/_2$ in. at the base. This made a cone of $^3/_{16}$ in. base × 1 in. high which gave slightly lower softening points than the $^1/_4$ in. × 1 in. cone; however, the average difference of 11° is quite negligible in comparison with other factors.

SERIES 2—Molybdenum furnace No. 2 was built in the same manner as No. 1. On repeating some of the tests that had been made in furnace No. 1, it was found that considerably higher softening points were being obtained, although all the test conditions were apparently the same as before. The entire series was, therefore, repeated, with the result that most of the samples softened at from 50 to 100° higher than in Series 1; in 4 samples of rather high iron content the softening point was raised 200°.

The cause of this variation was finally traced to

[1] 99.8 per cent hydrogen and 0.2 per cent ($CO_2$ + $O_2$ + $N_2$)—Analysis by G. A. Burrell and G. G. Oberfell.

a difference in the amount of water vapor present with the hydrogen in the furnace atmosphere. Considerable trouble was experienced from water collecting in the hydrogen exit pipe of the No. 1 furnace. Moisture also collected in the water-cooled observation tube at the front of the furnace. After rebuilding the furnace little or no condensation of water was noticed. The effect of a larger proportion of water vapor in

TABLE VIII—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MOLYBDENUM FURNACE NO. 1, USING TWO SIZES OF CONES—SERIES 1

Rate of heating, 2° per minute; 100 mesh ash; cones inclined 35° from vertical

| | Softening Point in °C. | | | | |
|---|---|---|---|---|---|
| | Cone 1 | Cone 3 | | | Difference |
| | 1/4 in. × 1 in. | 3/16 in. × 1 in. | Averages | | in average |
| Ash No. | Duplicates | Duplicates | Cone 1 | Cone 3 | values |
| 1 | 1123 | 1123 | 1123 | 1123 | 0 |
| 2 | 1430 1417 | | 1430 | 1417 | −13 |
| 3 | 1444 1470 | 1396 | 1457 | 1396 | +61 |
| 4 | 1227 | 1248 1220 | 1227 | 1234 | −7 |
| 5 | 1234 | 1241 1220 | 1234 | 1231 | + 3 |
| 6 | 1350 | 1340 1331 | 1350 | 1336 | +14 |
| 7 | 1580 1600 | 1580 1580 | 1590 | 1580 | +10 |
| 8 | 1318 | 1263 | 1318 | 1263 | +55 |
| 9 | 1213 | 1199 | 1213 | 1199 | +14 |
| 10 | 1185 | 1192 | 1185 | 1192 | −7 |
| 11 | 1220 | 1220 | 1220 | 1220 | 0 |
| 12 | 1068 | 1060 | 1068 | 1060 | + 8 |
| 13 | 1217 | 1217 | 1217 | 1217 | 0 |
| 14 | 1320 1331 | 1300 1331 | 1326 | 1316 | +10 |
| 15 | 1167 | 1161 | 1167 | 1161 | + 6 |
| 16 | 1241 | 1241 | 1241 | 1241 | 0 |
| 17 | 1192 | 1179 | 1192 | 1179 | +13 |
| 18 | 1199 | 1185 | 1199 | 1185 | +14 |
| 19 | 1562 | 1558 1558 | 1562 | 1558 | + 4 |
| | | | | Average, | +11 |

the hydrogen atmosphere of furnace No. 1 would be to retard the formation of metallic iron to a greater extent than in furnace No. 2. Consequently more ferrous oxide would be available to lower the softening temperature of the ash in the first series. As shown in Fig. 10, the largest differences occurred in Samples 12, 1, 5 and 8 containing 36, 33, 19 and 18 per cent

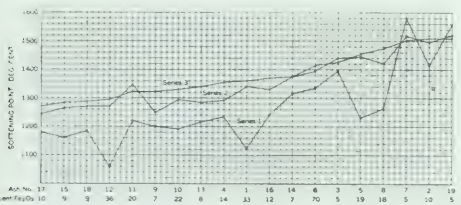


FIG. 10—COMPARISON OF THREE SERIES OF SOFTENING TEMPERATURES OBTAINED IN MOLYBDENUM FURNACE, SHOWING EFFECT OF WATER VAPOR

ferric oxide, respectively. The smallest differences were usually found with those samples which contained 7 per cent or less of ferric oxide.

The above deductions were further verified by examining polished sections of the fused cones under the microscope; in general, more metallic iron was visible in Series 2, than in the corresponding cones of Series 1. Also, some of the fused cones from both series were pulverized and analyzed. The results are given in Table IX.

TABLE IX—PERCENTAGES OF IRON IN CONES FROM SERIES 1 AND 2

| | Percentages Fe—Series 1 | | | Percentages Fe—Series 2 | | |
|---|---|---|---|---|---|---|
| Ash No. | Metallic | Ferrous | Ferric | Metallic | Ferrous | Ferric |
| 1 | 13.9 | 10.3 | 1.6 | 19.1 | 18.2 | Trace |
| 4 | 1.4 | 7.1 | None | 2.2 | 6.1 | None |

All the softening points determined in Series 2 are reported in Table X. Heating at the rate of 5° per minute tends to give somewhat higher softening points, the maximum difference being 65° and the average difference being 10°. The average difference of duplicate determinations (24°) was practically the same as was obtained with the 1/4 in. × 1 1/2 in. cones in the various furnaces previously described.

SERIES 3—Here the test conditions were changed by grinding the ash to an impalpable powder instead

TABLE X—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MOLYBDENUM FURNACE NO. 2 AT TWO DIFFERENT RATES OF HEATING—SERIES 2

100 mesh ash; 3/16 in. × 1 in. cone inclined 35° from vertical

| | Softening Point in °C | | | | |
|---|---|---|---|---|---|
| | 2° rate | | | Difference of duplicates | Difference of average values 5° and 2° rates |
| Ash No | 5° rate | Duplicates | Av. | 2° rate | |
| 1 | | 1340 | 1340 | | |
| 2 | | 1492 1502 | 1497 | 10 | |
| 1x[a] | 1440 | 1414 | 1414 | | +26 |
| 3 | | 1440 | 1440 | | |
| 4 | | 1263 1304 | | | |
| | | 1309 | 1292 | 46 | |
| 4x | 1234 | 1248 | 1248 | | −14 |
| 5 | 1448 | 1445 | 1445 | | + 3 |
| 5x | 1414 | 1402 | 1402 | | +12 |
| 6 | | 1410 1380 | 1395 | 30 | |
| 7 | | 1520 1516 | 1518 | 4 | |
| 8 | | 1375 1441 | | | |
| | | 1435 1434 | 1421 | 66 | |
| 9 | | 1248 1248 | 1248 | 0 | |
| 10 | | 1283 1304 | 1294 | 21 | |
| 11 | | 1335 1360 | 1348 | 25 | |
| 12 | | 1271 1271 | 1271 | 0 | |
| 12x | 1402 | 1345 1380 | 1363 | 35 | +39 |
| 13 | | 1271 1295 | 1283 | 24 | |
| 13x | 1390 | 1380 | 1380 | | +10 |
| 14 | | 1350 1402 | 1376 | 52 | |
| 14x | 1295 | 1300 1331 | 1316 | 31 | −21 |
| 15 | | 1271 1260 | 1266 | 11 | |
| 15x | 1402 | 1380 | 1380 | | +22 |
| 16 | | 1322 1336 | 1330 | 14 | |
| 16x | 1345 | 1360 | 1360 | | −15 |
| 17 | | 1241 1245 | 1243 | 4 | |
| 17x | 1360 | 1295 | 1295 | | +65 |
| 18 | | 1279 1263 | 1271 | 16 | |
| 18x | 1287 | 1279 | 1279 | | + 8 |
| 19 | | 1540 1502 | 1521 | 38 | |
| 20 | 1615 | 1621 | 1621 | | − 6 |
| 21 | 1601 | 1615 | 1615 | | −14 |
| 23 | 1520 | 1474 | 1474 | | +46 |
| 25 | 1173 | 1167 | 1167 | | + 6 |
| 30 | 1355 | 1350 | 1350 | | + 5 |
| 31 | 1313 | 1258 | 1258 | | +55 |
| 32 | 1365 | 1340 | 1340 | | +25 |
| 33 | 1390 | 1380 | 1380 | | +10 |
| 35 | 1470 | 1463 | 1463 | | + 7 |
| 36 | 1309 | 1300 | 1300 | | + 9 |
| 37 | 1300 | 1295 | 1295 | | + 5 |
| 38 | 1304 | 1291 | 1291 | | +13 |
| 39 | 1295 | 1291 | 1291 | | + 4 |
| 40 | 1360 | 1350 | 1350 | | +10 |
| 41 | 1370 | 1365 | 1365 | | + 5 |
| 42 | 1345 | 1340 | 1340 | | + 5 |
| 43 | 1328 | 1334 | 1334 | | − 6 |
| 44 | 1328 | 1328 | 1328 | | 0 |
| 45 | 1331 | 1322 | 1322 | | + 9 |
| 46 | 1340 | 1338 | 1338 | | + 2 |
| 47 | 1328 | 1335 | 1335 | | − 7 |
| 48 | 1350 | 1353 | 1353 | | − 3 |
| [a] Intrinsic ash | | | Average, | 24 | +10 |

of 100 mesh, and by mounting the cone in a vertical position instead of at an inclination of 35°.

The softening temperatures obtained on heating at rates of 10, 5 and 2° per minute are given in Table XI. The average difference between a 5° and 2° rate of heating was 12° as compared with 10° in Series 2. Heating at the rate of 10° per minute caused an average increase of 40° in the softening point over that obtained with a 2° rate.

In Table XII and Fig. 10 is given a comparison of the three series of softening-temperature determinations made in the molybdenum furnaces at a 2° rate of heating. The average difference of 110° between Series 1 and 2 is attributed to the higher proportion of water vapor in Furnace 1 which retarded the reduction of ferrous oxide to metallic iron. The average increase of 21° of Series 3 over Series 2 is exactly the same as the average increase of the softening interval,[1] *i. e.*,

[1] Difference in temperature of initial and of final deformation point.

the temperatures of initial deformation were the same in both series. Therefore, the higher results of the last series seem to be largely due to placing the cone in a vertical position, rather than to the finer grinding

TABLE XI—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MOLYBDENUM FURNACE NO. 2, AT THREE DIFFERENT RATES OF HEATING—SERIES 3

Ash ground to an impalpable powder; 3/16 in. × 1 in. cone placed in a vertical position

| Ash No. | Softening Point in °C. Rate per minute 10° | 5° | 2° | Difference in duplicates 5° | 2° | Difference in average values 10° and 2° | 5° and 2° |
|---|---|---|---|---|---|---|---|
| 1 | 1382 1414 | 1380 1390 | 1365 1355 | | | | |
| | Av. 1398 | Av. 1385 | Av. 1360 | 10 | 10 | +38 | + 25 |
| 2 | .. | .. | 1520 1502 | | | | |
| | 1562 | 1520 | Av. 1511 | .. | 18 | +51 | + 9 |
| 3 | | | 1440 1414 | | | | |
| | 1460 | 1414 | Av. 1427 | | 26 | +33 | — 13 |
| 4 | 1409 | 1360 | 1355 | | | +54 | + 5 |
| 5 | 1502 | 1462 | 1455 | | | +47 | + 7 |
| 6 | 1421 | 1402 | 1414 | | | + 7 | — 12 |
| 7 | 1540 | 1502 | 1502 | | | +38 | 0 |
| 8 | | 1486 1470 | 1478 1470 | | | | |
| | 1520 | Av. 1478 | Av. 1474 | 16 | 8 | +46 | — 4 |
| 9 | | 1313 1375 | 1313 1331 | | | | |
| | 1365 | Av. 1344 | Av. 1322 | 62 | 18 | +43 | + 22 |
| 10 | 1380 | 1340 | 1331 | | | +49 | + 9 |
| 11 | 1402 | 1427 | 1322 | | | +80 | +105 |
| 12 | 1322 | 1300 | 1295 | | | +27 | + 5 |
| 13 | 1402 | 1350 | 1340 | | | +62 | + 10 |
| 14 | 1427 | 1402 | 1375 | | | +52 | + 27 |
| 15 | 1300 | 1291 | 1283 | | | +17 | + 8 |
| 16 | 1380 | 1380 | 1370 | | | +10 | + 10 |
| 17 | 1295 | 1271 | 1271 | | | +24 | 0 |
| 18 | 1340 | 1340 | 1287 | | | +53 | + 53 |
| 19 | | 1520 1525 | 1520 1502 | | | | |
| | 1540 | Av. 1523 | Av. 1511 | 5 | 18 | +29 | + 12 |
| 39 | | 1271 | 1283 | | | | — 12 |
| 42 | | 1318 | 1313 | | | | + 5 |
| 33 | | 1390 | 1390 | .. | .. | .. | — |
| | | | Average, | 23 | 16 | +40 | +12 |

of the ash. A vertical cone would have a larger bending interval than one inclined 35° from the vertical.

To obtain further information on the relative effect of fineness of ash and inclination of cone, two special series of experiments were made in which only one of these factors was varied at a time. The data obtained are given in Tables XIII and XIV.

TABLE XII—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MOLYBDENUM FURNACES 1 AND 2, SHOWING EFFECT OF WATER VAPOR AND INCLINATION OF CONE

Rate of heating was 2° per minute

SERIES 1—Molybdenum furnace No. 1; 100 mesh ash; 3/16 in. × 1 in. cones inclined 35° from vertical position. Water collected in exit tube of furnace.

SERIES 2—Molybdenum furnace No. 2; 3/16 in. × 1 in. cones inclined 35° from the vertical position; 100 mesh ash. No water in exit tube.

SERIES 3—Molybdenum furnace No. 2; ash ground to an impalpable powder; cones in vertical position. No water in exit tube.

| Ash No. | Softening Point in °C. 100 mesh Series 1 Furnace No. 1 | Series 2 Furnace No. 2 | Powder Series 3 Furnace 2 | Difference in average values between series 1 & 3 | 2 & 3 | Average softening interval in °C. for series 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|
| 1 | 1123 | 1340 | 1355 | —232 | —15 | 11 | 92 | 92 |
| 2 | 1417 | 1497 | 1511 | — 94 | —14 | 27 | 47 | 96 |
| 3 | 1396 | 1440 | 1427 | — 31 | +13 | 46 | 44 | 69 |
| 4 | 1234 | 1292 | 1355 | —121 | —63 | 39 | 21 | 55 |
| 5 | 1220 | 1445 | 1455 | —235 | —10 | 28 | 31 | 115 |
| 6 | 1340 | 1395 | 1414 | — 74 | —19 | 40 | 35 | 34 |
| 7 | 1580 | 1518 | 1502 | + 78 | +16 | 29 | 51 | 68 |
| 8 | 1263 | 1421 | 1474 | —211 | —53 | 29 | 40 | 64 |
| 9 | 1199 | 1248 | 1322 | —123 | —74 | 24 | 28 | 91 |
| 10 | 1192 | 1294 | 1331 | —139 | —37 | 13 | 21 | 9 |
| 11 | 1220 | 1348 | 1322 | —102 | 26 | 50 | 30 | 51 |
| 12 | 1060 | 1271 | 1295 | —235 | —24 | 20 | 44 | 147 |
| 13 | 1217 | 1283 | 1340 | —123 | —57 | 25 | 56 | 49 |
| 14 | 1316 | 1376 | 1375 | — 59 | + 1 | 22 | 31 | 88 |
| 15 | 1161 | 1266 | 1283 | —122 | —17 | 34 | 28 | 49 |
| 16 | 1241 | 1330 | 1370 | —129 | —40 | 33 | 65 | 48 |
| 17 | 1179 | 1243 | 1271 | — 92 | —28 | 12 | 25 | 30 |
| 18 | 1185 | 1271 | 1287 | —102 | —16 | 15 | 50 | 28 |
| 19 | 1558 | 1521 | 1511 | + 47 | + 10 | 26 | 56 | 103 |
| | | | Average, | —110 | —21 | 28 | 42 | 63 |

EFFECT OF FINENESS OF ASH—The effect of grinding to an impalpable powder was barely appreciable in an average reduction of 6° in the softening points of the series. The principal advantage of finer grinding was in obtaining a more plastic and intimate mixture which could be molded into more substantial cones.

EFFECT OF INCLINATION OF CONE—The effect of varying the position of the cone from vertical to an inclination of 45° was more appreciable, giving in some cases a lowering of 64° in the softening point.

TABLE XIII—EFFECT OF FINENESS OF ASH

Molybdenum furnace No. 2; 3/16 in. × 1 in. cone in a vertical position Rate of heating, 2° per minute

| Ash No. | Softening Point in °C. 100 Mesh | Powder | Diff. | Ash No. | Softening Point in °C. 100 Mesh | Powder | Diff. |
|---|---|---|---|---|---|---|---|
| 39 | 1291 | 1283 | + 8 | 67 | 1223 | 1185 | +38 |
| 9 | 1248 | 1304 | —56 | 68 | 1216 | 1205 | +11 |
| 42 | 1340 | 1313 | +27 | 69 | 1251 | 1237 | +14 |
| 48 | 1380 | 1390 | —10 | 70 | 1259 | 1263 | — 4 |
| 8 | 1435 | 1481 | —46 | 71 | 1327 | 1300 | +27 |
| 19 | 1519 | 1510 | + 9 | 72 | 1368 | 1350 | +18 |
| 2 | 1492 | 1520 | —28 | 73 | 1380 | 1370 | +10 |
| 64 | 1108 | 1101 | + 8 | | | | |
| 65 | 1155 | 1127 | +28 | | | Average, | + 6 |
| 66 | 1174 | 1173 | + 1 | | | | |

A slight inclination of not to exceed 25° gave the same result as a vertical cone. The most satisfactory indication was obtained by mounting the cone with one side vertical, which usually caused the cone to bend towards that side. An important objection to mounting the cone at any considerable inclination, as 35 or 45°, is that certain ashes shrink before they reach

TABLE XIV—EFFECT OF INCLINATION OF CONES

Molybdenum furnace No. 2; 3/16 in. × 1 in. cone; ash ground to an impalpable powder; rate of heating, 2° per minute

| Ash No. | Softening Point in °C. Inclined from vertical 45° | 25° | Vertical position | Difference 45° and vertical | 25° and vertical |
|---|---|---|---|---|---|
| 39 | 1287 | 1283 | 1283 | + 4 | 0 |
| 42 | 1295 | 1313 | 1304 | — 9 | +9 |
| 9 | 1248 | 1304 | 1313 | —65 | —9 |
| 33 | 1396 | 1390 | 1390 | + 6 | 0 |
| 8 | 1414 | 1481 | 1478 | —64 | +3 |
| 19 | 1494 | 1510 | 1502 | — 8 | +8 |
| 2 | 1520 | 1520 | 1520 | 0 | 0 |
| | | | Average, | —19 | +2 |

their softening temperature which allows the cone to fall over to a still larger inclination and thus indicate a premature down point.

EFFECT OF DEXTRIN BINDER—The results of a few experiments made to show the effect of not burning out the dextrin binder before placing the ash cone in the molybdenum furnace are given in Table XV.

TABLE XV—EFFECT OF DEXTRIN BINDER

Molybdenum furnace No. 2; 3/16 in. × 1 in. cone inclined 35° from vertical; 100 mesh ash; rate of heating, 2° per minute

| Ash No. | Softening Point in °C. Not ignited | Ignited at 850° C. | Difference |
|---|---|---|---|
| 2 | 1492 | 1502 | —10 |
| 15 | 1260 | 1271 | —11 |
| 8 | 1435 | 1434 | + 1 |
| 8 | 1430 | 1434 | — 4 |
| | | Average, | — 6 |
| No. 8 + 1 per cent dextrin | 1427 | | |
| No. 8 + 10 per cent dextrin | 1420 | | |

The maximum apparent effect was a lowering of 11° in the softening point. Mixing 10 per cent of dry dextrin with the ash caused a reduction of only 14°. However, the conclusion that dextrin causes no material effect would apply only under the condition of determining the softening point in hydrogen and water-vapor mixtures as was done in the above cited experiments.

EFFECT OF COMBINED 5° AND 2° RATE OF HEATING—A series of tests was made in which the furnace temperature was increased at the rate of 5° per min. until deformation began. The rate was then reduced to 2° per min. until the cone was down. As shown by

Table XVI, the results approximate those obtained

TABLE XVI—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN MOLYBDENUM FURNACE NO. 2, AT TWO DIFFERENT RATES OF HEATING

Ash ground to an impalpable powder; $^3/_{16}$ in. × 1 in. cone in vertical position

| Ash No. | Softening Point in °C: 2° per min. until cone was down | 5° rate until deformation began then 2° rate until cone was down | Difference |
|---|---|---|---|
| 58 | 1199 | 1220 | +21 |
| 50 | 1220 | 1217 | + 3 |
| 49 | 1520 | 1514 | + 6 |
| 55 | 1380 | 1370 | +10 |
| 28 | 1390 | 1394 | — 4 |
| 52 | 1448 | 1478 | —30 |
| 61 | 1365 | 1370 | — 5 |
| | | Average, | — 6 |

with the usual 2° rate. The combined rate has the advantage of shortening the time of a determination.

### F—PLATINUM RESISTANCE FURNACE

All the foregoing softening temperatures were determined in atmospheres which had more or less reducing action on the ferric oxide in the ash. This reduction was probably least in the Meker furnace. It would have been possible to direct a stream of air through the muffle chamber and thus remove any furnace gases which penetrated through the walls of the muffle. Such a procedure, however, would still leave some

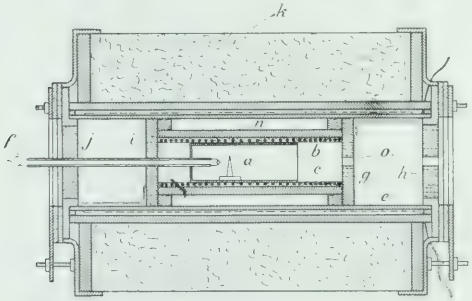


FIG. 11—SECTION THROUGH PLATINUM RESISTANCE FURNACE

*k*, Heraeus tube furnace, type B; *e*, porcelain tube, 2 $^5/_8$ inch inside diameter, 12 inches long, wound with platinum-foil heating element; *n*, alundum tube, 1 $^1/_2$ in. inside diameter, 6 in. long, $^3/_{16}$ in. wall; *c*, 17 ft. of $^3/_{100}$ in. diameter platinum wire wound on the inside of tube *n*, six turns to the inch in the middle and closer at the ends to partly compensate for radiation at the ends; *b*, alundum extraction thimble No. 5811, 30 mm. diameter, 80 mm. long; *j*, *i*, *g* and *h*, alundum disks; *o*, observation hole; *f*, Pt-PtRh thermo-element; *a*, ash cone.

doubt as to the complete removal of all traces of reducing gases. Therefore, a special platinum-wire resistance furnace (Fig. 11) was built in which there could be no question as to reduction, and in which accurate temperature measurements could be made.

The essential feature of this furnace is the platinum-wire resistor (*c*) wound on the inside of the alundum tube (*n*), which is then placed in the heating tube of a standard 110-volt Heraeus platinum-resistance furnace, and the two heaters connected in series. By this arrangement it was possible to attain a maximum temperature of 1500° C., repeatedly, without endangering the heating elements. A constant current of 12.5 amperes heated the furnace from 30 to 1450° in 63 minutes. During this interval the e. m. f. across the furnace terminals increased from 32 to 109 volts. The temperature of the space between the two heaters reached 1100°.

The inner heater was built by winding the platinum wire on a solid wood mandril 1 $^1/_4$ in. in diameter, with six turns to the inch in the middle and closer at the ends. The wire was then covered with a smooth coating of alundum cement, and the whole inserted in the alundum tube *n*. The space between the wire and tube was filled with cement. After drying slowly, the wood mandril was burned out in a muffle, and the exposed platinum wire covered with a thin slurry of alundum cement.

The temperature measurements in this furnace were more accurate than those in any of the others previously described, as shown by the following considerations:

1—The reading error of the thermo-element and millivoltmeter is less than 3° as compared with 5 to 15° in Wanner optical pyrometers.

2—No reducing gases being present, the bare hot-junction of the thermo-element could be placed very near the cone.

3—The temperature did not vary more than 5° for a distance of 1 inch on all sides of the cone, as was shown by exploration with the thermo-element.

4—A small crystal of pure diopside was placed on a sheet of platinum in the position usually occupied by the cone, and the furnace heated to 1387° as indicated by the thermo-element. After 10 minutes the crystal was removed from the furnace and found unchanged. It was then replaced in the furnace as before and the temperature held at 1392° for 10 minutes. On removal from the furnace the diopside was melted into a glassy globule. Since the melting point of diopside is 1391°, the temperature measurement was correct to within 5°.

TABLE XVII—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN THE PLATINUM RESISTANCE FURNACE AT THREE DIFFERENT RATES OF HEATING—SERIES 1

Atmosphere of air; 100 mesh ash; $^3/_{16}$ in. × 1 in. cone inclined 35° from vertical

| Ash No. | Softening Point in °C: 10° rate | 5° rate | 2° per min Duplicates | | Av. | Diff. in duplicates | Difference in average values: 10° and 2° | 5° and 2° |
|---|---|---|---|---|---|---|---|---|
| 1 | .. | .. | 1363 | 1367 | 1365 | 4 | .. | .. |
| 4(*b*) | .. | .. | 1160 | 1140 | 1150 | 20 | .. | .. |
| 4 | .. | .. | 1380 | 1385 | 1383 | 5 | .. | .. |
| 5(*a*) | 1465 | 1456 | 1450 | .. | 1450 | .. | +15 | + 6 |
| 5 | .. | .. | 1435 | 1430 | 1433 | 5 | .. | .. |
| 6(*a*) | 1415 | 1411 | 1395 | .. | 1395 | .. | +20 | +16 |
| 8 | .. | .. | 1435 | 1437 | 1436 | 2 | .. | .. |
| 9 | .. | .. | 1405 | 1385 | 1395 | 20 | .. | .. |
| 10 | .. | .. | 1300 | 1280 | 1290 | 20 | .. | .. |
| 10(*a*) | 1300 | 1302 | 1270 | .. | 1270 | .. | +30 | +32 |
| 11 | .. | .. | 1385 | 1375 | 1380 | 10 | .. | .. |
| 12 | .. | .. | 1330 | 1320 | 1325 | 10 | .. | .. |
| 15 | .. | .. | 1380 | 1380 | 1380 | 0 | .. | .. |
| 16 | .. | .. | 1300 | 1303 | 1302 | 3 | .. | .. |
| 16(*a*) | 1310 | 1310 | 1303 | 1303 | 1303 | 0 | + 7 | + 7 |
| 17 | .. | .. | 1335 | 1313 | 1324 | 22 | .. | .. |
| 17(*a*) | 1294 | 1305 | 1273 | .. | 1273 | .. | +21 | +32 |
| 18 | .. | .. | 1370 | 1345 | 1358 | 25 | .. | .. |
| | | | | | Average, | 10 | +19 | +19 |

(*a*) A second sample from the same lot of coal.
(*b*) Intrinsic ash, from coal that floated on a zinc-chloride solution of 1.35 specific gravity.

Following the same procedure as in the molybdenum-furnace experiments, two series of tests were made in the platinum furnace. In Series 1, Table XVII, the ash was ground to 100 mesh and molded into $^3/_{16}$ in. × 1 in. cones which were inclined 35° from the vertical.

In Series 2, Table XVIII, the ash was ground to an impalpable powder and the cones were mounted in

TABLE XVIII—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN PLATINUM RESISTANCE FURNACE AT THREE DIFFERENT RATES OF HEATING—SERIES 2

Atmosphere of air; ash ground to an impalpable powder; 3/16 in. × 1 in cone placed in a vertical position

| | Softening Point in °C. Rates per minute | | | Difference between rates | |
|---|---|---|---|---|---|
| Ash No. | 10° | 5° | 2° | 10° and 2° | 5° and 2° |
| 1 | 1382 | 1380 | 1365 | +17 | +15 |
| 4 | 1405 | 1405 | 1400 | + 5 | + 5 |
| 5 | .. | 1490 | 1490 | .. | 0 |
| 6 | 1475 | 1470 | 1458 | +17 | +12 |
| 8 | 1460 | 1460 | 1450 | +10 | +10 |
| 9 | 1440 | 1430 | 1425 | +15 | + 5 |
| 10 | 1320 | 1313 | 1310 | +10 | + 3 |
| 11 | 1398 | 1400 | 1400 | — 2 | 0 |
| 12 | 1390 | 1375 | 1335 | +70 | +55 |
| 13 | .. | .. | 1500 | .. | .. |
| 15 | 1407 | 1407 | 1407 | 0 | 0 |
| 16 | 1330 | 1333 | 1322 | + 8 | +11 |
| 17 | 1335 | 1345 | 1343 | — 8 | + 2 |
| 18 | 1405 | 1405 | 1400 | + 5 | + 5 |
| | | | Average, | +12 | + 9 |

a vertical position. As reported in Table XIX, the effect of grinding to an impalpable powder and mounting the cones vertically was to increase the

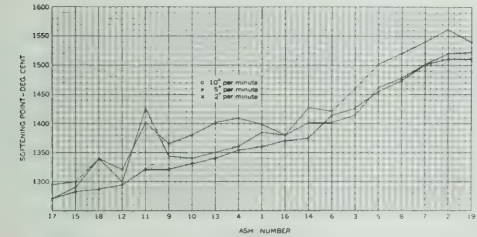


FIG. 12—EFFECT OF RATE OF HEATING ON THE SOFTENING TEMPERATURE IN AN ATMOSPHERE OF HYDROGEN

average softening point of Series 2, 19°, and the average softening interval 11°. The largest deviation in duplicate results was 30°; the average deviation was 10°—a better agreement than was obtained in any of the other furnaces. Also, varying the rate of heating from 2 to 10° per minute had less effect on the tests in air than those made in hydrogen, as shown in Figs. 12 and 13.

TABLE XIX—COMPARISON OF TWO SERIES OF SOFTENING TEMPERATURES OBTAINED IN PLATINUM RESISTANCE FURNACE SHOWING EFFECT OF INCLINATION

Rate of heating 2° per minute; 3/16 in. × 1 in. cones

| | Softening Point in °C. | | | | |
|---|---|---|---|---|---|
| | Series 1 | Series 2 | Av. softening interval °C. | | Diff. in av. values. |
| | 100 mesh ash cones inclined 35° from vertical | Powdered ash Cones vertical | Series 1 | 2 | Series 1 and 2 |
| Ash No. | | | | | |
| 1 | 1365 | 1365 | 45 | 65 | 0 |
| 4 | 1383 | 1400 | 48 | 30 | —17 |
| 5 | .. | 1490 | .. | 50 | .. |
| 6 | 1433 | 1458 | 55 | 58 | —25 |
| 8 | 1436 | 1450 | 26 | 10 | —14 |
| 9 | 1395 | 1425 | 35 | 55 | —30 |
| 10 | 1290 | 1310 | 35 | 40 | —20 |
| 11 | 1380 | 1400 | 25 | 20 | —20 |
| 12 | 1325 | 1335 | 35 | 80 | —10 |
| 13 | .. | 1500 | .. | 60 | .. |
| 15 | 1380 | 1407 | 45 | 67 | —27 |
| 16 | 1302 | 1322 | 32 | 82 | —20 |
| 17 | 1323 | 1343 | 54 | 63 | —20 |
| 18 | 1358 | 1400 | 53 | 60 | —42 |
| | | | Average, 41 | 52 | —19 |

### EFFECT OF VARIOUS ATMOSPHERES

In Table XX is given a comparison of average softening points obtained in different atmospheres under otherwise similar conditions. The maximum differences range from 143 to 425° C. In 13 samples which softened below 1500° in the platinum furnace, 8 gave

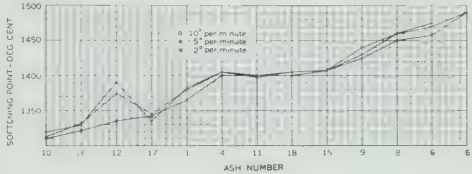


FIG. 13—EFFECT OF RATE OF HEATING ON THE SOFTENING TEMPERATURE IN AIR

their highest results in the strongly reducing carbon-monoxide atmosphere of the Northrup furnace (see Fig. 14); and five gave their highest results in the oxidizing atmosphere of the platinum furnace.

TABLE XX—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN DIFFERENT FURNACES SHOWING EFFECT OF VARIOUS ATMOSPHERES

Rate of heating, 2° per minute

| | Softening Point in °C. 100 mesh ash 1/16″ × 11/2″ Cones inclined 35° from vertical | | | | | Powdered ash 3/16″ × 1″ Cones Vertical position | | |
|---|---|---|---|---|---|---|---|---|
| | Carbon | Molybdenum | | Muffle | Meker | | Plat- | |
| Furnace Ash No. | CO+ $CO_2$+N | No. 2 H | No. 1 $H_2$+$H_2O$ | Air from-bustion gases | | Northrup CO+N | inum Air | Max. Diff. |
| 1 | 1090 | 1360 | 1123 | 1192 | | 1131 | 1365 | 275 |
| 2 | 1593 | 1511 | 1417 | .. | .. | 1645 | Above 1500 | 228 |
| 3 | 1562 | 1427 | 1396 | .. | | 1502 | Above 1500 | 166 |
| 4 | 1306 | 1355 | 1234 | 1226 | 1305 | 1360 | 1400 | 174 |
| 5 | 1356 | 1455 | 1220 | 1320 | 1376 | 1645 | 1490 | 425 |
| 6 | 1179 | 1414 | 1340 | 1318 | .. | 1455 | 1458 | 279 |
| 7 | 1638 | 1502 | 1580 | .. | .. | 1645 | Above 1500 | 143 |
| 8 | 1166 | 1474 | 1263 | 1251 | 1343 | 1562 | 1450 | 395 |
| 9 | 1249 | 1322 | 1199 | 1284 | 1318 | 1440 | 1425 | 241 |
| 10 | 1167 | 1331 | 1192 | 1199 | .. | 1385 | 1310 | 218 |
| 11 | 1139 | 1322 | 1220 | 1214 | .. | 1185 | 1400 | 261 |
| 12 | 1088 | 1295 | 1060 | 1182 | .. | 1080 | 1335 | 276 |
| 13 | 1322 | 1340 | 1217 | .. | 1273 | 1520 | 1500 | 303 |
| 14 | 1424 | 1375 | 1316 | .. | 1417 | 1551 | Above 1500 | 235 |
| 15 | 1250 | 1283 | 1161 | .. | 1186 | 1427 | 1407 | 264 |
| 16 | 1341 | 1370 | 1241 | .. | 1212 | 1470 | 1322 | 258 |
| 17 | 1220 | 1271 | 1179 | .. | 1182 | 1390 | 1343 | 211 |
| 18 | 1250 | 1287 | 1185 | .. | 1204 | 1455 | 1400 | 270 |

The lowest results for 18 samples were distributed among the different furnaces as follows:

| | | | |
|---|---|---|---|
| Molybdenum furnace No. 1 | 10 | Northrup furnace | 1 |
| Molybdenum furnace No. 2 | 1 | Muffle furnace No. 2 | 1 |
| Carbon resistance furnace | 4 | Meker furnace | 1 |

### APPEARANCE OF CONES SOFTENED IN VARIOUS ATMOSPHERES

(*a*) PLATINUM FURNACE, AIR ATMOSPHERE—In Fig. 15 are shown the various ways in which cones of different ashes deform on heating in air in the platinum

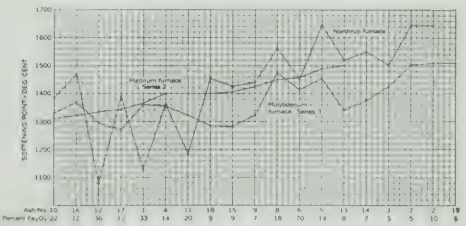


FIG. 14—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN NORTHRUP, PLATINUM, AND MOLYBDENUM FURNACES

furnace. The manner of deformation is somewhat characteristic for each individual ash. No. 59 illustrates the typical Seger cone bend, No. 26 the type

which fuses to a lump, No. 29 the intumescing type. No. 7 is an ash which did not soften at 1500°. The

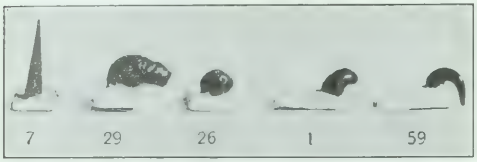


FIG. 15

color of the fused cones varied from a buff, or reddish brown, to a glossy black. The black cones were magnetic.

(*b*) MOLYBDENUM FURNACES, HYDROGEN ATMOSPHERE—Fig. 16 illustrates typical forms from the molybdenum furnace (hydrogen atmosphere). Owing to the reducing atmosphere, these cones almost always developed a pronounced vesicular structure. In some cases as in ash No. 3, the swelling due to the evolution of gas prevented the cone from bending in the normal manner. This is one of the reasons for the somewhat larger variations between duplicate determinations in re-

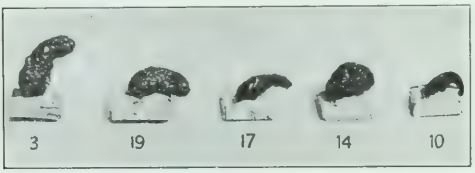


FIG. 16

ducing atmospheres. The fused cones were usually light to dark gray or grayish black in color; they had a vitreous luster and invariably showed iron globules on examination under the microscope.

(*c*) NORTHRUP FURNACE, CARBON MONOXIDE AND NITROGEN ATMOSPHERE—The cones fused in the Northrup furnace (CO atmosphere) varied from a dark gray to a brownish black or metallic black color. The surface lacked the vitreous luster of the cones fused in air or hydrogen. Carbon was deposited on the cones and base in increasing quantity as the

FIG. 17

temperature exceeded 1400°, as shown by the blackened base of ash No. 8 (Fig. 17) which was heated to 1550°.

Another peculiarity in the Northrup series was the softening and swelling of the thick bottom portion of some of the cones before the apex began to soften. Ash No. 4 began swelling at the base at 1200°, heating was continued at the rate of 2° per minute until a temperature of 1375° was reached, when the current was interrupted and the furnace allowed to cool. As shown in Fig. 17, fusible constituents appeared to separate and run down the sides of the cone, leaving a refractory skeleton standing. However, on breaking the cone it appeared that the irregular contour was due to the evolution and expansion of gases in the interior of the softening slag. The expanded bottom was a thin-shelled bubble of slag, as was the case in ashes 15, 8 and 17.

The first perceptible swelling of the lower part of ash No. 8 took place at 392° below the point where it finally bent over in the position shown in the photograph.

The earlier fusion of the thick part of the cone may be due to the inability of the carbon monoxide to penetrate and reduce the iron oxide in the interior to metallic iron as rapidly as in the thin upper part. This phenomenon of irregular softening was noted only in the Northrup and carbon-resistance furnaces.

### G—DOWN-DRAFT CERAMIC KILN

Several years before the present investigation was begun, one of the authors had occasion to determine the relative softening temperatures of a number of ashes and clinkers. Through the kindness of A. V. Bleininger these tests were made in a 6-foot down-draft kiln at the Pittsburgh station of the Bureau of Standards. The ash was ground to 100 mesh, molded into $^1/_2$ in. × $2^1/_2$ in. cones and mounted in two rows, one above the other, in the middle of the muffle space of the kiln. The muffle space was 26 in. long × 26 in. wide × 30 in. high. The temperatures were read from two thermo-elements, one in each row of cones. The rate of heating such a large kiln was necessarily

TABLE XXI—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN DOWN-DRAFT CERAMIC KILN WITH THOSE OBTAINED IN PLATINUM RESISTANCE FURNACE

KILN: 100 mesh ash; $^1/_2$ in. × $2^1/_2$ in. cones; rate of heating, 100° per hour; inclined 25° from vertical.

PLATINUM FURNACE: Ash ground to an impalpable powder; $^3/_{16}$ in. × 1 in. cones placed in vertical position; rate of heating, 5° per minute to first visible softening, then 2° per minute to softening point.

| Sample No. | | Softening Point in °C: Kiln | Platinum furnace | Diff. | Softening Interval in °C: Kiln | Pt. furn. |
|---|---|---|---|---|---|---|
| 63 | | 1198 1173 1194 1214 | | | | |
| | Av.. | 1194 | 1270 | —76 | 7 | 70 |
| 59 | | 1166 | 1190 | —24 | 3 | 30 |
| 56 | | 1163 | 1210 | —47 | 3 | 35 |
| 57 | | 1179 | 1250 | —71 | 2 | 25 |
| 62 | | 1255 | 1300 | —45 | 36 | 50 |
| 60 | | 1256 1257 | 1290 | —33 | 14 | 40 |
| | Av.. | 1257 | | | | |
| 29 | | 1347 1348 | 1380 | —32 | 12 | 55 |
| | Av.. | 1348 | | | | |
| 27 | | 1342 1258 1360 | 1420 1397 | | | |
| | Av.. | 1320 | 1409 | —89 | 13 | 46 |
| 26 | | 1356 | 1410 | —54 | 5 | 60 |
| 54 | | 1275 1265 | | | | |
| | Av.. | 1270 | 1350 | —80 | 51 | 25 |
| 51 | | 1296 1288 | | | | |
| | Av.. | 1293 | 1370 | —77 | 36 | 50 |
| 53 | | 1219 | 1280 | —61 | 9 | 30 |
| | | | Average. | —57 | 16 | 43 |

slow. Heating was begun in the evening, the gas burners being so adjusted that by morning a temperature of 800 to 900° was reached. The temperature was then increased at the rate of 100° per hour until the last cone was down. An oxidizing atmosphere was maintained by admitting a large excess of air around the gas burners.

The results obtained in the kiln are given in Table XXI, together with results obtained on the same samples

of ash in the platinum furnace under strictly oxidizing conditions. The consistently lower softening points obtained in the kiln may be attributed to the much slower rate of heating, and also the possibility of some slight reduction by products of incomplete combustion. Considering the difference in test conditions the agreement is remarkably close.

### SUMMARY AND CONCLUSIONS

The effect of various factors on the softening temperature of a number of typical coal ashes has been studied in eight different furnaces, having atmospheres of varying degrees of oxidation and reduction. The influences of the more important factors are summarized as follows:

I—SIZE AND SHAPE OF CONE—Cones that measured $1/4$ in. $\times$ $1\,1/2$ in. gave closer duplication and from 10 to 50° lower average softening points than $1/4$ in. $\times$ 1 in. cones; $3/16$ in. by 1 in. cones gave practically the same results as $1/4$ in. by $1\,1/2$ in. cones. The more slender cones were more satisfactory in giving shorter and more definite softening intervals; they also gave less trouble from intumescence due to evolution of gases from the melting ash. In reducing-atmosphere tests, the surrounding gases penetrated a thin cone more uniformly than one with a wide base.

II—FINENESS OF ASH—Ash ground to an impalpable powder tended to soften at a slightly lower temperture than 100 mesh ash. The difference averaged 6° and in no case exceeded 40°. Ash pulverized to at least 200 mesh could be molded into more substantial cones than 100 mesh material.

III—INCLINATION OF CONES—Mounting the cones with a considerable inclination, 35 or 45° from the vertical, led in some cases to premature deformation points, which were caused by a further bending over due to shrinkage of the cone in its base, rather than deformation due to softening and flowing of the ash. Vertical or nearly vertical cones were free from this source of error, and gave the most concordant indications.

IV—RATE OF HEATING—In general, slower rates of heating gave lower softening points. Rates slower than 2° per minute are too time-consuming for practical consideration. Rates faster than 10° per minute led to inaccurate temperature measurements. Varying the rate of heating from 2 to 10° per minute caused less increase of softening temperature in oxidizing atmospheres than in reducing atmospheres of hydrogen (see Figs. 12 and 13). A 2° rate of heating gave the most uniform results; however, heating 5° per minute to initial deformation and then reducing to 2° per minute gave practically the same results and saved considerable time.

V—OXIDIZING OR REDUCING ATMOSPHERE—The atmosphere in which the ash was heated proved by far the most important factor in causing large variations in the softening temperature. As pointed out in the introductory theoretical discussion, the highest softening points were obtained, either in an atmosphere of air (platinum furnace), or in a strongly reducing atmosphere of carbon monoxide (Northrup furnace) which prevented the iron oxide from acting as a fluxing agent by reducing it to metallic iron before the softening of the ash began.

The lowest softening temperatures were obtained in those atmospheres of mixed gases in which reduction of ferric oxide proceeded mainly to ferrous oxide, the most active phase of iron as regards slag formation at lower temperatures. Such a condition apparently existed in the muffle furnace No. 2, the molybdenum furnace No. 1, and in many of the carbon resistance furnace determinations. The maximum variation in softening temperatures due to different atmospheres ranged from 143 to 495° C. (see Table XX and Figs. 4, 6, 8, 10, 12, 13 and 14).

### STANDARD METHODS FOR DETERMINING THE SOFTENING TEMPERATURE OF ASH

Obviously, the statement that an ash has a "fusing" or softening temperature of 1500° means nothing unless the exact conditions of making the test are defined. The method must, therefore, be carefully standardized in all its details before comparable results may be secured by different workers. The most important consideration is the atmosphere in which the test shall be made. From the standpoint of securing results that can be duplicated in different laboratories, the softening temperature in air, as was determined in the platinum furnace, is undoubtedly the most satisfactory standard; but unfortunately, ash forming in a fuel bed is not free from the effect of reducing gases. Consequently, clinkering may take place under conditions of partial reduction similar to those which prevailed when the low softening points were obtained in the molybdenum or gas furnaces. Therefore, the lowest softening temperature of an ash under such conditions as will reduce the ferric oxide to the ferrous form should give the most promising relation to clinker formation under furnace conditions. Such a method will be described in a subsequent paper.

### ACKNOWLEDGMENTS

The authors desire to express their deep appreciation of the assistance and of the many helpful suggestions received from G. A. Hulett, consulting chemist of the Bureau of Mines, and from A. V. Bleininger, of the Pittsburgh station of the Bureau of Standards.

The observations in the Northrup-furnace series and the platinum-furnace series of Table XXI were made by Alex. L. Feild. Some of the molybdenum-furnace tests were made by W. A. Mueller. The chemical analyses were made by H. H. Hill, W. A. Selvig and F. D. Osgood, all of this laboratory.

A number of the coal samples used in this investigation were furnished by Mr. E. G. Goodwin, Chief Fuel Inspector of the Southern Railway.

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## PHYSICAL CONSTANTS OF GAS OILS AND DERIVED TARS[1]

By WALTER F. RITTMAN AND GUSTAV EGLOFF
Received January 4, 1915

In connection with a general study of the behavior of hydrocarbons under different temperatures and

[1] Published with the permission of the Director of the Bureau of Mines.

TABLE I—PHYSICAL CONSTANTS OF GAS OILS AND DERIVED TARS AND THEIR DISTILLATES

All Data for 20° C. unless indicated otherwise. Charge for distillations 400 cc

| | Gas Oil Number 1 | Gas Oil Number 2 | Gas Oil Number 3 | Gas Oil Number 4 |
|---|---|---|---|---|
| Specific gravity at 15.5° C | 0.872 | 0.858 | 0.872 | 0.860 |
| Surface tension (dynes per cm.) | 28.60 | 28.40 | 28.54 | 28.91 |
| Viscosity (specific) | 2.3 | | 2.11 | 1.68 |

| Temp. C | Cc. | Vol. % | Sp. gr. 15.5 °C. | Sr. T. dynes | Refr. ind. | Cc. | Vol. % | Sp. gr. 15.5 °C. | Sr. T. dynes | Refr. ind. | Cc. | Vol. % | Sp. gr. 15.5 °C. | Sr. T. dynes | Refr. ind. | Cc. | Vol. % | Sp. gr. 15.5 °C. | Sr. T. dynes | Refr. ind. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 150 | 3.5 | 0.9 | 0.790 | 22.40 | 1.416 | 5.0 | 1.3 | 0.788 | 22.22 | 1.419 | 4.5 | 1.1 | 0.759 | 21.59 | 1.412 | 3.0 | 0.8 | 0.775 | 23.38 | 1.426 |
| 200 | 6.0 | 1.5 | 0.800 | 24.30 | 1.434 | 4.5 | 1.1 | 0.798 | 24.29 | 1.442 | 8.7 | 2.2 | 0.778 | 23.79 | 1.434 | 12.5 | 3.1 | 0.794 | 24.32 | 1.437 |
| 225 | 4.5 | 1.1 | 0.809 | 25.57 | 1.441 | 8.0 | 2.0 | 0.814 | 25.97 | 1.448 | 9.0 | 2.3 | 0.799 | 25.22 | 1.448 | 19.0 | 4.8 | 0.815 | 25.36 | 1.446 |
| 250 | 17.0 | 4.2 | 0.818 | 26.28 | 1.454 | 22.5 | 5.6 | 0.824 | 26.87 | 1.453 | 12.0 | 3.0 | 0.817 | 26.23 | 1.455 | 25.5 | 6.4 | 0.832 | 26.43 | 1.454 |
| 275 | 21.5 | 5.4 | 0.836 | 27.60 | 1.464 | 25.0 | 6.2 | 0.832 | 27.41 | 1.458 | 24.5 | 6.1 | 0.837 | 27.18 | 1.464 | 27.0 | 6.8 | 0.845 | 27.07 | 1.462 |
| 300 | 49.0 | 12.2 | 0.849 | 28.12 | 1.472 | 32.0 | 8.0 | 0.842 | 27.86 | 1.464 | 39.5 | 9.9 | 0.851 | 28.06 | 1.472 | 38.0 | 9.5 | 0.853 | 27.67 | 1.469 |
| Mixed distillate | 101.5 | 25.4 | 0.837 | 27.16 | 1.463 | 97.0 | 24.2 | 0.828 | 26.90 | 1.458 | 98.2 | 24.6 | 0.830 | 25.77 | 1.462 | 125.0 | 31.4 | 0.833 | 26.60 | 1.458 |

| | Tar Oil Number 1 | Tar Oil Number 2 | Tar Oil(a) Number 3 | Tar Oil Number 4 |
|---|---|---|---|---|
| Specific gravity at 15.5° C | 1.071 | 1.090 | 1.122 | 1.086 |
| Surface tension (dynes per cm.) | 33.83 | 34.83 | 36.55 | 37.6 |
| Viscosity (specific) | 4.04 | 11.86 | 10.9 | 5.60 |

| Temp. C | Cc. | Vol. % | Sp. gr. 15.5 °C. | Sr. T. dynes | Refr. ind. | Cc. | Vol. % | Sp. gr. 15.5 °C. | Sr. T. dynes | Refr. ind. | Cc. | Vol. % | Sp. gr. 15.5 °C. | Sr. T. dynes | Refr. ind. | Cc. | Vol. % | Sp. gr. 15.5 °C. | Sr. T. dynes | Refr. ind. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 150 | 7.5 | 1.9 | 0.870 | 27.49 | 1.491 | 3.0 | 0.8 | | | | 5.0 | 1.2 | | | | 12.5 | 3.1 | 0.874 | 27.44 | 1.499 |
| 200 | 17.5 | 4.4 | 0.903 | 29.44 | 1.520 | 3.5 | 0.9 | 0.940 | 30.26 | 1.531 | 6.5 | 1.6 | 0.942 | 30.28 | 1.532 | 28.0 | 7.0 | 0.916 | 29.13 | 1.529 |
| 225 | 26.0 | 6.5 | 0.930 | 30.95 | 1.541 | 4.5 | 1.1 | 0.956 | 32.44 | 1.562 | 12.5 | 3.1 | 0.977 | 33.66 | 1.557 | 27.5 | 6.9 | 0.956 | 30.69 | 1.553 |
| 250 | 45.0 | 11.2 | 0.975 | 32.39 | 1.569 | 17.0 | 4.2 | 0.984 | 33.31 | 1.576 | 26.0 | 6.5 | 1.012 | 35.21 | 1.572 | 45.5 | 11.4 | 0.986 | 32.16 | 1.576 |
| 275 | 33.0 | 8.2 | 0.983 | 32.61 | 1.572 | 49.0 | 12.3 | 0.993 | 33.51 | 1.582 | 43.0 | 10.8 | 1.027 | 35.69 | 1.585 | 42.0 | 10.5 | 0.998 | 32.84 | 1.587 |
| 300 | 29.0 | 7.2 | 0.995 | 32.95 | 1.579 | 24.0 | 6.0 | 1.010 | 33.79 | 1.589 | 25.0 | 6.3 | 1.047 | 36.08 | 1.594 | 23.0 | 5.8 | 1.018 | 33.25 | 1.597 |
| Mixed distillate | 158.0 | 39.4 | 0.970 | 31.95 | 1.562 | 101.0 | 25.3 | 0.983 | 32.20 | 1.578 | 118.0 | 29.5 | 0.968 | 34.10 | | 178.5 | 44.7 | 0.968 | 31.66 | 1.566 |

(a) Much difficulty was experienced in distilling tar oils Nos. 2 and 3, due to the presence of water.

pressures it was considered advisable to make a study of the properties of gas oils and derived tars as formed in the carbureted water-gas process.

With this end in view samples were procured of the oils used by plants producing carbureted water gas in four cities of widely different geographic locations. In addition samples of the tars resulting from the cracking of these identical oils were obtained. Samples of oil and tar were in each case taken from the run of the same day. Information from the gas companies indicated that the tars represented about 15 to 20 per cent of the original oils.

TABLE II—SURFACE TENSIONS OF VARIOUS OIL AND TAR CONSTITUENTS

| Substance Formula | B. P. °C. | Surface tension(b) Value | At °C. | Determinations made by |
|---|---|---|---|---|
| Water, $H_2O$ | 100 | 73.01 | 20 | Sentes(c) |
| Water, $H_2O$ | 100 | 72.69 | 20 | Morgan(d) and McAfee |
| PARAFFINS(a) | | | | Isolations made by |
| Pentane, $C_5H_{12}$ | 38 | 16.0 | 11 | Warrener(e) |
| Hexane, $C_6H_{14}$ | 71 | 20.0 | 11 | Schorlemmer,f |
| Heptane, $C_7H_{16}$ | 98.4 | 23.5 | 12 | Young and Francis(g) |
| Isoheptane, $C_7H_{16}$ | 91.5 | 23.4 | 12 | Crossley(h) |
| Octane, $C_8H_{18}$ | 125.5 | 24.3 | 11 | Schorlemmer(i) |
| Nonane, $C_9H_{20}$ | 149.5 | 24.9 | 14 | Warren(j) |
| Decane, $C_{10}H_{22}$ | 173.0 | 25.8 | 13 | Mabery(k) |
| Undecane, $C_{11}H_{24}$ | 194.5 | 26.4 | 14 | Mabery(k) |
| Dodecane, $C_{12}H_{26}$ | 214.0 | 27.2 | 12.8 | Mabery(k) |
| Tridecane, $C_{13}H_{28}$ | 234.0 | 27.9 | 14 | Mabery,k |
| Tetradecane, $C_{14}H_{30}$ | 252.5 | 28.7 | 13 | Mabery(k) |
| Pentadecane, $C_{15}H_{32}$ | 270.5 | 29.4 | 13.3 | Mabery(k) |
| Hexadecane, $C_{16}H_{34}$ | 287.5 | 29.8 | 13 | Mabery(k) |
| UNSATURATED(b) | | | | |
| Amylene, $C_5H_{10}$ | | 17.21 | 16.5 | Mendelejeff |
| | | 15.13 | 36.8 | |
| Cetene, $C_{16}H_{32}$ | | 27.14 | 15.0 | Mendelejeff |
| Acenaphthene, $C_{12}H_{10}$ | | 31.36 | 128 | Dutoit and Friederich |
| | | 26.60 | 178 | |
| AROMATIC(b) | | | | |
| Benzene, $C_6H_6$ | | 28.28 | 18.1 | Walden |
| | | 29.86 | 17.5 | Volkman |
| | | 28.83 | 11.4 | Renard and Guye |
| | | 30.24 | 20.0 | Morgan |
| | | 29.31 | 11.2 | Ramsay and Shields |
| Toluene, $C_7H_8$ | | 29.07 | 12.5 | Volkman |
| | | 28.52 | 17.5 | Volkman |
| Xylene, $C_8H_{10}$ 1 : 2 | | 32.20 | 13.8 | Feustal |
| 1 : 3 | | 28.97 | 15.7 | Dutoit and Friederich |
| 1 : 4 | | 30.22 | 14.0 | Feustal |
| Mesitylene, $C_9H_{12}$ | | 27.92 | 7.4 | Dutoit and Friederich |
| | | 18.74 | 108.4 | Dutoit and Friederich |
| Naphthalene, $C_{10}H_8$ | | 27.98 | 127.0 | Dutoit and Friederich |
| | | 22.86 | 177.2 | Dutoit and Friederich |
| Phenol, $C_6H_5OH$ | | 38.55 | 30 | Morgan and Egloff |
| o-Cresol $C_7H_7OH$ | | 38.21 | 12.5 | Renard and Guye |
| m-Cresol | | 37.78 | 9.0 | Bolle and Guye |
| p-Cresol | | 37.80 | 32.2 | Feustal |
| MISCELLANEOUS(b) | | | | |
| Mercaptan | | 23.63 | 2.0 | Ramsay and Shields |
| Mercaptan | | 21.62 | 16.0 | Ramsay and Shields |
| Thiophene | | 36.20 | 30.0 | Shiff |
| Thiophene | | 33.10 | 20.0 | Shiff |
| Molten paraffin | | 30.56 | 54.0 | Quincke |
| Wax | | 33.40 | 68.0 | Quincke |

(a) Washburne, *Bull. Am. Inst. Mining Eng.*, **1914**, p. 2367.
(b) These data were gathered from Landolt and Bornstein, Castell-Evans, Tables Annuelles Internationales de Constantes, and the original literature.
(c) *Jour. Phys.*, **1897**, p. 183.
(d) *J. Am. Chem. Soc.*, **33** (1911), 1284.
(e) *Proc. Am. Acad.*, **27**, 56–92.
(f) *Ber.*, **3** (1870), 615.
(g) *Jour. Chem. Soc.*, **1898**, p. 921.
(h) *Chem. Zentr.*, **99**, 2, 474.
(i) *Berichte*, **1870**, p. 615.
(j) *Zeit. phys. Chem.*, **242**, 1.
(k) *Am. Chem. Jour.*, **19**, 419.

## EXPERIMENTAL

The following methods of examination were applied

TABLE III—SPECIFIC GRAVITIES AND REFRACTIVE INDICES OF VARIOUS OIL AND TAR CONSTITUENTS

| Paraffins | B. P. °C. | Sp. gr. | Refractive index at °C. | Value |
|---|---|---|---|---|
| Hexane(a) | 68 | 0.665 | 14.8 | 1.378 |
| Heptane(b) | 92/94 | 0.709 | 15.0 | 1.404 |
| Oktane(a) | 125.5 | 0.707 | 15.1 | 1.401 |
| Nonane(b) | 136/138 | 0.740 | 15.0 | 1.421 |
| Decane(a) | 173 | 0.728 | 14.9 | 1.411 |
| Tetradecane(c) | 126 (12 mm.) | 0.770 | 20.0 | 1.431 |
| Hexadecane(c) | 151 (12 mm.) | 0.780 | 20 | 1.436 |
| Oktodecane(a) | 174 (12 mm) | 0.779 | 27 | 1.439 |
| OLEFINES | | | | |
| Hexylene(a) | .... | 0.689 | 15.2 | 1.400 |
| Oktylene(a) | .... | 0.726 | 16 | 1.416 |
| Decylene(a) | .... | 0.773 | 17 | 1.439 |
| AROMATICS | | | | |
| Benzene(d) | 80.4 | 0.876 | 20 | 1.501 |
| Toluene(e) | 110.3 | 0.871 | 14.7 | 1.499 |
| Ethyl benzene(d) | 134.0 | 0.875 | 14.5 | 1.499 |
| o-Xylene(d) | 142.0 | 0.885 | 14.1 | 1.508 |
| m-Xylene | 139.0 | 0.869 | 15.7 | 1.500 |
| p-Xylene | 138.0 | 0.866 | 14.7 | 1.499 |
| N-Propyl benzene | 158.5 | 0.866 | 15.7 | 1.494 |
| Isopropyl benzene | 153.0 | 0.863 | 15.1 | 1.495 |
| Mesitylene | 164.5 | 0.865 | 14.6 | 1.497 |
| Pseudocumene | 170.0 | 0.883 | ... | 1.507 |
| Cymene | 175.0 | 0.862 | 13.7 | 1.511 |
| Isobutyl benzene | 167.0 | 0.872 | 17.5 | 1.496 |
| NAPHTHENES | | | | |
| Cyclohexane(f) | 80.8 | 0.779 | 19.5 | 1.427 |
| Methylpentamethylene(g) | 72.0 | 0.750 | 20.0 | 1.411 |
| Methylhexamethylene(h) | 101.0 | 0.769 | 20.0 | 1.424 |
| Isohexamethylene(i) | 101.0 | 0.756 | 19.0 | 1.418 |
| Dimethylpentamethylene(j) | 93/96 | 0.754 | 20.0 | 1.413 |
| Hexahydro-m-xylene(k) | 117/118 | 0.758 | 17.0 | 1.419 |
| Ethyl cyclohexane(l) | 130 | 0.799 | 4.0 | 1.433 |
| 1,3-Dimethylhexamethylene (m) | 120 | 0.769 | 20.0 | 1.423 |
| 1,1-Dimethylhexamethylene (m) | .... | 0.773 | 18.0 | 1.424 |
| 1,4-Dimethylhexamethylene (n) | 118.2 | 0.769 | 20.0 | 1.424 |
| 3-Methyl-1,2,5-hexahexene | 142/44 | 0.781 | 20.0 | |
| 1,3,5-Trimethyl cyclohexane | 134/36 | 0.788 | 4.0 | 1.426 |
| Monanaphthene(o) | 170/172 | 0.773 | 16.0 | 1.433 |
| 1,3-Diethylhexamethylene | .... | 0.796 | 22.0 | 1.439 |
| Isobutylcyclohexane | 157 | 0.804 | 21.0 | 1.447 |

(a) Landolt and Jahn, *Z. phys. Chem.*, **10** (1892), 303.
(b) Bartoli and Stracciati, *Ann. chim. phys.*, **7** (1886), 382.
(c) Ubbelohde and Agthe, Dip. Karlsruhe, 1912.
(d) Kuops, *Liebig's Ann.*, **248** (1888), 175; Barbier and Rowe, *Bull. soc. chim.*, **3** (1890), 255; Weegman, *Z. phys. Chem.*, **2** (1888), 237.
(e) Landolt and Jahn, *Z. phys. Chem.*, **10** (1892), 303.
(f) Zelinsky, *Chem. Z.*, **1901**, II, 985.
(g) Zelinsky, *Ber.*, **30** (1897), 387.
(h) Generosow and Zelinsky, *Ibid.*, **30** (1897), 1539.
(i) Zelinsky and Rudsky, *Ibid.*, **29** (1896), 403.
(j) *Ibid.*, **30** (1897), 1540.
(k) Wischin, Naphthene, Braunschweig, **1901**, p. 58.
(l) Ubbelohde and Malexa, Karlsruhe, Dissertation, 1912.
(m) Zelinsky and Naumon, *Chem. Z.*, **1899**, 341.
(n) Zelinsky, *Ber.*, **40** (1907), 3277.
(o) Zelinsky and Rudewitz, *Ibid.*, **28** (1895), 1343.

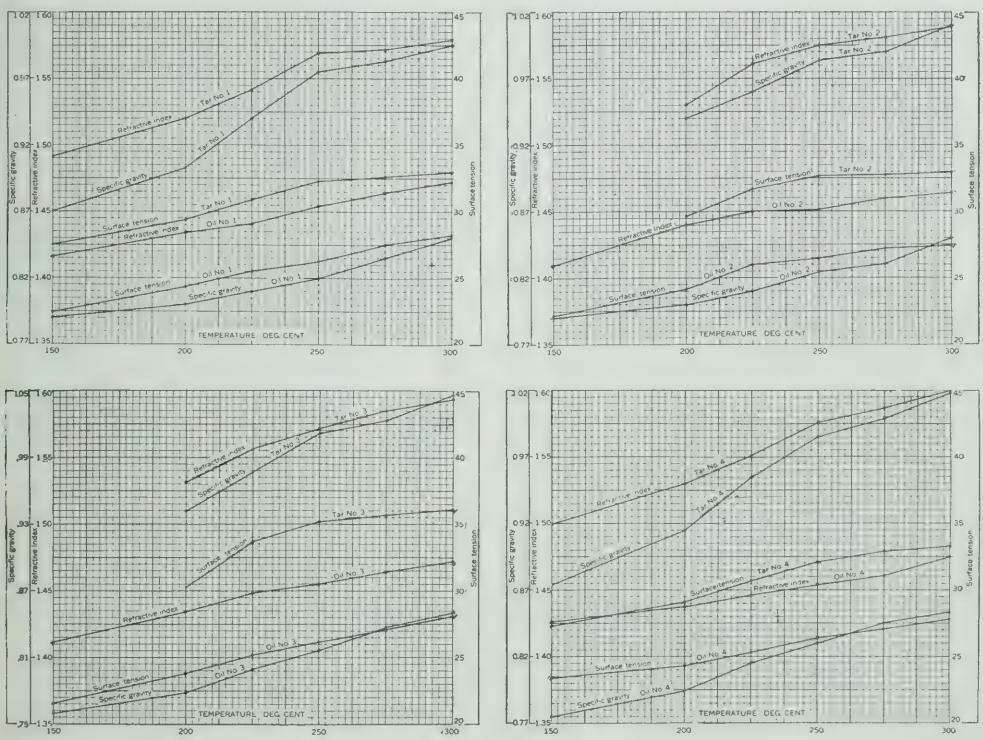
as indicated, with the results given in Table I:

| Method | Applied to |
|---|---|
| 1 Fractional distillation | Original oils and tars |
| 2 Determinations of specific gravity | Original samples and distillation cuts |
| 3 Determinations of viscosity | Original oils and tars |
| 4 Determinations of surface tension | Original samples and distillation cuts |
| 5 Determinations of refractive index | Distillation cuts |

DISTILLATIONS were made in 500 cc. glass flasks arranged with moderately efficient fractionating columns of aluminum beads.[1] Cuts were made at 150° C., 200° C. and thereafter at 25° intervals up to 300° C.; original charges of 400 cc. were used. The results obtained show that the tars have a larger percentage of constituents boiling below 300° than the original oils. When high-boiling petroleum hydrocarbons are subjected to increased temperatures, decomposition can take place in at least two ways: (1) a simple splitting into aliphatic hydrocarbons of smaller molecular weight; (2) a combination of splitting and subsequent polymerization into ring compounds. The results of such decomposition are determined by the prevailing conditions of temperature, pressure, concentration, contact surface and time.

SPECIFIC GRAVITY determinations were made at 15.5° C. with a Westphal balance having a plummet of 1 cc. displacement. The figures representing gravities run up steadily with increase in boiling temperature of the distillation cuts. The gravities of the tars are much higher than those of the oils, showing that aromatic hydrocarbons have been formed. These are of higher density for a given volatility than are the aliphatic hydrocarbons found in the original oils.

SURFACE TENSION measurements were made by the Morgan[1] drop-weight method. The results are given in dynes per centimeter. Again the figures for the tars, and distillation cuts derived from them, are higher than the analogous ones for the original oils. In general, surface tension is a property which increases with specific gravity, though experience has indicated the ease with which small quantities of certain impurities influence the former constant.




CURVES SHOWING RELATIONS BETWEEN PHYSICAL CONSTANTS OF GAS OILS AND DERIVED TARS

REFRACTIVE INDICES were measured by means of the Pulfrich Refractometer, at a temperature approximating 20° C. The values found show relations similar to those of specific gravity and surface tension. The accompanying sets of curves plotted according to the values obtained for the various oils and tars are typical and show that refractive indices vary with volatility.

The data obtained by the various methods, as given collectively in Table I, summarize clearly the differences in the properties of the two classes of products.

For purposes of comparison, the surface tensions, specific gravities and refractive indices of a number of hydrocarbons, both aliphatic and aromatic, have

[1] Rittman and Dean, THIS JOURNAL, 7 (1915), 185.

[1] *J. Am. Chem. Soc.*, 33 (1911), 349 and 643.

been collected from the literature and are given in Tables II and III.

CONCLUSIONS

I—The striking differences between the constituents of an aliphatic oil and its derived tar are made evident by the characteristic differences between volatility-gravity, volatility-refractive index, and volatility-surface tension relations.

II—The experiments reported herewith again verify the well-known information that aromatic hydrocarbons can be formed from the aliphatic hydrocarbons occurring in petroleum.

III—The various physical constants of typical gas oils and derived tars have been measured and tabulated.

The experimental work connected with the determinations reported in this paper was carried out in the laboratories of the Departments of Physical Chemistry and Industrial Chemistry of Columbia University, New York.

CHEMICAL SECTION OF PETROLEUM DIVISION
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## THE TIME FACTOR IN MAKING OIL GAS

By M. C. WHITAKER AND C. M. ALEXANDER
Received April 1, 1915

The production of oil gas is dependent upon certain chemical laws which relate to gas reactions in general and which embody the principles of both thermodynamics and chemical kinetics.

In an investigation on the effect of the variables, temperature, pressure, and concentration on the thermal decomposition of petroleum and petroleum distillates, Whitaker and Rittman[1] have carefully considered the theoretical principles of thermodynamics as applied to gas reactions. Their experimental results verified their theoretical conclusions and showed that the principles of thermodynamics apply to the decomposition of petroleum hydrocarbons as well as to more simple reactions.

In the above work, however, conclusions were drawn on the assumption that chemical equilibrium was attained under the experimental conditions adopted. It then became a question whether or not equilibrium was reached. Undoubtedly this question could be answered by the application of the principles of chemical kinetics, which introduced the time factor. In the present study of oil gas production, therefore, four variables—time, temperature, pressure and concentration—are recognized.

Difficulties were foreseen, however, in the accurate adjustment of the above variables in commercial plants and a basis for control was sought which would fall within the range of engineering requirements. Under constant temperature and pressure conditions, the time factor, which can be controlled by variation of the rate of oil feed, offers the most available means for the study of the thermal decomposition of petroleum and petroleum distillates on the basis of the principles of chemical kinetics.

Design of apparatus is fixed for any one construction and hence remains a constant factor while the variables are controllable within certain operating limits. The concentration factor above is considered in the sense of changes involved in the admixing of other substances with the initial material, such as the decomposition of oil in an atmosphere of hydrogen, carbon monoxide, etc.

[1] This Journal, **6** (1914), 383, 472.

THEORETICAL

According to chemical kinetics, a reaction tending toward a state of equilibrium will require time to reach such a state.

A reversible reaction may be represented thus:

$$n_1A_1 + n_2A_2 \rightleftarrows n_1'A_1' + n_2'A_2' \ldots$$

Such an equation represents two reverse reactions, each with a separate reaction velocity:

$$v = k(A_1)^{n_1}(A_2)^{n_2} \ldots \qquad v' = k'(A_1')^{n_1'}(A_2')^{n_2'} \ldots$$

The difference between these two velocities at any moment of time under constant conditions will give a certain change per unit of time in one direction or the other toward equilibrium. This change per increment of time, $\frac{dx}{dt}$, is commonly shown as follows:

$$\frac{dx}{dt} = v - v' = k(A_1)^{n_1}(A_2)^{n_2} \ldots - k'(A_1')^{n_1'}(A_2')^{n_2'} \ldots$$

in which $k$ and $k'$ are the velocity constants of the two reverse reactions, $(A_1)$, $(A_2)$, etc., are the concentrations of the reacting substances, and $n_1$, $n_2$, etc., their respective molecular exponents as obtained from a properly balanced equation.

The above velocity constants vary with temperature[1] and as a result temperature has a very marked effect upon the reaction velocities of the two reverse reactions. The effect of temperature on a number of gas reactions has been very carefully studied by Bodenstein[2] and the fundamental equations applied mathematically to the experimental results.

At equilibrium, the velocities of the opposing reactions are equal and hence the change per increment of time, $\frac{dx}{dt}$, must become zero.

$$\frac{dx}{dt} = v - v' = k(A_1)^{n_1}(A_2)^{n_2} \ldots - k'(A_1')^{n_1'}(A_2')^{n_2'} \ldots = 0$$

$$\text{Hence,} \qquad \frac{k}{k'} = \frac{(A_1')^{n_1'}(A_2')^{n_2'} \ldots}{(A_1)^{n_1}(A_2)^{n_2} \ldots} = K,$$

where K is the equilibrium constant. Thus chemical equilibrium deals only with the end state of a reaction and time is not a factor.

Where time is not considered the relations between the state of equilibrium and the thermal values of a reaction can be worked out by the application of thermodynamics. Such relations have been developed by Nernst,[3] Mayer and Altmayer,[4] and others[5] and expressed in terms of mathematical formulas from which equilibrium compositions can be calculated: *e. g.*, the Nernst approximate formula:

[1] Trautz, *Z. Elektrochem.*, **18** (1912), 513; *Z. physik. Chem.*, **68** (1909), 295; **74** (1910), 747, Zellinek, *Z. anorg. Chem.*, **49** (1906), 229.

[2] Bodenstein, *Z. physik. Chem.*, **29** (1899), 147, 295, 315, 429, 665; Bodenstein and Wolgast, *Ibid.*, **61** (1908), 422.

[3] W. Nernst, "Theoretische Chemie"

[4] Mayer and Altmayer, *Ber.*, **40** (1907), 2134.

[5] H. von Wartenberg, *Z. physik. Chem.*, **61** (1907), 366.

$$\log K_p = \log \frac{p_1'^{n_1'} p_2'^{n_2'} \ldots}{p_1^{n_1} p_2^{n_2} \ldots}$$

$$= \frac{Q_p}{4.751\,T} + 1.75(\Sigma n' - \Sigma n) \log T + (\Sigma n'C' - \Sigma nC)$$

By the use of such formulas the ultimate composition representative of equilibrium conditions is obtained. This final composition, according to the principles of chemical kinetics, represents the end point of a reaction which can be attained only through a sufficient lapse of time. As applied to the production of oil gas, a progressive decomposition, in which time is an important factor, should proceed to an ultimate state of equilibrium.

The reactions taking place in the decomposition of petroleum hydrocarbons by heat are numerous and not definitely known. In the industries based on these decomposition reactions, as in the making of oil gas, carbureting water gas, and cracking petroleum for light distillates, the chemical nature of only the initial materials and the final products are determined, and this does not give any definite knowledge concerning the intermediate reactions. The breaking down of hydrocarbons of high molecular weights to simpler hydrocarbons apparently consists in numerous consecutive and concurrent reactions,[1] but their actual course from the initial material to the final products has not been established. Even in the absence of such knowledge, the theoretical principles of chemical kinetics which apply to single reactions should also hold in the case of the numerous reactions involved in the thermal decompositions of petroleum hydrocarbons.

The importance of the variable time in a few related decompositions has been shown by a number of investigators. Lewes[2] finds that the decomposition of ethylene is dependent not only upon temperature and pressure but also on rate of flow. Clement[3] has shown the importance of the time factor in the manufacture of producer gas. Hempel's[4] experiments with gas oils at temperatures between 700 and 900° C. have demonstrated further the influence of the rate of oil feed upon the composition of the products. J. F. Tocher[5] has also shown some results of a change in the rate of oil feed. A technical application of the time factor can be found in the experiments of Jones.[6]

In varying the rate of oil fed into a retort or furnace for the production of oil gas, one varies the time during which any portion is heated and hence the time allowed for the reaction. With a very slow rate of oil feed, the reaction would attain an equilibrium composition representative of the heating zone conditions. With increasing rates of oil feed the time allowed for reaction is shortened and the products obtained correspond to an earlier stage of the decomposition. The composition of oil gas is therefore dependent upon the time allowed for chemical change. Hence the study of the time factor in the making of oil gas should yield interesting and practical results.

[1] Berthelot, *Ann. chim. phys.* (**1866** to **1877**); Thorpe and Young, Liebig's *Ann.*, **165** (1872), 1; *Proc. Roy. Soc.*, **21** (1873), 184; Norton and Andrews, *Am. Chem. J.*, **8** (1886), 1; Armstrong and Miller, *J. Chem. Soc.*, **49** (1886), 74; Lewes, *J. Soc. Chem. Ind.*, **11** (1892), 584; Haber, *Ber.*, **29** (1896), 2691; *J. Gasbel.*, **34**, 377, 435, 452; Worstall and Burwell, *Am. Chem. J.*, **19** (1897), 815; Bone and Coward, *J. Chem. Soc*, **93** (1908), 1197; Hempel, *J. Gasbel.*, **1910**, p. 53; Kramer and Spilker, *Ber.*, **33** (1910), 2265; Lewes, *Trans. Chem. Soc.*, **69** (1892), 322; *Proc. Roy. Soc.*, **55** (1894), 90; **57** (1905), 394, 450; Bone, *J. Gasbel.*, **51** (1908), 803; Engler, *Ber.*, **30** (1897), 2908.

[2] Lewes, *Proc. Roy. Soc.*, **55** (1894), 90; **57**, 594.

[3] Clement, *Bull.* **30** (1909), D. of Ill. Eng. Exp. Sta.

[4] Hempel, *J. Gasbel.*, **1910**, pp. 53, 77, 101, 137 and 155.

[5] J. F. Tocher, *J. Soc. Chem. Ind.*, **13** (1894), 231.

[6] Jones, *Am. Gaslight J.*, **99** (1913), 273.

## EXPERIMENTAL CONSIDERATIONS

A study of the reactions of gases moving through heated vessels, the method which was used in this investigation and is representative of practice in oil gas production, involves certain features of design which are dependent upon the theoretical considerations of reaction velocity. During the passage of any heating-zone-composition through the cooling zone, there will be a certain change in composition due to a reversal of reactions.[1] The extent of this reversal will depend on the time required in the cooling zone to arrest the reactions. Hence the more quickly these gases are cooled after leaving the heating zone, the more nearly will the product obtained be representative of the heating zone conditions. The efficiency of the cooling zone in arresting the reversal of reactions is materially increased in some of the decomposition reactions by the separation of carbon in the solid phase, making it possible to obtain as the product a gas mixture which very closely approximates the composition of the mixture in the heating zone. It is thus evident that reaction velocity is important not only in the heating zone, but also in the cooling zone.

Further essential considerations in the attainment of a product representative of heating zone conditions are those of convection and diffusion. As shown by Langmuir,[2] diffusion and convection act in a way that is equivalent to decreasing the reaction velocity. Convection currents may be set up by differences in temperatures or irregularities in design, the results of which will tend to shorten the time of contact for some of the molecules in the heating zone. The effect of diffusion increases with temperature as the coefficient of diffusion varies approximately with the square of the absolute temperature. Considering the heating zone or cooling zone separately, raising the temperature increases the diffusion effect and is in a sense equivalent to shortening the time of contact. This effect may be a material consideration in the heating zone but would be almost negligible in the cooling zone. On the other hand, when one considers the mutual effect of the two zones, diffusion offers an advantage, due to the differences in the partial pressures of the reacting substances. Differences in partial pressures cause those substances whose proportions increase with rise in temperature to diffuse from the heating zone to the cooling zone and *vice versa* those substances whose proportions decrease with rise in temperature diffuse in the opposite direction. Hence, this effect aids also in obtaining products more nearly corresponding to the heating-zone-composition.

[1] Nernst, *Z. anorg. Chem.*, **49** (1906), 213.

[2] Langmuir, *J. Am. Chem. Soc.*, **30** (1908), 1742.

### OIL GAS APPARATUS

The design and construction of an apparatus suitable for carrying out the study of the behavior of hydrocarbon vapors under the conditions outlined in the foregoing theoretical discussion involved many important considerations. In such an apparatus it was desired to provide for working with constant temperatures up to 2300° C.; for pressures ranging from —15 lbs. to 100 lbs. gauge per sq. in.; for constant rates of oil feed over a large range; for suitable means of collecting the resultant products; and for numerous other requirements.

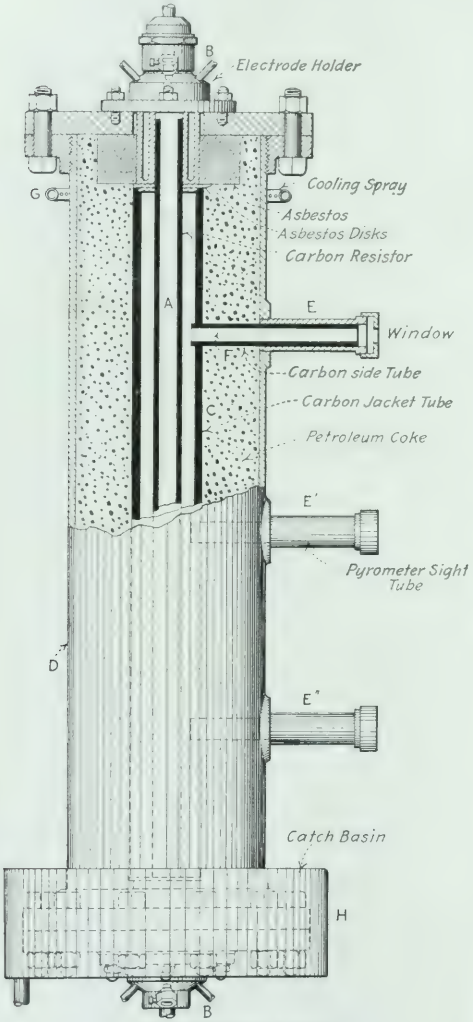


FIG. I RESISTANCE FURNACE

### THE FURNACE

An electrically heated carbon tube resistance furnace, illustrated in Fig. I, was constructed. This furnace embodies the use of a carbon tube resistor held by water-jacketed electrode holders and surrounded by heat-insulating material enclosed by an iron furnace body which is provided with suitable accessory mechanisms for electrical and water-cooling connections, feed and discharge apparatus, and observation of temperatures and pressures.

The carbon tube[1] resistor (A) is 46 in. long, 1 in. inside diameter, with 0.25 in. wall. Deducting the electrode holder contact length, about 4 in. at each end, this gives a heating zone of 38.5 linear inches with 120 sq. in. heating surface and a volume equal to 30.5 cu. in. or about 500 cc. This tube is copper plated externally at each end to give a suitable contact surface of 18 sq. in. with each electrode holder.

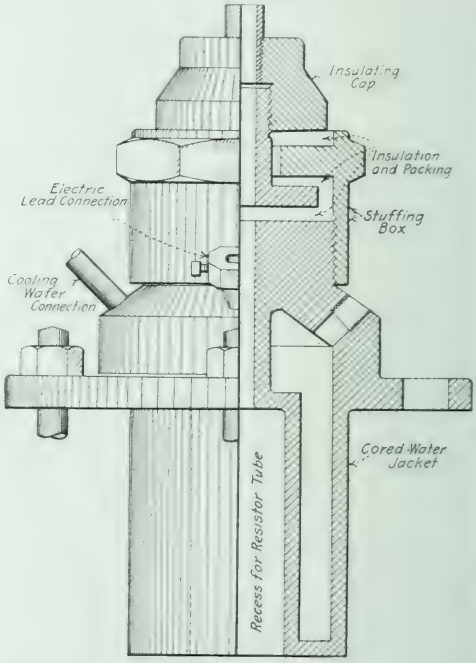


FIG. II—ELECTRODE HOLDER

The electrode holders (BB) are integral bronze castings with cored water jackets and with flanges for bolting to the furnace heads. The construction is shown in some detail in Fig. II. Into the main body of the holder outside of the flanges, are drilled and tapped the water-jacket connections and binding posts for the electric leads. The outside ends are further provided with carefully insulated stuffing boxes and caps in order to separate the heating element, electrically, from the feed and discharge mechanisms of the assembled apparatus. The flanges, bolts, and nuts are insulated with sheet mica to isolate the heating element from the furnace casing.

The resistor tube is surrounded by a large concentric

[1] Carbon tubes were obtained from the National Carbon Co.

carbon tube (C), 3 in. inside diameter and 0.50 in. wall, which is insulated from the electrode holders by asbestos disks. This construction leaves an annular dead gas space of 0.75 in. around the resistor. Between this large carbon tube and the furnace casing powdered petroleum coke is packed for heat insulation.

The furnace body (D) is made from extra heavy wrought iron pipe with screwed and peened flanges at each end. To these are bolted blank companion flanges centrally bored to receive the bodies of the electrode holders and faced to seat the flanges. The electrode holders are each held in position by six 0.5 in. stud bolts drilled and tapped into the furnace heads. As above stated the mountings of the electrode holders are mica-insulated from any contact points with the furnace casing. Three solid bosses,

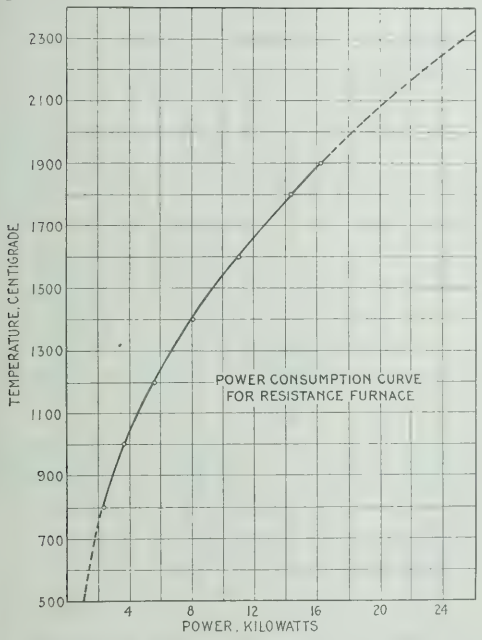


FIG. III—POWER CONSUMPTION CURVE FOR RESISTANCE FURNACE

3 in. diameter by 0.5 in. thick, are autogenously welded on the outside walls of the furnace casing and are drilled and tapped for 1 in. brass extensions which serve as sight tubes (EE′E″).

These extension tubes register with and support carbon side tubes (FF′F″), 0.75 in. inside diameter and 0.125 in. wall, which connect the sight tubes with the annular space around the resistor. The outer ends of the sight tubes are provided with glass windows 0.25 in. thick. This combination gives a straight way view into the resistor chamber at three points along its length.

The water-cooling system for the furnace casing consists of a perforated yoke of water pipe (G) at the top for spray cooling and an annular catch basin (H) at the bottom.

### OPERATION AND TEST OF FURNACE

The power required to heat the furnace is derived from a single phase, 60 cycle, 50 kw. alternating current generator, having a range of 5 to 100 volts which can be regulated within narrow limits by a switchboard and rheostat combination. Thus the temperature of the furnace can be readily controlled. Power was measured by the use of a portable Weston ammeter, voltmeter, and wattmeter placed in close proximity to the furnace. The readings from these three instruments made it possible for the operator to determine the power consumption of the furnace and to check the proper working of the apparatus.

Ordinarily it required about an hour to heat the furnace to a constant temperature after the power had been turned on. The high temperatures are measured by sighting through the observation tube windows with a Wanner optical pyrometer; no temperature corrections are necessary. The low temperatures are measured by replacing the glass windows by small stuffing boxes through which pyrods are inserted. The power used for the various temperatures is shown in Fig. III. This furnace has been tested at various temperatures ranging from 500 to 2300° C. and held constant at such temperatures for several hours at a time. In these tests the readings at the three different observation points agreed. In one of the tests the furnace was held at 1600° C. for four hours without requiring any regulation of the power. A hydrostatic pressure test fo 200 lbs. per sq. in. was made on the assembled furnace with the feed and discharge mechanisms attached.

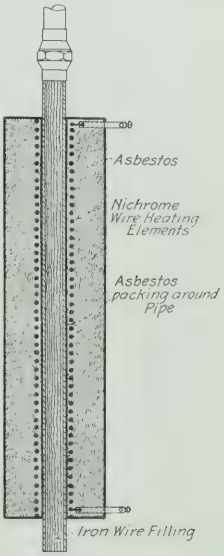


FIG. IV—PREVAPORIZER

The carbon resistor is the only part of the furnace which requires renewal. Yet a single tube has been used for fifty runs at various temperatures. Whenever it is necessary to renew the resistor, the electrode holders are removed and a new tube fitted.

### PREVAPORIZER

The object of the prevaporizer is to vaporize the oil before it enters the heating zone of the furnace.

The prevaporizer, Fig. IV, consists in a $^3/_8$ in. brass pipe 18 in. long, containing a bundle of iron wire for spreading the oil. It is electrically heated from the outside by 8 turns to the inch of No. 18 B. & S. nichrome resistance wire properly insulated from the tube by four wrappings of asbestos paper. For heat conservation the whole is surrounded by standard 85 per cent

magnesia pipe covering. The power required for heating the prevaporizer is furnished from a separate direct current line and regulated by the use of a lamp bank.

Prevaporization was found to be an essential feature as experiments showed that even when the heating zone temperature of the furnace was 1400° C. and the rate of oil feed 50 drops per minute, the oil dropped directly through the heated carbon tube and came out at an equal rate with very little vaporization; this result was apparently due to spheroidal effect and lack of contact with the heated surface. With a solid or vapor passing through the tube under the same conditions,

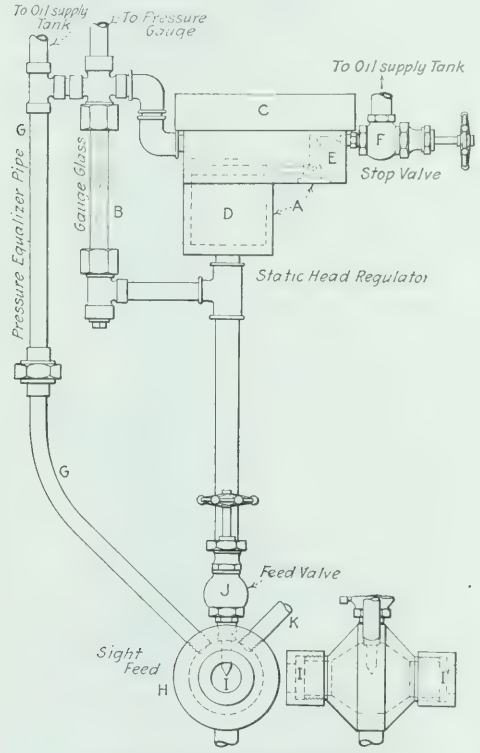


FIG. V—STATIC HEAD AND FEED REGULATOR

the solid would become heated by radiation and the vapor mainly by conduction. Prevaporization was found to be incomplete at very high rates of oil feed, *i. e.*, the prevaporizer has a maximum capacity. As an additional precaution, at high feed rates, the wire filling of the prevaporizer was extended into the heating zone of the furnace.

### STATIC HEAD AND FEED REGULATOR

The object of the static head and feed regulator is to provide for an accurate and steady rate of oil feed which in turn controls the time factor.

The static head regulator, shown in Fig. V. is made up of a specially designed cast brass casing, A, with a gauge glass, B, and a screw cap, C, which may be removed for internal adjustment. The inside mechanism consists of a cork float, D, which operates a needle valve, E. This constant level regulator is also connected with the oil supply tank, the feed mechanism, the pressure equalizer pipe, and the pressure gauge. Valve F is a stop-valve to be closed when the apparatus is not in use.

The sight-feed regulator H is constructed from a brass casting provided with two glass windows, II', and an angle needle valve, J, to regulate the rate of oil feed. Connections are made from this with the static head regulator, prevaporizer, and pressure equalizer and admixture pipes as shown in Fig. V.

A constant head of oil is necessary in order that a fixed opening of the feed valve J may give a definite and uniform rate of oil feed. This is accomplished by the cork float D operating the needle valve E, which admits oil from the storage tank at a rate equal to the rate of feed. In order to insure the proper working of this mechanism, a gauge glass, B, is provided, which registers the oil level. This level has been found to vary not more than $^1/_8$ in. regardless of the level in the oil supply tank. The oil feed is regulated to the desired rate by adjusting the needle valve J, according to observations made through the windows I.

Table I contains data taken from some of the experimental runs and serves to show the range of accuracy of oil feed obtained by this mechanism:

TABLE I RANGE OF ACCURACY OF OIL FEED

| Test | Rate of feed per minute | Period of test | Variation |
|---|---|---|---|
| 1 | 8 drops | 3 hrs. | None |
| 2 | 100 drops | 2 hrs. | 1 drop |
| 3 | 5.4 cc. | 1 hr. | None |
| 4 | 15.8 cc | 30 min. | 0.5 cc. |
| 5 | 69.0 cc. | 8 min. | None |

The pressure of the whole system is equalized by a pressure equalizing pipe, G, which communicates the furnace pressure through the sight feed to the static head regulator and the oil supply tank.

Pipe K is used for recirculating the gases made or for admixing other material with the oil.

### OIL SUPPLY TANK

The oil supply tank (see Fig. VI), with a capacity of 600 cc., is made from standard 1.5 in. brass pipe and fittings. To this a gauge glass is connected and provided with a parallel meter stick carrying a sliding pointer. This arrangement is calibrated for volume and enables the operator to verify the uniformity of the rate of oil flow and hence the accuracy of the constant head apparatus.

### GAS HOLDERS

The gas holders are balanced bell holders with water seal. These are calibrated and provided with a meter stick and pointer in order to facilitate the recording of the rate of gas generation during a run.

### FEED AND DISCHARGE MECHANISM

Both the oil feed mechanism and the condensing system are carried on the supporting framework by swinging arms. The connections to the furnace at their respective ends are made through ground joint

unions. When cleaning, renewals or repairs to the furnace are necessary, the unions may be disconnected and the mechanism swung aside without disturbing the furnace.

### ASSEMBLY AND OPERATION

The arrangement of the complete apparatus ready for operation is shown in Fig. VI. At the beginning

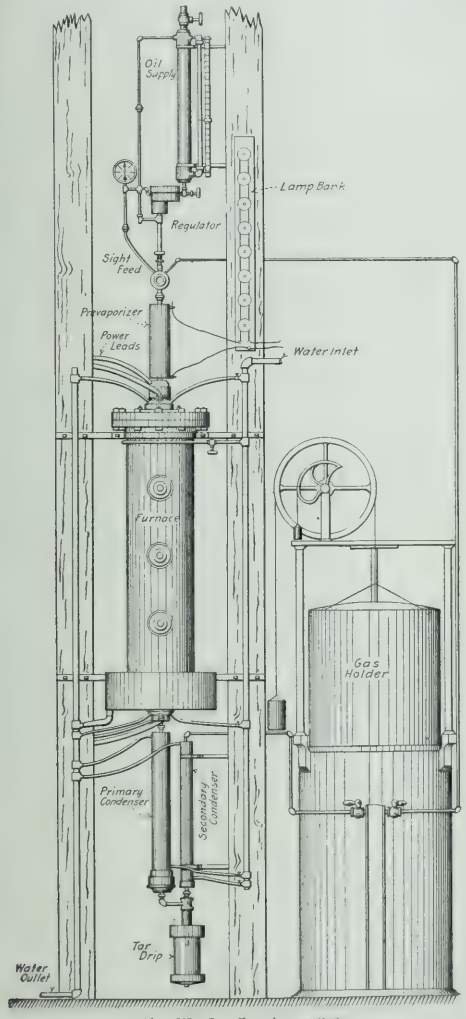


FIG. VI—OIL GAS APPARATUS

of an experiment the oil tank is first filled with oil; after the feed valve has been adjusted to the desired rate of oil feed, oil-tank readings are taken at definite intervals of time.

The oil passes from the supply tank to the static head regulator and out through the feed adjusting valve to the prevaporizer. From here the vaporized oil is carried directly into the heating zone of the furnace.

The oil gas runs were made over a range of constant temperatures from 800° to 1600° C.

Temperature observations, during a run, showed that the feed end of the resistor was 50° to 100° C. cooler than the center and discharge points which remained practically the same. This lower temperature of the feed end of the reaction chamber is obviously due both to the heating up of the oil vapors and to the large amount of heat required for the endothermic reactions taking place in this part of the tube. Furthermore, the deposition of carbon here may reduce the resistance and hence lower the temperature.

TABLE II—RECORDS OF RUNS AT DIFFERENT RATES OF OIL FEED

SLOW RATE OF OIL FEED

| Time | K. W. | Temp. ° C. | Gauge pressure Lbs. per sq. in. | Oil rate Cc. per min. | Gas rate Liters per min. |
|---|---|---|---|---|---|
| 11.15 | 4.0 | 1010 | 0 | 2.1 | ... |
| 11.20 | ... | .... | 0 | 2.1 | 2.0 |
| 11.25 | ... | 1000 | 0 | 2.0 | 1.9 |
| 11.30 | ... | .... | 0 | 2.0 | 1.7 |
| 11.35 | ... | .... | 0 | 2.1 | 1.8 |
| 11.40 | ... | 1000 | 0 | 2.2 | 1.8 |
| 11.45 | ... | .... | 0 | 2.0 | 1.9 |
| 11.50 | 4.1 | .... | 0 | 2.1 | 1.8 |
| 11.55 | .... | 1010 | 0 | 2.2 | 1.8 |
| 12.00 | .... | .... | 0 | 2.1 | 1.8 |
| 12.05 | .. | 1000 | 1 | 2.1 | 1.7 |
| 50 min. | | | | 105 cc. | 92 liters |

| PERCENTAGE GAS ANALYSIS—SLOW RATE OF FEED—MARCH 8, 1915 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $CO_2$ | Ill. | $O_2$ | CO | $H_2$ | $C_nH_{2n+2}$ | $N_2$ (diff.) | Total | Carbon | Tar |
| 0.6 | 6.7 | 0.8 | 1.0 | 54.5 | 29.0 | 7.4 | 100 | Little | Trace |
| or ... | 7.5 | ... | ... | 60.5 | 32.0 | ... | 100 | ..... | ..... |

MODERATE RATE OF OIL FEED

| Time | Temp., ° C. | Gauge pressure Lbs. per sq. in. | Oil rate Cc. per min. | Gas rate Liters per min. |
|---|---|---|---|---|
| 4.10 | 1000 | 0 | 14.0 | ... |
| 4.12 | ... | 0 | 13.5 | 5.8 |
| 4.14 | .... | 0 | 13.5 | 5.8 |
| 4.15 | .... | 0 | 13.0 | 6.2 |
| 4.20 | .... | 0 | 13.5 | 6.5 |
| 4.25 | .... | 0 | 13.5 | 5.3 |
| 4.30 | .... | 0 | 13.5 | 6.3 |
| 4.35 | 1000 | 0 | 13.0 | 6.5 |
| 25 min. | | | 240 cc. | 160 liters |

| PERCENTAGE GAS ANALYSIS—MODERATE RATE OF FEED—APRIL 16, 1915 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $CO_2$ | Ill. | $O_2$ | CO | $H_2$ | $C_nH_{2n+2}$ | $N_2$ (diff.) | Total | Carbon | Tar |
| 0.1 | 19.2 | 0.0 | 0.8 | 44.3 | 35.2 | 0.4 | 100 | Little | 125 cc. |
| or ... | 19.5 | ... | ... | 44.8 | 35.7 | ... | 100 | .... | ... |

RAPID RATE OF OIL FEED

| Time | Temp. ° C. | Gauge pressure Lbs. per sq. in. | Oil rate Cc. per min. | Gas rate Liters per min. |
|---|---|---|---|---|
| 3.30 | 1000 | 0 | 44.0 | ... |
| 3.32 | .... | 0 | 44.5 | 13.0 |
| 3.36 | .... | 0 | 44.5 | 13.2 |
| 3.38 | .... | 0 | 45.0 | 13.3 |
| 3.41 | 1000 | 0 | 44.5 | 13.3 |
| 11 min. | | | 490 cc. | 445 liters |

| PERCENTAGE GAS ANALYSIS—RAPID RATE OF FEED—APRIL 16, 1915 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $CO_2$ | Ill. | $O_2$ | CO | $H_2$ | $C_nH_{2n+2}$ | $N_2$ (diff.) | Total | Carbon | Tar |
| 0.0 | 35.0 | 0.6 | 1.8 | 21.8 | 36.0 | 4.8 | 100 | Trace | 245 cc. |
| or ... | 37.7 | ... | ... | 23.5 | 38.8 | ... | ... | ..... | ... |

The measurement of the high temperatures by the optical pyrometer offered no difficulties as there were no fumes present in the furnace.

The hot gases are discharged from the reaction chamber directly into the primary condenser where the reactions are arrested by the cooling. From here the gases go through the tar drip which is followed by a secondary condenser and thence out to the gas holders, where the rate of gas generation is noted at definite intervals of time. The condensates from both the primary and secondary condensers run into the same tar drip from which they may be readily removed at the end of each experiment.

Typical records of runs are shown in Table II.

### GAS SAMPLING AND ANALYSIS

The gas from the runs was collected in the balanced bell gas holders already described. Care was always taken to saturate the seal water with a similar gas previous to the collection of the run from each experiment. Before taking a sample of gas from the holders for analysis, the product was allowed to stand a sufficient length of time for complete mixing by diffusion and for the settling out of any tar or carbon that might have been carried over.

The gas samples were analyzed by the standard methods[1] with a few modifications to meet special requirements. The Hempel equipment was used in all analyses and the order of procedure was as follows:

1—Absorption of the carbon dioxide with KOH solution.

2—Absorption of the illuminants with fuming sulfuric acid (23 per cent free $SO_3$).

3—Absorption of the oxygen by alkaline pyrogallol.

4—Absorption of the carbon monoxide by two ammoniacal cuprous chloride solutions.

5—Partial combustion of the hydrogen by passing 20 to 30 cc. of the remaining gas mixed with the proper proportion of pure oxygen over palladium black heated to 70° to 80° C.

6—Explosion of the remaining hydrocarbon-oxygen mixture.

The partial combustion of hydrogen in gas mixtures containing percentages above 90 per cent was difficult on account of the danger of explosion. In such cases the mixture was exploded directly and calculated as hydrogen and methane from the formulas,

$$\text{cc. of } H_2 = \frac{2\text{T. C.} - 4CO_2}{3} \text{ and cc. of } CH_4 = CO_2,$$

where T. C. = total contraction noted directly after the explosion and $CO_2$ = contraction due to absorption with KOH after explosion.

In the partial combustion of hydrogen followed by the explosion of the residual gas mixture, it was often difficult to obtain an explosion by using air as the source of oxygen. This difficulty was avoided, however, by the use of pure oxygen in such an amount that, after the removal of the hydrogen by the palladium black treatment, an explosive mixture remained.

From the total contraction and the carbon dioxide found by explosion, the volume of saturated hydrocarbons was calculated by the following formula:[2]

$$V = \frac{2\text{T.C.} - CO_2}{3}$$

This gave the total volume of all the saturated hydrocarbons: methane, ethane, propane, etc. From the V and the $CO_2$ a mean value of $n$ for the type formula $C_nH_{2n+2}$ was obtained, which gave an indication of the nature of the hydrocarbons present, that is, $n = \frac{CO_2}{V}$.

There is no proof that the saturated hydrocarbons do not contain hydrocarbons of higher molecular weight than ethane. The true percentages of each of the $C_nH_{2n+2}$ hydrocarbons can be determined only by the fractional distillation methods of Burrell[1] and his associates, of the U. S. Bureau of Mines.

In common analytical practice, when the hydrogen is separated by partial combustion, the remaining gas is assumed to contain only methane and ethane and is calculated as such. This obviously would give an error dependent upon the amount of heavier hydrocarbons present.

For the calculation of the respective volumes of ethane and methane present on the above assumption, the following formulas were used:

$$\text{cc. of } C_2H_6 = \frac{4CO_2 - 2\text{ T. C.}}{3} \text{ and}$$

$$\text{cc. of } CH_4 = CO_2 - 2\ C_2H_6.$$

### THE TIME FACTOR

The experimental values found in this investigation are considered on the assumption that the true time factor is a function of the rate of oil feed. As stated above, the true time factor, which represents the interval of time in which the reactions progress, is dependent upon the theoretical considerations of reaction velocity. It is substantially a function indirectly proportional to the rates of oil feed; *i. e.*, an increase in the rate of oil feed decreases the time of reaction.

On the other hand, the rate of gas production might be considered as a means of obtaining a better approximation of the true time factor. This would necessitate the calculation of the volumes of the gases to the reaction zone conditions. Furthermore, tars would have to be considered, in case of their formation. Such a method, even if both tars and gases were considered, would not give a value approximating the true time factor, as the original oil vapors occupy a much smaller volume than their decomposition products; in fact decomposition in the reaction zone proceeds with a continuous increase in volume. It is apparent then that this basis of a time factor would be impractical either for experimental study or for technical purposes. For these reasons the time factor as based on the rate of oil feed was selected for this investigation as it offers a comparative value for theoretical considerations and is an easily measured quantity, as well as a readily controllable variable for practical work.

### EXPERIMENTAL

A water-white kerosene, boiling between 150–290° C., was used in all experimental runs.

All runs were made at atmospheric pressure, any variation of which was indicated by the pressure gauge.

The complete gas analyses always showed varying percentages of carbon dioxide, carbon monoxide, and air (*e. g.*, see Analyses in Table II), so that the figures for illuminants, hydrogen, and saturated hydrocarbons did not present these constituents in their proper relationships. This difficulty was overcome by recalculating the analyses to the illuminant-hydrogen-saturated hydrocarbon basis (see Analyses in Table II) and all subsequent data are presented from this view point.

[1] Dennis, "Gas Analysis," 1913.

[2] DeVolderc and DeSmet, *Z. anal. Chem.*, **49** (1910), 661.

[1] Burrell and Seibert, *J. Am. Chem. Soc.*, **36** (1914), 1537; Burrell and Robertson, THIS JOURNAL, **7** (1915), 17, 210

EFFECT OF RECIRCULATION OF GASEOUS PRODUCTS

In this investigation it was necessary first to prove that in the production of oil gas, chemical equilibria are not obtained, for if such were not the case, a study of the time factor would be valueless. This point was proved by runs at slow rates of oil feed, so as to allow a considerable time for reaction, and subsequent recirculations of the products. Slow rates of oil feed were selected because, if equilibria were not established at such rates, it is self-evident that they would not be established at higher rates with correspondingly less time for reaction.

In experimental data given in Table III three different rates of oil feed at the same temperature, 1200° C., were selected and the recirculations (*a* and *b*) made at rates equal to their respective rates of gas

TABLE III—GAS GENERATION AND RECIRCULATION AT 1200° C.

| Run No. | Oil rate Cc. per min. | Gas rate Liters per min. | Gas Analyses (Percentages) Illum. | $H_2$ | $C_nH_{2n+2}$ |
|---|---|---|---|---|---|
| 1 | 1.1 | 1.25 | 0.0 | 92.5 | 7.5 |
| 1*a* | ... | 1.25 | 0.0 | 94.0 | 6.0 |
| 2 | 2.4 | 2.4 | 1.1 | 90.5 | 8.4 |
| 2*a* | ... | 2.4 | 0.0 | 92.8 | 7.2 |
| 2*b* | ... | 2.4 | 0.0 | 93.2 | 6.8 |
| 3 | 6.0 | 5.3 | 1.5 | 88.2 | 10.3 |
| 3*a* | ... | 5.3 | 0.5 | 88.9 | 10.1 |
| 3*b* | ... | 5.3 | 0.0 | 90.5 | 9.5 |

generation. Rates that gave practically no tar were selected; this was necessary because tars, if present, undoubtedly take part in the reactions in the heating zone.

A consideration of the general velocity equation in conjunction with the above data will show some interesting relations between reaction velocity and gas recirculation.

$$\frac{dx}{dt} = k(A_1)^{n_1}(A_2)^{n_2} \ldots - k'(A_1')^{n_1'}(A_2')^{n_2'} \ldots$$

Here the rate of change is dependent upon the respective velocity constants of the reverse reactions and the concentrations of the reacting substances. For any one temperature the velocity constants have a fixed value. Should the decomposition reactions have completed themselves or come to equilibrium, $dx/dt$ would have been equal to zero, but the above data shows that this was not the case, and hence equilibrium was not attained. As the reactions approach equilibrium, the respective velocities of the two reverse reactions become more nearly equal, *i. e.*, the rate of change, $dx/dt$, is a decreasing function as equilibrium is approached. The results in Table III show this effect quite conclusively, as the change in the second recirculation is less than that in the first.

In case one considers the reactions to proceed to completion in one direction only, the same theoretical conclusions hold.

In the above gas mixtures, with no illuminants present, the saturated hydrocarbon percentages were found to consist entirely of methane. The reaction involved at such a stage of the decomposition consists only in the decomposition of methane into carbon and hydrogen. The equilibrium composition of this reaction at 1200° C. (calculated according to the formulas of Nernst or Mayer and Altmayer) should show not more than 0.3 per cent methane, as has been experimentally proved by many investigators.[1] The reason that this value was not obtained in the above experiments is that sufficient time was not allowed for the reactions to reach equilibrium. The intervals of reaction time in the runs in Table III calculated from the gas rates, temperature, pressure and volume of heating zone, amounted to only a few seconds—5, $2^1/_2$ and 1 second, respectively—for Nos. 1, 2 and 3. Equilibrium compositions could be attained only by the lapse of many minutes in the heating zone. This emphasizes the fact that equilibrium compositions are not obtained in oil gas practice and further that it would be impractical to run an oil gas generator at such rates of oil feed as would even approximate equilibrium compositions.

CHANGE OF COMPOSITION WITH RATE OF OIL FEED AT CONSTANT TEMPERATURE

The changes of composition with the rate of oil feed at constant temperature are plotted from the experimentally determined data in Fig. VII. In general, these curves show that a decrease in the oil rate, *i. e.*, an increase in the time of reaction, at any one constant temperature, results in a greater degree of decomposition.

For any two temperatures that can be compared with reference to percentage of any one selected constituent, the higher temperature will result in an equivalent degree of the decomposition at a much higher rate of oil feed. However, the total compositions of the gases produced at the different temperatures are not strictly comparable, *i. e.*, the percentages of illuminants or saturated hydrocarbons for equal percentages of hydrogen are not the same. This is apparently due to different reactions taking place at the different temperatures and to the unequal effect of the different temperatures on the velocities of the various reactions.

It will be noted that at low temperatures and at high rates of oil feed a decrease or increase in the oil rate has comparatively little effect on the percentages of hydrogen or illuminants in the gaseous products. This suggests that there must be a minimum percentage of each constituent at these temperatures. Yet one must not conclude from these facts that the decompositions at the low temperatures proceed in abrupt stages, as this phenomenon finds explanation in a more close consideration of the true time factor. From Fig. IX it will be seen that the rates of gas generation do not undergo material change over a considerable range of oil feed. On the assumption that the volumes of the tars in the heating zone are approximately equal, then the reaction periods for the high rates of oil feed are almost the same and should give gaseous products of similar compositions.

In accordance with the theoretical considerations, the maximum decomposition at any one temperature can be attained only at equilibrium, which is char-

[1] Bone and Jerdan, *J. Chem. Soc.*, **71** (1897), 41; **79** (1901), 1042; Mayer and Altmayer, *Ber.*, **40** (1907), 2134; H. von Wartenberg, *Z. physik. Chem.*, **61** (1907), 366; Bone and Coward, *J. Chem. Soc.*, **93** (1908), 1197. **93** (1908), 1975; Pring, *J. Chem. Soc.*, **97** (1910), 498; Pring and Fairlie, *Ibid.*, **99** (1911), 1796; **101** (1912), 91; also THIS JOURNAL, **4** (1912), 812.

acteristic of an extremely long time for reaction. The curves in Fig. VII point toward such equilibrium compositions at the slow rates of oil feed. Such compositions can in all probability be attained in the heating zone at extremely slow rates of oil feed but experimental results would not verify this on account of the reversal of reactions which would take place in the cooling zone.

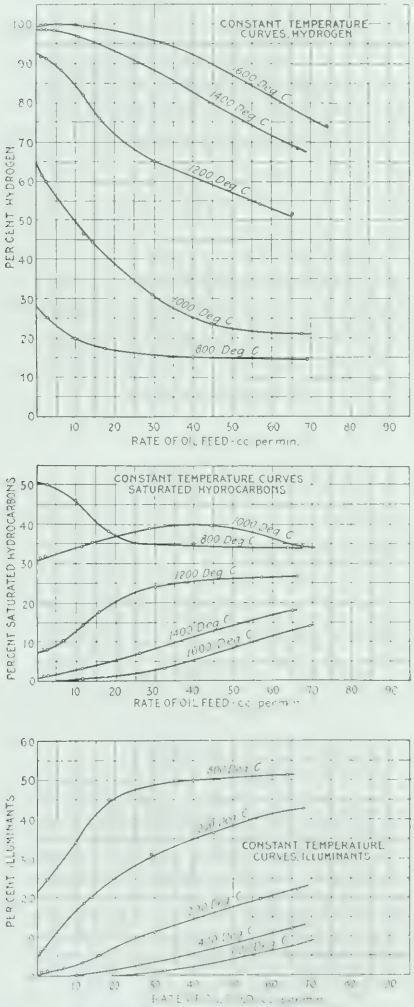


FIG. VII—CONSTANT TEMPERATURE CURVES

CHANGE OF COMPOSITION WITH TEMPERATURE AT CONSTANT RATES OF OIL FEED

In general, the constant feed curves[1] in Fig. VIII show that increase in temperature results in a greater degree of decomposition and that there are definite

[1] Plotted from values obtained by interpolation from the curves in Fig. VII.

temperatures at which maximum and minimum percentages of the various constituents of the gas mixtures exist. The maxima for hydrogen and the minima for saturated hydrocarbons indicate to a complete decomposition of the oil into carbon and hydrogen. The minima for illuminants exist at a lower temperature than the minima for saturated hydrocarbons at the same rates of oil feed, *i. e.*, in the complete thermal

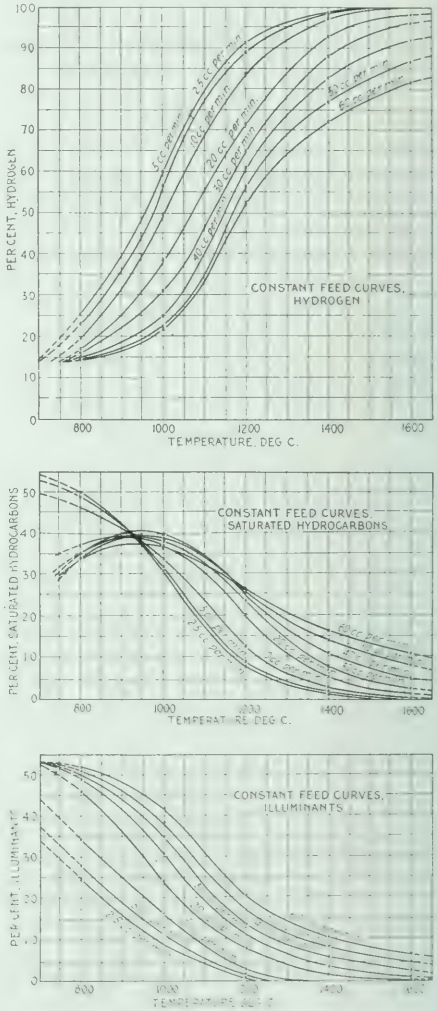


FIG. VIII—CONSTANT FEED CURVES

decomposition of hydrocarbon oils into carbon and hydrogen, the illuminants disappear before the saturated hydrocarbons. The curves for hydrogen and for illuminants seem to indicate minima and maxima, respectively, as shown by the extrapolations. On the other hand, the percentages of saturated hydro-

carbons show true maxima dependent upon the rate of oil feed and the temperature.

PRODUCTION OF HYDROGEN

Table IV shows that at 1600° C., with increasing rates of oil feed, the percentages of hydrocarbons in the resulting gases decrease until a maximum of de-

TABLE IV—PRODUCTION OF HYDROGEN AT 1600° C.

| Run No. | Oil rate Cc. per min. | Gas rate Liters per min | Gas Analyses (Percentages) Illum. | $H_2$ | $C_nH_{2n+2}$ |
|---|---|---|---|---|---|
| 1 | 69.0 | 54.0 | 11.8 | 73.1 | 15.1 |
| 2 | 32.4 | 34.0 | 1.6 | 96.0 | 2.4 |
| 3 | 11.5 | 13.0 | 0.0 | 99.2 | 0.8 |
| 4 | 6.8 | 8.3 | 0.0 | 100.0 | 0.0 |
| 5 | 2.4 | 2.9 | 0.0 | 100.0 | 0.0 |
| 6 | 0.27 | .... | 0.2 | 98.6 | 1.2 |
| 7 | 0.15 | .... | 0.7 | 96.8 | 2.5 |

composition is reached, when the oil is completely decomposed into carbon and hydrogen.

As stated above, under the recirculation of gas, even at 1200° C. the hydrocarbons should be completely decomposed into carbon and hydrogen, but to attain such a result at this temperature would require many minutes in the heating zone. On the other hand, this complete decomposition is realized at 1600° C. in a comparatively short reaction period, due to the great increase in the rate of decomposition at the high temperature over that at the lower temperature so that the shorter time in the heating zone is sufficient for the complete decomposition.

With any design of generator for the production of hydrogen by the direct decomposition of hydrocarbon oils, the time in the heating zone must be such as to favor complete decomposition at the desired temperature. This temperature has both a minimum and a maximum value dependent upon the principles of thermodynamics and upon practical reasons, respectively. The minimum is that lowest temperature at which equilibrium composition represents complete decomposition; *i. e.*, about 1200° C., at which temperature a long time would be necessary to complete the reaction. The maximum is that limited by economical design and practical temperatures.

In Runs 6 and 7, made at very slow rates of oil feed, there are small percentages of hydrocarbons present. This is apparently due to a reversal of reactions as in the theoretical consideration it was concluded that if the rate of cooling was slow the reactions would reverse toward that equilibrium composition corresponding to a lower temperature.

In view of these results the range of complete decomposition is limited not only by temperature but also by definite rates of oil feed which have a maximum and a minimum limit. The maximum is that rate at which the time allowed for reaction is just sufficient for complete decomposition. The minimum is that rate at which the time required to arrest the reactions in the cooling zone is sufficiently long to cause a measurable reversal of reactions. For any temperature at which complete decomposition is possible, these limiting rates will have different values.

From these considerations it seems that the direct decomposition of hydrocarbon oils might become a future source of large quantities of hydrogen, but difficulties would be encountered in the commercial application of such a process. These obstacles would consist mainly in the economical heating of the reacting substances to the necessary high temperature and in the purification of the resulting gas. Economical heating could probably be attained by the use of a counter-current system. Purification would be necessary in order to remove the oxygen and sulfur compounds derived from the original oil.

Crossley[1] has reviewed the commercial hydrogen situation to date, but has omitted reference to the direct decomposition of oil as a possible source of hydrogen. A few patents[2] relating to such processes have been issued.

ILLUMINANTS

Table V consists of data taken from the curves of Fig. VII. These data show that it is possible to obtain gases containing equal percentages of illuminants at different temperatures by varying the rate of oil feed. At a given temperature and rate of oil feed a certain percentage of illuminants is obtained. Should it be desired to obtain a gas containing an equal percentage of illuminants at a higher temperature, it would be necessary to increase the rate of oil feed; this is strictly in accord with the theoretical principle of reaction

TABLE V—EQUAL PERCENTAGES OF ILLUMINANTS OBTAINED AT DIFFERENT TEMPERATURES BY VARYING THE RATE OF OIL FEED

| Temperatures ° C. | Oil rate Cc. per min. | Compositions of Gases (Percentages) Illum. | $H_2$ | $C_nH_{2n+2}$ |
|---|---|---|---|---|
| 800 | 14.0 | 40.0 | 18.5 | 41.5 |
| 1000 | 55.0 | 40.0 | 22.0 | 38.0 |
| 1000 | 14.0 | 20.0 | 44.4 | 35.6 |
| 1200 | 57.0 | 20.0 | 53.7 | 26.3 |
| 1000 | 3.5 | 10.0 | 58.2 | 31.8 |
| 1200 | 26.5 | 10.0 | 66.5 | 23.5 |
| 1400 | 55.5 | 10.0 | 74.0 | 16.0 |
| 1000 | 1.0 | 5.0 | 63.5 | 31.5 |
| 1200 | 14.0 | 5.0 | 78.5 | 16.5 |
| 1400 | 35.0 | 5.0 | 85.5 | 9.5 |
| 1600 | 50.0 | 5.0 | 87.0 | 8.0 |

velocity that increase in temperature increases rate of decomposition and hence it should be necessary to increase the rate of oil feed (equivalent to decreasing the time for reaction) in order to obtain the same percentage of illuminants in the resulting gas. However, gases containing equal percentages of illuminants do not necessarily contain equal percentages of the other constituents. This is apparently due to unequal effects of change of temperature on the various reactions involved in the decomposition. With a desired percentage of illuminants in view, then, it would be possible to increase materially the capacity of any oil gas generator by increasing the temperature a hundred or more degrees.

Experimentally it was found that a gas containing about 52.0 per cent illuminants could be obtained at 800° C. at a high rate of oil feed but at the same time a large amount of tar was produced.

GAS GENERATED

Fig. IX consists of two sets of curves, one showing the gas rates and the other the gas yields for the various rates of oil feed at constant temperature. The rates of gas generation and yields at 1600° C. are not shown, as runs at this temperature could not be maintained for a sufficiently long time to obtain accurate

[1] Crossley, *J. Soc. Chem. Ind.*, **33** (1914), 1135.

[2] Frank, U. S. Pat. 1,107,926 (1914); Ellis, U. S. Pat. 1,092,903 (1914).

data, on account of the choking of the furnace by the large amounts of carbon formed.

The gas rate curves show that at constant temperature an increase in the rate of oil feed does not result in a proportionate increase in the rate of gas generation but rather in a decreasing ratio of gas rate to oil rate. As a result, at low temperatures and high rates of oil feed the rates of gas generation do not show a material change over a considerable range. At 800° C. and at very high rates of oil feed the rate of gas generation actually becomes a decreasing function.

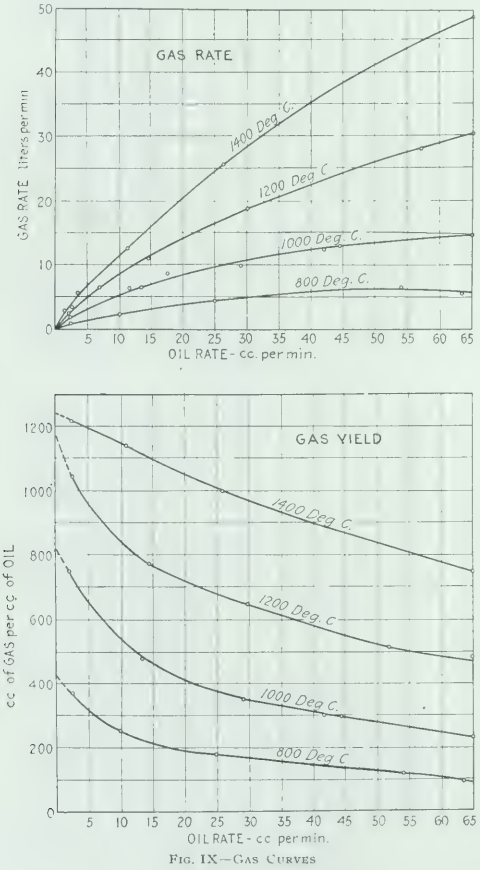


FIG. IX—GAS CURVES

tion. This is apparently due to the checking of the course of the reactions by the insufficient time interval allowed or to so exceeding the capacity of the furnace that the oil vapors are not heated to the temperature of the reaction zone.

The gas yield curves indicate that increase in temperature results in an increase of the yield of gas at any constant rate of oil feed. This is due to the more complete decomposition of the hydrocarbons, as shown by the compositions of the gases made at slow rate (Fig. VII). At constant temperature, decrease in the rate of oil feed will result in an increase in the yield of gas to whatever maximum is representative of the most complete decomposition to be attained at the given temperature. As stated previously a decrease in the rate of oil feed provides the longer reaction period necessary for final equilibrium. Since the most complete decomposition at any one temperature is characteristic of equilibrium composition, a maximum yield of gas can be obtained only at this final stage, although such yields of gas can not be realized experimentally on account of the above-mentioned reversal of reactions in the cooling zone.

### TARS

Tar yields could not be determined with accuracy in these runs as the high rates of gas generation in many of the experiments made it impossible completely to separate the tars from the gases with the apparatus at hand. In general, the tar yield increased with increase in the rate of oil feed at a given temperature and with a decrease in temperature at constant rates of oil feed. Above 1200° C., at slow rates of oil feed, no tars were obtained. The nature of the tars obtained at the various temperatures has not been investigated.

### CONCLUSIONS

I—The control of the composition of the products obtained in the manufacture of oil gas involves not only thermodynamics but also chemical kinetics.

II—In practice, equilibrium is not reached in the thermal decomposition of petroleum hydrocarbons. This is proved by the fact that a recirculation of the products, under the same conditions at which they were generated, results in a further change in composition.

III—The time factor, which is controlled by the rate of oil feed, is just as important as are the other variables (temperature, pressure and concentration), as it has been found that the compositions of the products obtained in making oil gas vary with the rate of oil feed. Hence, from the standpoint of practical operation of an oil gas plant, the rate of oil feed offers an easily accessible means of control.

IV—Maximum and minimum percentages of the various constituents in the products formed by the decomposition of petroleum and petroleum distillates by heat can be obtained by a proper adjustment of the variables.

V—Petroleum hydrocarbons can be completely decomposed into carbon and hydrogen only within well defined limits of the four variables. In this investigation the range of complete decomposition at a definite temperature and pressure was limited by definite rates of oil feed.

VI—Oil gases containing equal percentages of illuminants can be produced at different temperatures by varying the rate of oil feed. Such gas mixtures, although they have equal percentages of illuminants, do not in general have equal percentages of saturated hydrocarbons and hydrogen, *i. e.*, gases of equal illuminating values are not necessarily of equal thermal values.

VII—In an isothermal decomposition of petroleum hydrocarbons, maximum yields of gas and minimum yields of tar are characteristic of equilibrium compositions.

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## THE EFFECT OF THE MINERAL CONTENT OF WATER ON CANNED FOODS

By H. L. HUENINK AND EDWARD BARTOW

Received May 3, 1915

The quality of canned foods produced by certain factories is always superior to that produced by other factories. To be convinced of this fact it is only necessary to examine the product of a number of factories. It will become apparent that this difference is always present. In general, the character of the products put out by each factory is the same from year to year.

Canned-food brokers, who probably examine more canned food than any other class of people, often remark upon the consistent difference in quality, and frequently raise the question as to why it should exist.

There are, of course, numerous causes which may lead to differences in the quality of canned foods, such as climate conditions, character of the soil, mode of handling the crops, factory management, character of the water used in the process, etc. The climatic conditions and the character of the soil cannot be controlled, whereas the others may be entirely corrected in a scientifically managed factory.

One of the factors which may affect the quality of canned foods is the water used in processing. Water is used extensively in the canning industry for washing, soaking, blanching and making of brines and syrups. The foods are also sterilized in autoclaves in the presence of water and the action of its mineral constituents is probably greater here than at any other step in the process of canning.

With the hope that some important information may be gathered, whereby the quality of canned foods can be improved, we have begun a systematic investigation of the action of various salts occurring in water on canned foods.

Because beans could be canned during the winter months and also because baked beans are canned in far greater quantities than any other class of soaked vegetables, the preliminary investigation was made with beans. Beans were canned with distilled water and with University of Illinois tap water to determine the effect which would be produced by the presence of the salts in the water. The analysis of the University supply is shown in the accompanying table.

The beans canned with the University water were harder than those canned with distilled water and their color was very much darker. This shows that the dissolved salts in the water affect the quality of canned beans. To study the effect of the individual salts, pure salts dissolved in distilled water were used in experiments.

In canning beans, they are soaked over night, washed, placed in cans and covered with a syrup, the composition of which varies widely. Usually the syrup consists of water, salt, brown sugar and molasses.

| Ions | Parts per mil. | Hypothetical Combinations | Parts per mil. | Grains per gal. |
|---|---|---|---|---|
| Potassium, K | 2.6 | Potassium nitrate, $KNO_3$ | 1.1 | 0.06 |
| Sodium, Na | 29.0 | Potassium chloride, KCl | 2.9 | 0.17 |
| Ammonium, $NH_4$ | 2.3 | Sodium chloride, NaCl | 3.5 | 0.20 |
| Magnesium, Mg | 34.9 | Sodium sulfate, $Na_2SO_4$ | 3.6 | 0.21 |
| Calcium, Ca | 70.1 | Sodium carbonate, $Na_2CO_3$ | 60.5 | 3.52 |
| Iron, Fe | 1.0 | Ammonium carbonate, $(NH_4)_2CO_3$ | 6.1 | 0.36 |
| Aluminum, Al | 1.3 | Magnesium carbonate, $MgCO_3$ | 121.2 | 7.07 |
| Nitrate, $NO_3$ | 0.7 | Calcium carbonate, $CaCO_3$ | 175.2 | 10.22 |
| Chlorine, Cl | 3.5 | Iron carbonate, $FeCO_3$ | 2.1 | 0.12 |
| Sulfate, $SO_4$ | 2.5 | Alumina, $Al_2O_3$ | 2.5 | 0.15 |
| Silica, $SiO_2$ | 18.9 | Silica, $SiO_2$ | 18.9 | 1.10 |
| | | TOTAL | 397.6 | 23.18 |

Many brands are put up with tomato ketchup. In the soaking process the beans absorb a large amount of water, according to their dryness. The beans which were used in these experiments took up very nearly their own weight of water.

The beans were canned in 250 cc. flasks closed with cotton plugs. These containers were found very convenient for experimental work, and the method was found satisfactory. Beans canned simultaneously in the flasks and in regular No. 2 tin cans could not be distinguished from each other. The method of canning was as follows: 50 g. of dry navy beans were completely covered with water in a 250 cc. Florence flask and allowed to soak over night (about 12 hours). The excess water was then poured off and the beans rinsed several times. There were added 50 cc. of syrup, which was prepared as follows: 20 g. brown sugar, 2.5 g. NaCl, 5 cc. New Orleans molasses and water to make 100 cc. The flasks were plugged with cotton and sterilized in an autoclave for 65 minutes at 14 pounds pressure. The only variable in the experiments was the composition of the water which was changed in order that the effect of the soluble salts could be observed.

In the first series we used waters containing quantities of $CaCl_2$ ranging from 0 (distilled water) to 1000 parts per million, with differences of 100 parts per million between the samples. The results showed in a very striking manner a gradation in the hardness of the beans. The sample which had been processed with the distilled water was very tender and would grade "strictly fancy." Those processed with water containing 100 and with 200 parts per million of $CaCl_2$ were hard and tough and the criticism would be, "underprocessed." Beans of this character are often found on the market and are graded as "standards." The remaining samples, processed with water containing from 300 to 1000 parts per million of $CaCl_2$, were extremely hard and practically unmerchantable. The sample processed with 1000 parts per million of $CaCl_2$ was almost as hard as the uncooked beans. These differences were so marked that the samples could easily be placed in their proper order by one who did not know the quantities of $CaCl_2$ used. The experiment was repeated several times with the same results.

Three parallel series were then run with waters containing $CaCl_2$, $MgCl_2$ and $Na_2CO_3$, respectively. The concentrations again ranged from 0 to 1000 parts per million with differences of 100 parts per million between samples. The results from the $CaCl_2$ series were the same as in previous experiments. The results from the $MgCl_2$ series were very similar, although the differences were not so marked. The beans were harder as the concentration of the $MgCl_2$ increased, and the samples could easily be placed in their proper order by one who did not know the quantities of $MgCl_2$ used.

The $Na_2CO_3$ in the water was found to have a softening action. This fact is quite commonly known. No information, however, could be found concerning the concentration which might be advantageously used. The results showed a gradation in softness from the sample processed with distilled water to that processed with water containing 1000 parts per million $Na_2CO_3$. The former appeared to have received the proper amount of cooking, while the latter appeared to be greatly overcooked. The time of cooking these samples might have been adjusted so that the product in each case would have been "fancy." As the concentration of $Na_2CO_3$ increased it was also observed that the beans were darker in color. The use of $Na_2CO_3$ undoubtedly has some advantages, but this subject needs further investigation.

In order that a careful comparison could be made between effects of substances commonly found in waters, parallel series were run simultaneously, using waters containing $CaCl_2$, $CaSO_4$, $Ca(HCO_3)_2$, $MgCl_2$, $MgSO_4$, $Mg(HCO_3)_2$, $Na_2CO_3$ and $NaHCO_3$. The waters were made up with concentrations of 0, 50, 100, 200, 300, 500 parts per million expressed as $CaCO_3$.

The results indicate that the magnesium and calcium salts, when they are present in any of the forms above mentioned, have a hardening effect on the beans; that is, no difference could be detected in beans processed with water containing equivalent concentrations of calcium or magnesium whether a chloride, sulfate or bicarbonate. With bicarbonates of calcium or magnesium the gradation in hardness was not so marked and consistent as with the chlorides or sulfates. This may be due to the fact that calcium bicarbonate and magnesium bicarbonate solutions are unstable, causing the concentration to change during the soaking and heating. No difference could be detected between the beans canned with water containing magnesium salts and those canned with water containing calcium salts, when the quantities of the salts in solution were equivalent. It would seem, therefore, that the effects of the magnesium ion and of the calcium ion are identical.

The beans canned with the water containing $Na_2CO_3$ and those canned in water containing $NaHCO_3$ were compared and practically no difference could be detected. The same softening effect was observed in the cases when water containing $NaHCO_3$ was used as when $Na_2CO_3$ was used.

The authors expect to continue this work. Experiments will be made with various kinds of beans and other soaked vegetables as well as fresh vegetables, fruits and berries.

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## THE USE OF COPPER SULFATE IN THE PURIFICATION OF SWIMMING POOLS

By STANLEY JUDSON THOMAS

Received December 24, 1914

Within the past two or three years, numerous articles have been written relating to the sanitary conditions of indoor swimming pools. Studies have been made by Dr. William J. Lyster at the University of Pennsylvania, Dr. M. P. Ravenel of the University of Wisconsin, and by various other workers throughout our eastern colleges and universities. One fact is emphasized by all these authorities—that the danger of transmission of zymotic disease through the swimming pool is *real*. It is easy to see how a person suffering with walking typhoid may infect the limited amount of water in the pool and thus transfer the disease to many bathers, who consciously or unconsciously take the water into their mouths. This is but an example. We might carry it further and show how readily diphtheria, cholera, skin diseases, colds, and in fact almost any of our bacterial diseases may be contracted through this medium. It is not my intention to go into the subject of the general care and upkeep of a pool. The *American Physical Education Review* of December, 1912, and February, 1913, has several excellent articles in this connection. The fact is indisputable that, besides such general precautions as preliminary bathing with soap, inspection of the bather, and rejection of dirty bathing suits, etc., some chemical treatment of the water is necessary to safeguard the health of the bathers. What this chemical shall be is the question I shall attempt to answer.

Excellent articles have been written by Dr. Ravenel,[1] Mr. S. C. Markley[2] and others, recommending hypochlorite of lime as the disinfectant. As a precautionary treatment of public water supplies, there is no doubt that this chemical is without a peer. Innumerable examples could be given to show its efficacy. But it must be borne in mind that in the treatment of a public water supply more than 2 parts per million of "hypochlorite" is seldom necessary. This means about 0.6 part per million of available chlorine. When this maximum amount is used aeration of the water is necessary to remove the disagreeable odor and taste of the "hypochlorite." Now consider the use of this chemical in a swimming pool. Dr. Ravenel found that 1 part per million of available chlorine was necessary to sterilize the water. That means 3 parts per million of the hypochlorite, and as the usual method proposed is to dissolve the salt in the pool directly one can imagine the unpleasant odor and taste of the water. "Aeration" is effected, it is true, but "aera-

[1] Dr. M. P. Ravenel, "The Hygiene of Swimming Pools," *Proceedings of the Sixth Congress of the American School Hygiene Association*.

[2] S. C. Markley, "The Use of Chloride of Lime in the Purification of Swimming Pools," *American Physical Education Review*, VIII, 2.

tion" only releases the odor from the water into the enclosed room surrounding the pool.

The use of 2.5 parts per million "hypochlorite" was tried in the Taylor Gymnasium pool, at Lehigh University, and even at this dilution the odor was marked. That the treatment was not effective is shown by the results of the bacteriological analyses of the pool during the treatment (Table I):

TABLE I—BACTERIOLOGICAL EXAMINATION OF TAYLOR GYMNASIUM SWIMMING POOL

| Day and Time November, 1914 | | Count per cc. Gelatin | Agar | *B. coli* per cc. | Remarks |
|---|---|---|---|---|---|
| 8 | 12.00 M. | 50 | 10 | 0 | Fresh water. |
| 9 | 9.00 A.M. | 200 | 1400 | 0 | 3 men had been in the pool. |
| 10 | 10.30 A.M. | 2700 | 1500 | 50 | |
| 10 | 11.15 A.M. | 3000 | 5300 | 200 | 40 men in pool since last sample. |
| 10 | 2.00 P.M. | 2 | 5 | 0 | 2.5 p. p. m. hypochlorite added at 11.30 A.M. No one in pool since 11.15. |
| 10 | 5.45 P.M. | 50 | 800 | 0 | |
| 11 | 3.00 P.M. | 400 | 1000 | 340 | |
| 12 | 5.00 P.M. | 800 | 3000 | 400 | |
| 13 | 2.30 P.M. | 100 | 500 | 100 | 3000 gal. fresh water added. |
| 13 | 2.45 P.M. | 0 | 3 | 0 | Sample taken after 2.5 p. p. m. hypochlorite were added. |
| 14 | 5.00 P.M. | 50 | 400 | 10 | |

From these results it may be seen that, though 2.5 parts per million of hypochlorite of lime purifies the water shortly after its introduction into the pool, it soon loses its germicidal properties and is unable to destroy the bacteria which are constantly being brought in by new bathers. To add 2.5 parts per million of the "hypochlorite" every day would probably solve the problem from a bacteriological standpoint, but the odor would be too offensive for this form of treatment to be considered.

This pool is equipped with a double unit mechanical filter in which alum is used as a coagulant. By this refiltration system the water is always kept clear. The bacterial content of the pool cannot be kept low, however, by this treatment alone. The idea was conceived, and acted upon, of using a small amount of copper sulfate in connection with the alum treatment, not, however, by mixing the copper sulfate with the alum, but by introducing it directly into the pool after the completion of the alum coagulation, which removes the carbonates and bicarbonates that would otherwise hinder the action of the copper sulfate. The result of using 0.4 part per million of copper sulfate proved to be very satisfactory, as will be shown later.

I shall now discuss the use of copper sulfate as a germicide and attempt to show its advantage over hypochlorite of lime as a disinfectant of swimming pools.

In a paper written in the early 80's, Carl von Naegeli,[1] one of the greatest German botanists of the past century, showed how exceedingly sensitive certain living plants are to minute quantities of various metals. He found that certain Spirogyra are unable to resist the toxic effect of one part of copper to one thousand million parts of water, and that minute quantities of other metals, such as silver, lead, tin, iron and mercury, manifested "oligodynamic"[2] properties. Israel and Klingmann,[1] in 1897, studied the effect of copper on certain bacteria, Spirogyra and animal forms. Bacteria and Spirogyra were very sensitive and were easily killed with dilute solutions. In the case of the animal forms, while the toxic effects were visible in most cases with dilute solutions, Vorticella and a few others required a larger amount of the metal. Locke found that traces of copper contained in water distilled in copper vessels were sufficient to destroy Tubifex (one of the annelid worms) and tadpoles. Cushing,[2] in 1899, gave a good description of the work done up to that time along this line.

The fact that these discoveries were of great economic importance was first brought out by Dr. George T. Moore of the U. S. Department of Agriculture. In 1904 the U. S. Department of Agriculture, Bureau of Plant Industry, published[3] the results of Dr. Moore's experiments with copper sulfate as an algicide and disinfectant in polluted water. In that paper it was recommended that copper sulfate be used in the dilution of one part to one thousand parts of water. In December of the same year, *The American Journal of Pharmacy* published an article by Dr. Moore[4] and one by Dr. Henry Kraemer,[5] of the Philadelphia College of Pharmacy. In his paper, Dr. Moore reviewed thoroughly the *practical* application of copper sulfate in municipal water supplies, chiefly as an algicide. The first reservoir so treated was that of the Winchester Water Co. at Winchester, Ky. The success of the treatment is best given in Dr. Moore's own words:

"In June, 1903, our attention was called to the condition of the reservoir at Winchester, Ky. This supply was constructed in 1890, and after the first three years a strong odor and taste were noticeable in the water during the hot summer months. This condition gradually increased until the water attained such a degree of offensiveness as to make its use for any purpose almost intolerable. Aeration and mechanical filtration were tried without effect, and it seemed that the only hope for relief was to abandon the entire reservoir and go ten miles to the Kentucky River for the source of a new supply. The cost, however, was too great to be considered, and for this reason the difficulty was considerably increased. A microscopical examinaton of the water showed that the odor and taste were due to the presence of one of the blue-green algae, and it was believed that the application of copper sulfate at the rate of about 1 to 5,000,000 would be sufficient to destroy these forms; consequently, there being no objection on the part of either the water board or the health authorities, a treatment was made, and the results have been everything that could be desired. Within three or four days the odor disap-

[1] "Ueber oligodynamische Erschemungen in lebenden Zellen," von Naegeli.

[2] "Oligodynamic"—derived from two Greek words meaning the force within a small quantity of a substance.

[1] Israel and Klingmann, "Oligodynamische Erschemungen (v. Naegeli) an pflanzlichen und thiereschen Zellen," Virchow's *Archiv.*, **1897**, pp. 293–340.

[2] Cushing, "Pharmacology and Therapeutics," **1899**, p. 159.

[3] "A Method of Destroying or Preventing the Growth of Algae and Certain Pathogenic Bacteria in Water Supplies," by Moore and Kellerman, U. S. Department of Agriculture, Bureau of Plant Industry, *Bull.* **64.**

[4] "A New Method for the Purification of Water Supplies," by Dr. George T. Moore (an address given before the American Philosophical Society, Oct. 21, 1904), *American Journal of Pharmacy*, **76** (1904), 553.

[5] "The Copper Treatment of Water," by Prof. Henry Kraemer, *American Journal of Pharmacy*, **76** (1904), 574.

peared and the water was perfectly clear. This summer at about the same time it was feared that the algal growth was reappearing, and for this reason another slight treatment was made, but with this exception no copper has been added to the water since the original treatment in June, 1903, and it has remained perfectly clean and sweet."

After citing numerous other examples of the efficiency of copper sulfate as an algicide Dr. Moore says: "Very naturally after it was noted that the algae were so susceptible to infinitesimal quantities of copper, it seemed worth while to test the effect of this metal upon typhoid and cholera germs, these being the two pathogenic forms which are most commonly conveyed by water. As the result of some 500 or 600 experiments, it was demonstrated that, while these bacteria were not as sensitive as the algae, still the dilution necessary to produce death was sufficiently great to warrant the belief that under certain conditions efficient sterilization of large bodies of water could be brought about."

Dr. Kraemer, in corroborating Dr. Moore's results, goes further into the effect of copper sulfate on the human system. He points out that the salt was most beneficial in removing algae from watercress beds, while not harming the cress, and adds: "It seems to me that this is in a measure due to the fact that in the algae the entire individual is comprised in a single cell, which performs all the vegetable as well as the reproductive functions, and being entirely surrounded by the water containing the copper sulfate, all the life processes of the plant are affected, there being no way for it to distribute the solution to other cells, and thus by a dilution minimize the toxic action of the copper." Dr. Kraemer allowed copper foil to dissolve in water in conducting his experiments. While this has the toxic power of the sulfate it has not its added power of sedimentation. His results are conclusive in showing that the intestinal bacteria like colon and typhoid are completely destroyed by placing clean copper foil in the water containing them.

Mr. Alfred M. Quick,[1] in 1904, gave the results of the use of copper sulfate in Lake Clifton of the Baltimore Water works. On July 28, *B. coli* were present in 1 cc. of the water. The next day copper sulfate in the dilution of 1 : 6,390,000 was used. On August 3rd, analysis showed *B. coli* absent. James M. Caird[2] showed the results of the use of $1^1/_2$ parts per million of copper sulfate in the water supply of Elmira, N. Y. On June 24th, analysis showed *B coli* 2 per cc. and the total count was 315 per cc. On June 30th, after treatment, *B. coli* were absent and the total count was 18 per cc.

In April, 1905, in a Bulletin[3] of the U. S. Department of Agriculture, Moore and Kellerman supplemented Dr. Moore's previous article and gave a complete description of all phases of the question. Numerous reports from cities upon the effect of the treatment are given. Notable among these is one from Columbus, Ohio. A badly polluted water supply had caused for over a year an almost continuous epidemic of typhoid fever. The copper sulfate treatment was resorted to but later discontinued "after the daily papers published glaring accounts of the dangers attendant upon such treatment." A tabulation of the data shows clearly the results of the use and non-use of copper sulfate. The salt was used in the dilution of 1 part in 1,500,000.

| | Month | Typhoid cases reported |
|---|---|---|
| No copper used | June | 24 |
| No copper used | July | 33 |
| Copper used after 19th | August | 52 |
| Copper used | September | 16 |
| Copper used | October | 16 |
| Copper used | November | 8 |
| Copper used | December | 4(*a*) |
| Copper discontinued after 5th | January | 91 |
| No copper used | February | 376 |
| No copper used | To March 27th | 279 |

(*a*) 17 cases were reported, but only 4 were users of city water.

The chief objections to the use of copper sulfate were based on the fact that it *might* be harmful to man. Aside from the puerile charges against it that have been made by certain ignorant advertisers a few doctors maintained that nothing was known of the effect of continued use of the salt. It would be impossible even to refer to most of the literature that has been published relating to the harmlessness of this treatment. Dr. Moore and Dr. Kraemer have both collected statements from the leading toxicologists in this and many foreign countries which answer fully all objections.

Dr. Henry Kraemer published an article[1] in 1905, showing the amounts of metallic copper normally contained in over a hundred foods. If these foods can be eaten with impunity, it may be easily seen what slight chance there is of being poisoned by the small amount of copper we use for water purification. Dr. Kraemer's results, Table II, show the quantities of copper in milligrams found in a kilogram of the foods, which corresponds to parts per million in a tabulation of the results obtained in its use in water. As metallic copper comprises only 25 per cent of copper sulfate these results must be quadrupled if an exact comparison is to be made.

TABLE II—QUANTITY OF METALLIC COPPER IN MILLIGRAMS PER KILOGRAM OF VARIOUS FOODS

| | | | | | |
|---|---|---|---|---|---|
| Almonds (15) | 36.8 | Egg, yolk (11) | 5.6 | Milk, cow (12) | 1.6 |
| Apricots (15) | 1.0 | Egg, white (11) | 7.2 | Oatmeal (19) | 4.27 |
| Cherries (15) | 2.3 | Figs(15) | 15.1 | Peas, French (7) | 59.4 |
| Cocoa, pure, no husk (18) | 47.0 | Grapes, Catawba (19) | 1.01 | Potatoes (5) | 2.8 |
| Cucumbers (15) | 45.0 | Kidney, beef (12) | 4.0 | Strawberries (15) | 8.0 |

Add to this the statements of many eminent physicians[2] relating to the beneficial effects of copper as a curative measure for typhoid fever and cholera, and the exhaustive study made by Dr. Walker[3] of London, and our case seems to be complete. Dr. Burg of Paris visited or corresponded with every important copper mine and foundry in Europe where workmen could possibly become impregnated with copper. The results of his study lead to the following conclusions

[1] "The Use of Copper Sulfate in Lake Clifton," by A. M. Quick, *Engineering News*, **52**, 284.

[2] "Purification of the Water Supply at Elmira, N. Y.," by J. M. Caird, *Engineering News*, **52**, 34.

[3] "Copper as an Algicide and Disinfectant in Water Supplies," by Moore and Kellerman, U. S. Department of Agriculture, Bureau of Plant Industry, *Bull.* **76**.

[1] Henry Kraemer, Ph.D., "The Use of Copper in Destroying Typhoid Organisms and the Effects of Copper on Man," *American Journal of Pharmacy*, **77**, 6.

[2] Dr. Lucien F. Salomon, *New Orleans Medical and Surgical Journal*, June, 1902.

[3] Dr. A. deN. Walker, "The Prophylactic Power of Copper in Epidemic Cholera," London, 1883.

which he addressed to the Academy of Medicine and Sciences.

"1—Complete immunity from cholera of the immense majority of all workmen whose calling necessitates their being habitually in contact with copper dust.

"2—Copper and its alloys, brass and bronze, permanently applied to large surfaces of the common integument, are a most precious preventative, which ought in no wise to be neglected and can cause no inconvenience. If these means leave something to be desired as a prophylactic, it will probably be found expedient to reduce the metal to an impalpable powder and to ingest a few pinches.

"3—In the treatment of cholera, copper, opportunely administered, whether in copper filing alone or in any other form which experience shall determine, affords the greatest probability of proving in the hands of the physician a powerful means of cure."

Having been convinced that even in fairly large doses copper sulfate is harmless to the human system, I tried its germicidal effect in the Taylor Gymnasium pool. As the pool water at the time was being refiltered daily, a small amount of alum being added to aid the mechanical filter—I took the opportunity of first determining the efficiency of the alum treatment. As the copper treatment immediately followed the alum treatment, I have tabulated my results together.

Table III shows the results of the use of alum and of alum and copper sulfate.

TABLE III—BACTERIOLOGICAL EXAMINATION OF TAYLOR GYMNASIUM SWIMMING POOL

| Date 1914 | Gelatin count per cc. | *B. coli* per cc. | Additions | Date 1914 | Gelatin count per cc. | *B. coli* per cc. | Additions |
|---|---|---|---|---|---|---|---|
| 5/11 | 4 | 0 | | 5/20 | 8,000 | 1,000 | 1.0 p. p. m. alum per day |
| | | | | 21 | 6,000 | 50 | |
| 11 | 790 | 7 | 1.0 p. p. m. alum per day | 22 | 18,000 | 100 | |
| 12 | 9,000 | 180 | | 23 | 30,000 | 150 | |
| 13 | 18,000 | 100 | | 24 | 9,000 | 80 | |
| 14 | 48,000 | 90 | | 25 | 27,000 | 300 | |
| 15 | 16,500 | 250 | | 26 | 5,000 | 5 | 0.04 p. p. m. $CuSO_4$ per day |
| 16 | 6,900 | 400 | | 27 | 2,500 | 0 | |
| 17 | 36,000 | 400 | | 28 | 100 | 0 | |
| | | | | 29 | 2,000 | 4 | |
| 18 | 4,800 | 29 | 22,000 gallons fresh water | 30 | 500 | 0 | |
| | | | | 6/2 | 5,000 | 9 | |
| 19 | 10,000 | 200 | | 3 | 6,000 | 14 | |

| Average Per Week | Gelatin count per cc. | *B. coli* per cc. |
|---|---|---|
| 1st Alum treatment | 15,000 | 390 |
| 2nd 2.5 p. p. m. "hydrochlorite" | 1,500 | 148 |
| 3rd 0.4 p. p. m. $CuSO_4$ | 3,014 | 5 |

Although copper sulfate is slightly more expensive than hypochlorite of lime, about $1.00 per hundredweight, it is effective in much smaller quantities and hence is cheaper to use.

The germicidal action of the copper sulfate is probably that of a crystalloid, permeating the cell wall and thereby producing the toxic effects.

In the presence of the bicarbonate of magnesium and calcium the following reaction takes place:

$$CuSO_4 + Ca(HCO_3)_2 = CaSO_4 + Cu(OH)_2 + 2CO_2$$

This chemical change, while it destroys the toxic power of the salt, really aids in the ultimate purification of the water since the hydroxide formed acts as a coagulant uniting with the suspended organic matter.

SUMMARY

The advantages of copper sulfate over hypochlorite of lime as a disinfectant for swimming pools therefore may be summarized as follows:

I—It is more effective because it does not undergo chemical change readily. Hypochlorite owes its power to the chemical change and is afterwards useless.

II—It is not irritating to the eyes and mucous membranes as is "hypochlorite" if the latter is used in germicidal quantities.

III—It is cheaper.

IV—It has no odor. If all other conditions were equal this last fact alone would prove its great advantage over "hypochlorite."

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## THE VALUATION OF COMMERCIAL ARSENATE OF LEAD

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The practical value of the arsenates of lead as insecticides depends upon their arsenic content and their comparative insolubility in water which prevents them from being injurious to foliage. There are three arsenates known: the lead of hydrogen or "acid" arsenate, the basic or "neutral" arsenate, and the pyroarsenate. The latter salt is unimportant from a spray standpoint, since it is probably not present in the commercial brands upon the market, due to the fact that the pyro salt cannot exist in the presence of water and, thus far, has been prepared only by heating the pure hydrogen arsenate at high temperatures as shown by Tartar and Robinson.[1] Previous investigations by Tartar and Robinson[1] have shown that pure lead hydrogen arsenate can be prepared corresponding in composition to the theoretical formula $PbHAsO_4$, giving upon analysis 32.98 per cent arsenic oxide and 63.92 per cent lead oxide. The basic arsenate was also found to be of constant composition when prepared from pure salts and gave upon analysis 23.42 per cent arsenic oxide and 74.72 per cent lead oxide.

Practically, then, there are two kinds of lead arsenates: (1) the hydrogen, and (2) the basic arsenate generally used as a spray material; manufacturers of commercial brands usually produce one or the other form and label them as such. The hydrogen arsenate is found on the market under the trades name "acid" or "dibasic" arsenate of lead and the basic is commonly known as the "neutral," "triplumbic" or "tribasic" arsenate of lead. There are, however, many brands that do not specify either a hydrogen or a basic sample but are simply labeled "arsenate of lead."

In the analysis of the commercial brands of lead arsenates, the specific determinations usually required, as evidence that the product is not a violation of the Federal Insecticide Law, consist of an estimation of total arsenic oxide, total lead oxide, water-soluble arsenic oxide, and moisture. This is sufficient to ascertain whether the sample fulfills the requirements as demanded by law, but it does not give evidence of the exact nature of the sample.

[1] Tartar and Robinson, *J. A. C. S.*, **36** (1914), 1843.

For the true valuation of these commercial samples, therefore, methods for their complete analysis are necessary. It is not enough to know the total arsenic or lead content to ascertain the value of the spray material as an insecticide, but it is equally important to understand the forms in which these elements are combined, and to what extent they exist as such. For example, if a sample is found to contain lead combined in the form of the basic or hydrogen arsenate, the carbonate and the chloride, the proportion and the extent to which each compound is present is an important consideration, and the estimation of each of these forms is essential in the valuation of the insecticide. Any other substance or impurity that would also depreciate the value of the sample is a factor in its valuation. These impurities such as carbonates, chloride, acetates, water-soluble substances, etc., besides being adulterants may have an injurious effect upon foliage and hence depreciate the intrinsic value of the material as a spray. Haywood and McDonnell[1] have shown that the chlorides, sulfates, and carbonates of the alkali metals render the arsenic in certain varieties of commercial lead arsenate more soluble, and hence increase the liability to foliage injury. In order to make these estimations, new methods were devised at this Station and substituted in some cases where the old ones were found to be inaccurate. Comparisons of the methods employed are given in Table I.

It can be understood, after a consideration of the possibilities for the introduction of impurities and the existence of both arsenic and lead in different proportions to form several compounds, that the insecticidal values of various commercial arsenates are appreciably different. Recent investigations by H. F. Wilson,[2] Entomologist of this Experiment Station, have shown that the arsenates of lead have widely different insecticidal properties. The pure lead hydrogen arsenate, specially prepared in this laboratory, was found to kill more quickly, to remain in suspension longer and to be more easily applied. From what has been stated regarding impurities and the differences in the constitutions of the lead arsenates, it is of paramount importance to ascertain, as far as possible, the true nature of the commercial arsenates.

In view of the possibilities for the introduction of impurities and adulterations and the existence of the two arsenates in one product, a number of commercial samples were selected and a system for their total analysis devised. The following determinations were made: Moisture, total arsenic oxide, total lead oxide, lead hydrogen arsenate, water-soluble arsenic oxide and lead oxide, lead carbonate, water-soluble impurities, chlorides, sulfates, acetates, and acid-insoluble impurities. In order to make these determinations it was necessary to devise several new methods and change some of the old ones now in use.

## ANALYTICAL METHODS USED

For the determination of moisture, total arsenic oxide, and total lead oxide, the official method as outlined in Bureau of Chemistry *Bull.* **107,** 239, was found satisfactory.

Water-soluble arsenic oxide and lead oxide were determined by two different methods, one being the regular official method as given in Bureau of Chemistry *Bull.* **107,** 240, and the other devised at this Station which for convenience is designated as the "Oregon Station Method." This method is based upon the extreme insolubility of both hydrogen and neutral arsenates as shown by Tartar and Robinson.[1] It is carried out as follows: A convenient amount, 4 to 6 grams, of the sample is accurately weighed out and transferred to a 590 S. & S. filter paper, first macerating in a mortar with a little water until it has a consistency that permits pouring onto the filter. Distilled water is used to extract the soluble arsenic oxide and lead oxide. (It is imperative that no carbonic acid nor ammonia be present in the water as they may react with lead arsenate, liberating arsenic in a soluble form.) The water-soluble impurities are extracted from the sample by washing with hot water until about a liter of filtrate is obtained. It is then cooled, made up to 1000 cc. and an aliquot titrated with standard iodine solution after reduction with potassium iodide according to modified Gooch and Browning method. Should the filtrate come through cloudy it may be clarified by filtering through a Gooch, that has a thin layer of pure carbon black over the asbestos pad.

In the estimation of the amount of lead hydrogen arsenate in the presence of the basic salt, it is first necessary to remove any water-soluble arsenic oxide that may be present. Consequently, the residue, obtained by leaching the sample with hot water, in the Oregon Station method above, was used. The determination was then made by the method devised by Tartar and Robinson.[1]

Water-soluble solids or impurities were also determined by two different methods. In one case the official method as outlined in Bureau of Chemistry *Bull.* **107,** 240, was applied. In the other method employed, 200 cc. of the clear filtrate, obtained in the Oregon Station method for the water-soluble oxide and lead oxide as cited above, were evaporated to dryness in a platinum dish upon a steam bath, dried at 110° C. and weighed. This gave the amount of water-soluble solids including foreign impurities and the soluble arsenic oxide.

Lead carbonate was calculated from the amount of carbon dioxide found in the sample, the Bowser method[2] being used as a basis for the determination of the carbon dioxide. The procedure, revised and made applicable to lead arsenate, is briefly as follows: An apparatus similar to that described by Bowser is used. About 10 grams of the sample are introduced into an Erlenmeyer flask of 200 cc. capacity, and 50 cc. of water added and, after inserting the rubber stopper through which a thistle tube passes, about 5 cc. of concentrated hydrochloric acid are allowed to

[1] United States Department of Agriculture, Bureau of Chemistry, *Bull.* **131,** 46.

[2] Proceedings of the Entomological Society of British Columbia, July, 1913, p. 9.

[1] *Loc. cit.*

[2] THIS JOURNAL, **4** (1912), 203.

run in. The absorbing tower contains 5 cc. of a 50 per cent solution of potassium hydroxide. When all connections are secure a low flame is applied and about 25 cc. distilled over, titrated with normal acid to disappearance of the pink color of the phenolphthalein indicator, and finally with 0.1 *N* acid to neutrality with methyl orange indicator. Each cc. of 0.1 *N* acid used in the final titration is equivalent to 0.0267 gram of lead carbonate,[1] $PbCO_3$.

The acid-insoluble substances were estimated by dissolving 10 grams of the dry material in warm dilute nitric acid, 10 per cent strength. The insoluble matter was collected upon a Gooch, washed free of acidity, dried at 110° C. and weighed.

Chlorides were determined as follows: A convenient amount of the sample, usually 4 grams, was dissolved in warm dilute nitric acid and the insoluble impurities filtered off. Excess of standard silver nitrate was added to the filtrate and titration completed as in the Volhard method for the chlorine.

Acetates were tested for qualitatively by converting them into ethyl acetate and observing the characteristic odor. This was performed as follows: A convenient amount of sample was added to a hot solution of 5 cc. of sulfuric acid and 5 cc. of 95 per cent alcohol. This was then brought to a boil when, in the presence of an acetate, the characteristic odor of ethyl acetate is obtained. Should there be any free acetic acid in the sample it may be leached out with hot water and the acidity titrated against standard sodium hydroxide solution, using phenolphthalein as indicator.

The different commercial samples used as exemplary specimens were selected in such a manner that a representative product as manufactured by various firms was secured. Two of the six samples so obtained were the dry powdered type recently placed upon the market and the other four were the usual paste arsenates.

A total analysis of the several brands of commercial lead arsenate is given in Table I.

An examination of Table I as a whole shows that the commercial arsenates of lead differ to a considerable extent in their chemical composition. From the analysis, Samples 1 and 6 show the highest degree of purity, the former being almost a pure hydrogen arsenate in the powder form, while the latter is the same kind in the paste form. The small amounts of impurities present further indicate the high grade of both of these products. Samples 2 and 3 are mixtures of the hydrogen and basic salts, the hydrogen arsenate predominating in the former sample, and the basic arsenate in the latter. Although both of these brands contain small amounts of lead carbonate, free-arsenic oxide, and water-soluble impurities, the small extent to which these substances are present are indications of a fair product. Attention is called especially to Samples 4 and 5 which demonstrate the value and applicability of methods devised at this Station. Both of these arsenates contain a very high percentage of lead carbonate and soluble impurities. Sample 4 contains no lead combined as the hydrogen arsenate. Furthermore, since the ratio of total arsenic oxide to total lead oxide in the pure basic arsenate is 1 : 3.19, this sample shows a large excess of lead oxide. This excess could not be accounted for were it not for the detection and quantitative estimation of the lead carbonate in the sample. The absence of water-soluble arsenic oxide should also be noted: obviously this might be expected from a mixture of basic lead arsenate and lead carbonate, for the presence of lead in the above form would perhaps combine with any free arsenic acid, resulting in the formation of an insoluble arsenate. In fact, the absence of water-soluble arsenic oxide in neutral arsenates generally has been demonstrated by analyses of many samples received in this laboratory. Sample 5, on the other hand, is not a lead hydrogen arsenate since the ratio of total arsenic oxide to lead oxide is greater than that in the pure salt which is 1 : 1.9. Analysis shows, furthermore, that this excess of lead oxide is present in the form of the carbonate. Unlike Sample 4, it has an extraordinary amount of water-soluble arsenic oxide.

TABLE I—PERCENTAGE ANALYSES OF SAMPLES OF COMMERCIAL LEAD ARSENATE

| Sample No. | Moisture | Total $As_2O_5$ | Total PbO | Total $PbHAsO_4$ | Water soluble $As_2O_5$ | | Lead carbonate | Insoluble substance | Chlorine | Water-soluble impurities | | Water-soluble PbO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Official | Oregon Station | | | | Official | Oregon station | |
| 1 | 0.15 | 32.53 | 63.50 | 99.38 | 0.08 | 0.12 | None | 0.08 | None | 0.25 | 0.40 | None |
| 2 | 47.08 | 15.07 | 34.71 | 30.17 | 0.08 | 0.15 | 0.30 | 0.04 | 0.22 | 0.35 | 0.94 | None |
| 3 | 0.19 | 31.47 | 64.02 | 92.01 | Trace | Trace | 0.48 | 0.13 | None | 0.55 | 0.71 | None |
| 4 | 36.69 | 12.34 | 46.58 | Trace | Trace | Trace | 16.57 | 0.02 | 0.06 | 0.52 | 0.93 | None |
| 5 | 53.78 | 12.01 | 30.55 | 18.01 | 0.77 | 1.12 | 9.90 | 0.22 | 0.10 | 3.66 | 4.28 | None |
| 6 | 41.35 | 16.19 | 31.64 | 55.97 | Trace | Trace | None | 0.04 | None | 0.25 | 0.55 | None |

At this point, it might be well to make a comment upon the requirements of the Federal Insecticide Law with reference to the arsenates of lead. In brief, the requirements are: "It must not contain: (1) more than 50 per cent of water; (2) less than 12.5 per cent of arsenic oxide, $As_2O_5$; (3) more than 0.75 per cent of water-soluble arsenic oxide, $As_2O_5$." As stated above, the pure hydrogen arsenate as prepared in the laboratory, contains 32.98 per cent total arsenic oxide, and in the basic or neutral salt there is 23.42 per cent arsenic oxide, these being the highest per cents possible in a pure sample. On a 50 per cent water basis, therefore, the maximum amount of arsenic oxide possible in a hydrogen arsenate is 16.49 per cent and in the basic compound 11.71 per cent. Hence, it is plainly evident that the law was made without a sufficient knowledge of the exact composition of the two types of lead arsenates, for no manufacturer could make a neutral arsenate that contains 12.5 per cent total arsenic oxide on a 50 per cent water basis when the pure product as prepared in the laboratory could contain at the most only 11.71 per cent. In order to abide by the law, therefore, it would be necessary to reduce the moisture

[1] The lead may be otherwise combined than the normal carbonate but since the exact form was not ascertained it is reported as $PbCO_3$.

or increase the arsenic oxide by some means. To obviate this difficulty, therefore, a maximum per cent of total arsenic oxide in hydrogen or acid arsenate should be specified and another amount for the neutral or basic arsenate.

A comparison of the amounts of water-soluble arsenic obtained by each method shows that the greater percentage is always found by the Oregon Station method. From these figures it is obvious that all the water-soluble arsenic oxide is not obtained by the official method; nor are the results obtained by the Oregon Station method too high, due to possible hydrolysis or other chemical action upon the sample, for in the three cases, Samples 3, 4 and 6, where only a trace is reported present by the official method, identical results are obtained by the Oregon Station method. These latter results further substantiate the claim made in our previous paper that the pure arsenates of lead are extremely insoluble, and when there is any free-arsenic oxide found it is due to the arsenic being in the form of a soluble salt and not in the form of either the hydrogen or basic arsenate. It should also be noted that no soluble lead oxide was found by either method, which is further proof that the water-soluble arsenic oxide was not in the form of a soluble lead salt.

As additional proof that all the water-soluble arsenic oxide is not obtained by the official method, a glance at the two columns depicting the quantity of water-soluble solids or impurities found shows that the greater amount is consistently obtained by the Oregon Station method. It is quite evident from this that all soluble material is not taken out by the ordinary official method as outlined in Bureau of Chemistry *Bull.* **107.** In all cases here cited it is shown that the amount obtained by the Oregon Station method is nearly double that obtained by the official method. It is possible that in the official method the soluble substances present remained occluded or adsorbed by the arsenate of lead and were not removed by water at room temperature. If, however, successive portions of hot water are used as in the Oregon Station method, this difficulty is overcome and the soluble salts go into solution. In the samples listed in Table I, soluble impurities, in all probability, are composed of chiefly sodium and potassium arsenate since qualitative tests show the presence of these two bases. Other impurities than those found are probably due to impurities in the materials used in the preparation of the commercial arsenate.

Chlorides were found in three of the samples examined. In two of these cases the quantity present was in amounts worthy of note.

The per cent of acid-insoluble impurities in the six samples cited is negligible but these impurities should not, however, be considered an unimportant constituent, as other samples received in this laboratory have shown as high as 5 per cent. acid-insoluble material. When present to that extent it is an adulterant of no small consideration.

The tests for the presence of acetates, and sulfates likewise, gave negative results in these six samples. Other arsenates, analyzed previously in this laboratory, however, have shown that these substances are sometimes present to an extent that would depreciate the value of the arsenate as an insecticide. The detection and estimation of these impurities may be valuable because their presence with the arsenates of lead results in the liberation of water-soluble arsenic oxide.

SUMMARY

I—The necessity of more complete methods for the true valuation of commercial lead arsenates has been pointed out.

II—Satisfactory methods have been worked out and applied to commercial samples as follows:

1—Estimation of lead hydrogen arsenate in presence of the mixed salts.

2—The determination of lead carbonate.

3—New methods for water-soluble arsenic oxide and water-soluble impurities.

4—A method for acid-insoluble impurities.

5—The detection of acetates and the quantitative estimation of chlorides.

III—The application of these methods shows a wide variation in the composition of the commercial arsenates and gives a better valuation of them than the methods now in use.

IV—Comments have been made upon the inconsistencies of the Federal Insecticide Law.

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## A STUDY OF VAPORS FROM DRYING PAINT FILMS

BY E. H. KING

Received April 10, 1915

In a recent article appearing in THIS JOURNAL,[1] Mr. C. A. Klein, of Middlesex, England, criticized very severely an article communicated by Mr. H. A. Gardner,[2] of Washington. Mr. Gardner's communication contained the result of an investigation as to the "Composition of Paint Vapors."

It cannot be denied that the method of procedure in some instances was open to adverse criticism. Particularly is this the case in the method employed for determining carbon monoxide. In Gardner's method the vapors coming from the drying oil films were conducted first through fuming sulfuric acid, and the carbon monoxide then determined by passing the gases through heated iodine pentoxide. It is a fairly well-established fact that linseed oil films give off formic acid in drying and since fuming sulfuric acid decomposes this acid, setting carbon monoxide free, any conclusion that the monoxide determined has come from the drying films alone must be lacking in absolute accuracy. The point brought out by Klein on this is well taken.

The present writer has been investigating for eighteen months the vapors coming from different drying oils when ground with different kinds of pigments, and had detected very small quantities of carbon

[1] THIS JOURNAL, 7 [1915], 99.
[2] *Ibid.*, 6 [1914], 93.

monoxide in such drying films previous to the publication of Gardner's article. Since the appearance of Klein's criticism of this article it has seemed advisable to make known some of the results which have been obtained.

The method of obtaining the vapor for study in the first series of experiments was as follows: A box frame 2 ft. × 2 ft. × 4 ft. was constructed of pine, the ends, sides and top of which were made of glass. The floor

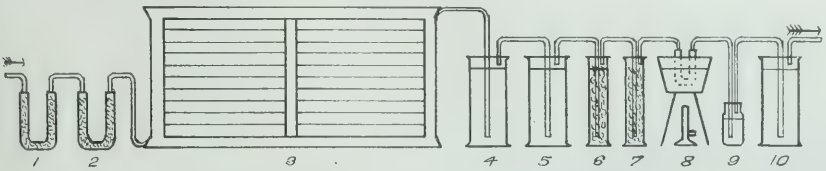


FIG. 1 APPARATUS USED FOR FIRST SERIES OF EXPERIMENTS

1, 6, and 7—Calcium Chloride
2—Potassium Hydroxide
3 Paint Case
4, 5, and 10—Barium Hydroxide
8—Iodine Pentoxide
9 Potassium Iodide

was coated with melted paraffin well rubbed into the grain of the wood, and the box was made air-tight by the use of a similar procedure. Glass rods fitted into holes bored in the wooden frame on the inside served as supports for eight glass plates about 1 1/2 ft. × 3 1/2 ft. which were covered with the films by spreading them on with a brush, due account being taken in each case of the amount of both pigment and oil used. In order to insure complete circulation of the air, freed of carbon dioxide by passing through alkalies, it was drawn in at the bottom of one end of this apparatus and out at the top of the other end. In one experiment a small motor and fan were placed inside, but this was found to be unnecessary. The apparatus was then closed and the air drawn through for several hours as a blank test to find if the absorbents or drying chamber gave off traces of carbon monoxide. No evidence of carbon monoxide was obtained.

with that in which the free iodine was absorbed in potassium iodide solution and titrated with standard sodium thiosulfate.

The vapors were drawn from the drying chamber into towers of standard barium hydroxide arranged to insure complete absorption. The alkali would, furthermore, absorb any volatile acids and retain any aldehydes which may have been liberated. They were then passed through calcium chloride drying tubes and finally through a U-tube containing iodine pentoxide mixed with asbestos fiber. The tube was kept in an oil bath at 150° C. The air was drawn from the outside but in this set of experiments no means of removing carbon monoxide was employed because it was deemed unnecessary to take such precautions. Air was drawn through by aspiration at the rate of about one liter per ten minutes. This was done for only about two hours per day on the average.

The films placed on the drying plates were composed of (1) basic white lead and linseed oil, (2) zinc oxide and linseed oil, and (3) a mixture of the two. The percentages of carbon dioxide and carbon monoxide were based on the percentage of the oil employed liberated as the corresponding oxide.

(1) 54 grams of basic white lead in 63.2 g. of oil gave off on drying 20 days, 1.00 per cent of the oil as carbon dioxide and 0.122 per cent as carbon monoxide.

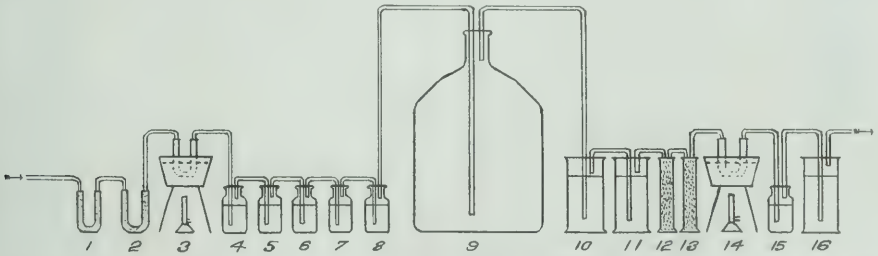


FIG. 2 APPARATUS USED FOR SECOND SERIES OF EXPERIMENTS

1, 12, and 13—Calcium Chloride
2 Potassium Hydroxide
3 and 11 Iodine Pentoxide
4 and 15 Potassium Iodide Solution
5, 6, 7, 8, 10, 11, and 16 Barium Hydroxide
9 Drying Paint

For some previously conducted investigations on carbon monoxide the present writer had already become familiar with the fact that iodine pentoxide would give off a small amount of iodine on being heated. In order to check this the carbon dioxide formed on passing the carbon monoxide through the iodine pentoxide was absorbed in standard barium hydroxide. It was found that the estimation of the carbon monoxide by this method checked very closely

(2) 86.62 grams of zinc oxide in 144.38 g. of oil evolved 0.60 per cent as carbon dioxide, and 0.0984 per cent as carbon monoxide upon drying 30 days.

(3) 42.12 grams of white lead when mixed with 42.12 g. of zinc oxide, with 84.15 g. of oil, gave off 0.077 per cent as carbon dioxide and 0.118 per cent as carbon monoxide. These films dried 17 days.

These results would indicate that the basic white lead tended to a greater destruction of the oil than

did the zinc oxide, or the lead and the oxide mixed. Later results, however, do not substantiate this.

Another series of determinations were made by the apparatus shown in Fig. 2, the essential differences being in the nature of the drying chamber and the use of a U-tube to take out any carbon monoxide which may have accidentally been present in the air. The drying bottle was a large acid carboy which contained 50 strips of glass plates $1^3/_4$ in. wide by 18 in. in length, which were coated and so spaced as to leave their surfaces free and exposed to the air drawn through. A part of the inside surface of the bottle was also coated with the drying films. Tube No. 3 contained fresh iodine pentoxide, while tube No. 14 was an old tube which had ceased to give off any iodine on being heated. The air was drawn through at the same rate as in the other tests.

Runs were made with (1) linseed oil alone and (2) linseed oil and basic white lead.

(1) 23 grams of linseed oil alone gave off 1.05 per cent as carbon dioxide, and 0.13 per cent as carbon monoxide.

(2) 30.21 grams of white lead in 26.79 g. of oil evolved 1.16 per cent of oil as carbon dioxide and 0.108 per cent as carbon monoxide.

In each of the above cases the film dried 15 days.

From these results it would appear that the oil itself gives off about, if not fully, as much of these two gases when drying alone as when mixed with some pigment.

In order to see the effect of sublimed white lead upon the amounts of these two gases set free a third drying chamber was used (see Fig. 3). This was a large cylinder, some six inches in diameter and three feet high, which was filled with carefully spaced glass plates about three or four inches wide and running the length of the cylinder. This was connected to the same kind of arrangement as in Fig. 2.

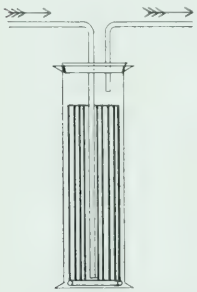

FIG. 3

25.6 grams of sublimed white lead in 35.4 grams of linseed oil set free 0.43 per cent of the oil as carbon dioxide, and 0.047 per cent as carbon monoxide, the films drying during six days.

This would show that sublimed white lead does not differ very much from either of the other pigments used.

In order to ascertain if this evolution of gases continues for a long period of time these chambers have been retained filled with the dried films and will be opened and tested for the presence of these gases from time to time over a period of at least one year.

The evidence points to the presence of carbon monoxide as one of the products given off in the drying of paint films. There is no basis for a statement especially favorable to any one pigment in this respect, as very small amounts of this gas appear to be produced in the presence of all those so far investigated. It is also to be conceded that the amount is so very small that great caution should be exercised in claiming it to be the agent effective as a poison. If the quantity mentioned in the above results is fairly well distributed with respect to its rate of liberation during the entire drying period of several days, as appears to be the case, no serious danger would be likely to arise in dwellings, as the gas would undoubtedly be too highly diffused and removed too rapidly to cause any harm.

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## PAINTS TO PREVENT ELECTROLYSIS IN CONCRETE STRUCTURES[1]

BY HENRY A. GARDNER

The use of protective paints upon metal that is to be embedded in concrete structures, in order to prevent any damage which might be caused by electrolysis, has been heretofore proposed. No tests have been made, however, as far as the writer is aware, which have determined what type of coating is best suited for the purpose. It would appear from first consideration that a paint capable of forming a film of high electrical resistance would be most efficient. Such films, however, generally present a high gloss surface and are apt to prevent the proper bonding of the concrete with the painted metal, thus doing more harm than good. It is chiefly for this reason that engineers have not generally adopted the use of paint upon reinforcing metal. In the experiments presented herein, a method for overcoming this objectionable feature of insulating paints is described, and data are presented on the relative insulating and bonding values of several different types of paint.

CORROSION CAUSES—Before describing these tests, it might be well to review briefly, for the benefit of those not thoroughly familiar with the subject, some of the conditions upon which metal corrosion depends. The ordinary forms of iron corrosion have been found to be due to auto-electrolysis, the presence of segregated impurities being responsible for differences in potential at certain areas, which set up galvanic action and cause solution and the formation of rust at the positive nodes. A similar but more rapid action takes place when an electric current is passed through an iron anode immersed in an electrolyte; *e. g.*, salt water. When damp cement contains an embedded iron anode, the cement acts as an electrolyte and the same rusting action takes place, regardless of the fact that concrete contains sufficient lime to inhibit corrosion when no electrical currents are present. With the electrolytic change of metal into oxide comes an increase in volume of the products of reaction, and there is developed an enormous expansive force or mechanical pressure, which is sufficient to crack the strongest forms of concrete.

SOURCE OF CURRENTS—Corrosion may therefore be expected, with its attendant results, when sufficiently high-voltage direct currents enter the iron of a new concrete building, either through contact with conductors of light and power circuits, contact with water or gas pipes carrying direct currents from grounded power lines, through defective insulation of electrical wiring, or from similar sources. That the damage is

[1] Presented before the Master Painters' Association of Pennsylvania, Philadelphia, Jan. 12, 1915.

greatest to new structures is due to the fact that the concrete is then damp and a better electrolyte than when it has become dry from age. That examples of reinforced concrete structures damaged from stray currents are not more common may be due to the fact that in many localities engineers are active in their endeavors to prevent high voltage currents from running wild. This fact, however, does not justify a disregard of what might happen in the future and what may now be happening to some structures which have not been carefully guarded against stray current electrolysis. That much of this damage may be prevented by the adoption of suitable forms of foundation waterproofing, exterior insulating joints for pipelines, isolation of lead-covered cables entering buildings, and other insulating devices is shown by Rosa, McCollum, and Peters[1] in what is probably the most valuable contribution to the subject of reinforcement electrolysis that has ever been published. Of equal importance, however, should be the safeguarding of the metal with suitable insulating and bonding paints, before it is embedded in cement. The adoption of this precaution, if followed by the use of the safety devices noted above, will guard against the causes which contribute to electrolysis and thus render our modern concrete structures safe from destruction by reinforcement corrosion.

FIG. I—PAINTED RODS
Specimen at left was "sanded"

## EXPERIMENTAL

SERIES I—The writer's investigations were made upon two separate series of concrete test cylinders. The first series were made by embedding, in concrete cylinders, painted iron rods $^1/_2$ in. in diameter and 12 in. long. Previous to painting, the rods were thoroughly cleaned from scale and rust. Two coats of paint were then applied, allowing a week's time for drying between coats. The painted rods were then placed in molds in an upright position, about 1 in. apart and 1 in. from the bottom of the molds. Cement mortar, prepared from one part of Portland cement and two parts of sand, was poured around the rods and tamped into place. After two days' time the molds were removed and the test pieces were repaired with cement mortar wherever defects were shown.

METHOD OF MAKING GOOD BONDING SURFACES—In making up the specimens for test, it occurred to the writer that the objection to using paints which dry upon metal to a gloss surface and which prevent proper bonding of the cement, might be overcome by applying to the painted surface, while it is still tacky (not dry), sharp particles of sand or similar material. Emery powder, abrasives, and fine quartz sand were among the substances tested. When allowed to drain upon a painted rod, the particles become attached to the paint and dry with it to form a rough surface resembling coarse sandpaper (see Fig. I). After thoroughly drying, the particles are solidly embedded in the paint, which thus presents a dull rather than a gloss film. Fine, clean, white sand was found most useful.

ARRANGEMENT OF TESTS—After ageing for a month, the pieces were connected in parallel and in series with

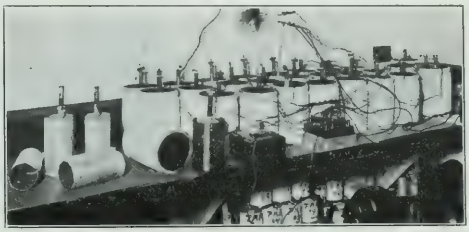


FIG. II—ARRANGEMENT OF SERIES II SPECIMENS IMMERSED
Iron molds for forming specimens shown at left. Specimen removed from jar shows surrounding iron cathode

resistance to reduce the voltage from 110 to 30 volts D. C. Current readings were made over a period of twenty-four hours. The current passing was small. The test cylinders were then placed in a shallow pan containing sufficient water to immerse the lower 2 in. of each specimen. After a week's test, the cylinders were disconnected and removed from the pan for observation. A few of the specimens showed small cracks near the bottom, where the wet cement had conducted the current to the greatest extent. The cylinders were then placed in separate earthenware jars and again connected up. The jars contained sufficient water to immerse the specimens up to within 1 inch of their top surfaces. They were left in circuit for ten days and current readings were made every twenty-four hours. Cracking was shown by nearly every cylinder which current readings proved to be carrying any appreciable amount of current. The fracture in every case started at the anode, extending radially to the edge of the cylinders and parallel to the electrode, gradually opening up as the tests were continued. The specimens were finally disconnected and removed for examination. (See Table I and Figs. III and IV.) Those which had been cracked by the electrolytic corrosion of the metal were easily split into two sections, disclosing the contained electrodes. The others, which did not show any cracking, were parted with a chisel, in order to make a comparative examination of the condition of the embedded metal.

SERIES II consisted of specimens made by embedding in concrete cylinders painted anodes $^3/_4$ inch in diameter and 12 inches in length. Previous to painting, the rods were thoroughly cleaned from scale and rust. They were painted with two coats of the same paints used in Series I. The rods were placed in molds $3^1/_2 \times 8$ in., in an upright position, and the same kind of Portland cement mixture used in Series I tests was placed around the rods and

[1] "Electrolysis in Concrete," Technologic Paper No. 18, U. S. Bureau of Standards.

tamped into place. The specimens for this series were very carefully prepared and presented a much better appearance than those used in Series II. After setting for two days, the molds were removed from the pieces which were then aged for a month. They were then placed in water for twenty-four hours, and the next day were put into individual earthenware jars containing sheet-iron cathodes coiled so as to surround but not touch the cylinders (see Fig. II). The jars were filled with sufficient water to cover the cylinders up to within one inch of their top surfaces. The specimens were connected up as in Series I. The tests were continued for 240 hours at 30 volts, during which time Nos. 4, 10, 11, 13, 15, 19, and 24 had developed cracks. The voltage was then increased to 55 and continued for 60 hours, at which time the tests were discontinued. (See Table I and Figs. V and VI.) Fig. VII shows the results of Series II in amperage hours.

face of each cylinder. After ageing for three weeks, the specimens were tested in a Riehlé testing machine, upon an iron block drilled in the center with a 1-inch hole. Each test specimen was placed in such a position that the lower end of the contained iron anode would be in alignment with the hole below. Pressure was applied until the painted iron rod was pushed away from the surrounding cement and the bond destroyed. (See Table I.)

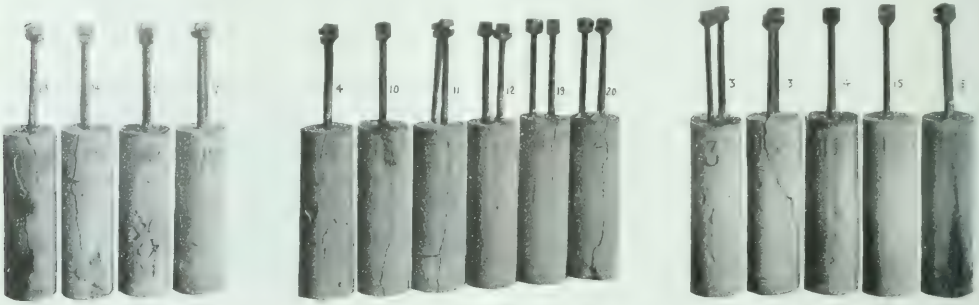



FIG. III—PART OF TEST CYLINDERS—SERIES I

Nos. 23 and 24 contained unpainted metal and show cracking: 1 and 17 illustrate protection afforded by insulating paints
Nos. 4, 10, 11, 12, 19 and 20 show cracking resulting from painting metal with various grades of water paints
Nos. 3, 13, 14, 15 and 16 contain rods coated with oil-pigment paints: while excellent protection for exposed structural steel, these paints are not so efficient for embedded steel subjected to electrolysis

OBSERVATIONS ON RESULTS

In the test specimens, where cracking had occurred, the anodes showed considerable rust, the paint coatings originally applied having been destroyed. On the cathodes in Series I the paint coatings were still intact, although some had apparently been affected by the moisture and the hydrated lime in the wet concrete, chalky surfaces being shown. Wherever there were small voids in the concrete, at or around the painted anodes, corrosion was most severe, and at such places

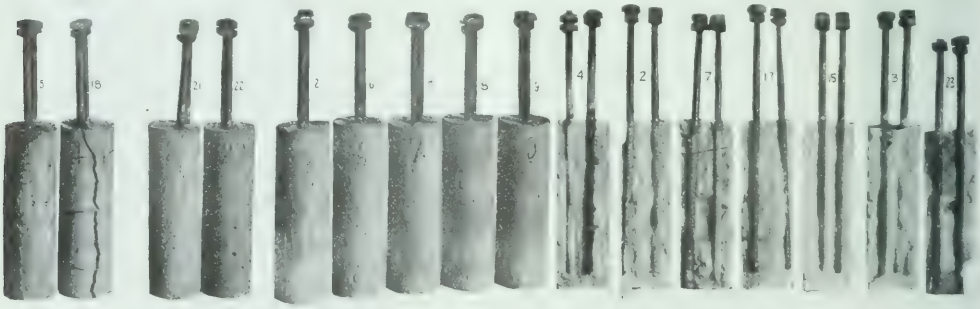



FIG. IV—PART OF TEST CYLINDERS—SERIES I

Nos. 5 (collodion), 18 (linseed oil), and 21 (gutta-percha solution) show insufficient protection of metal
No. 22 owes its good condition to the use of paint No. 9 (see Table)
Nos. 2, 6, 7, 8 and 9 contain metal coated with cement-steel compounds [illegible] unpainted and 4 water paints show great corrosion at anode: 3 and 15 (oil paints) show less corrosion: 2 (heat-treated [illegible] and trace in alcohol), 17 (special bitumen) and 15 (chromated iron oxide in oil) show practically no corrosion

SERIES III: TEST OF BONDING VALUE. In order to determine the comparative bonding strength shown by the various painted rods with the surrounding concrete, a series of test specimens was prepared, exactly duplicating those used for Series II, except that the rods were placed flush with the bottom surface of each cylinder. After ageing for three weeks, the specimens were tested in a Riehlé testing machine, upon an iron block drilled in the center with a 1-inch hole. Each test specimen was placed in such a position that the lower end of the contained iron anode would be in alignment with the hole below. Pressure was applied until the painted iron rod was pushed away from the surrounding cement and the bond destroyed. (See Table I.)

OBSERVATIONS ON RESULTS

In the test specimens, where cracking had occurred, the anodes showed considerable rust, the paint coatings originally applied having been destroyed. On the cathodes in Series I the paint coatings were still intact, although some had apparently been affected by the moisture and the hydrated lime in the wet concrete, chalky surfaces being shown. Wherever there were small voids in the concrete, at or around the painted anodes, corrosion was most severe, and at such places pitting was shown. The protective coatings upon the anode and cathode bars embedded in the concrete cylinders which did not crack and which carried but little current were later found to be in a very good state of preservation.

INCIDENTAL REACTIONS—The breaking down of a

TABLE I—RESULTS OF TESTS WITH VARIOUS PAINTS

| No. | Composition of Paints | Results in Series I<br>500-hour test | Results in Series II<br>300-hour test | Series III<br>Comparative bonding strength |
|---|---|---|---|---|
| | | Unpainted Blank Specimens | | |
| 23 | Electrodes not painted. | Cracked at end of 240 hours. Passed large amount of current throughout test. Anodes badly corroded and pitted. | Cracked at end of 96 hours. Passed large amount of current throughout test. Anodes badly corroded and pitted. | 2,010 lbs. |
| 24 | Electrodes not painted. | Cracked at end of 50 hours. Same condition as No. 23. | Cracked at end of 96 hours. Same condition as No. 23. | 2,750 lbs. |
| | Bituminous Paints | | | |
| 1 | Boiled, water-free coal tar, lime, Portland cement, and rosin, thinned with benzol. | No cracking shown. Passed only small amount of current. Some excretion of tar paint at anode. | No cracking shown. Passed only small amount of current | 1,530 lbs. |
| 17 | Blown residual petroleum oil fluxed with gilsonite, dissolved in benzol and turpentine. | No cracking shown. Passed only small amount of current. | No cracking shown. Passed only small amount of current. | 2,810 lbs |
| | Aqueous Paints | | | |
| 4 | Silicate of soda, 40° Bé. | Cracked at end of 240 hours. Very little resistance to current. | Cracked at end of 168 hours. Very little resistance to current. Examination of iron showed some clear areas and some pitted. | 700 lbs. |
| 10 | Liquid glue. | Cracked at end of 240 hours. Passed large amount of current throughout test. Considerable iron hydrate at top of specimen and permeated throughout concrete around anode. | Cracked at end of 96 hours. Passed large amount of current. Dense deposit of iron hydrate at top of test piece. Bad corrosion of metal shown. | 100 lbs. |
| 11 | 50% silicate of soda, 20° Bé., and 50% graphite ground together. | Cracked at end of 144 hours. Passed considerable current. Corrosion marked. | Cracked at end of 96 hours. Passed large amount of current. Corrosion marked. | Specimen faulty. |
| 12 | 50% silicate of soda, 20° Bé., and 50% iron oxide pigment ground together. | Cracked at end of 240 hours. Passed considerable current. Much corrosion. | Cracked at end of 192 hours. Passed considerable current. Much corrosion. | 1,870 lbs. |
| 19 | 5% aqueous solution of sodium resinate. | Cracked at end of 240 hours. Passed more current than one blank specimen. Much rust. | Cracked at end of 144 hours. Passed considerable current. Much rust. | 1,890 lbs. |
| 20 | 5% aqueous solution of sodium resinate ground with an equal weight of iron oxide. | Cracked at end of 240 hours Passed large amount of current. Much rust. | Cracked at end of 196 hours. Passed large amount of current. Much rust. | 2,580 lbs. |
| | Oil Paints | | | |
| 3 | Red lead in oil; 30 lbs. pigment to one gallon of raw linseed oil. | Did not crack, but large quantity of iron hydrate deposited at top surface of specimen, staining the concrete, showing weakened bond and corrosion. | Cracked at end of 192 hours. Considerable iron hydrate stain shown at surface of specimen throughout test. Iron quite badly corroded. | 1,370 lbs. |
| 13 | Chrome green 20% on 80% barytes base, ground in raw linseed oil (medium). | Cracked at end of 240 hours. Iron hydrate stain shown around anode at top surface of specimen early in test. Iron quite badly corroded. | Cracked at end of 192 hours. Same conditions observed as in Series I. | 790 lbs. |
| 14 | Blue lead in oil; 14 lbs. pigment to one gallon raw linseed oil. | No cracking shown. Resistance to current was not marked. Slight corrosion observed. Deposit of iron hydrate at surface of cylinder | No cracking shown. Same conditions observed as in Series I | 1,250 lbs. |
| 15 | Chromated iron oxide in oil; 12 lbs. pigment to one gallon raw linseed oil. | No cracking shown. Only slight corrosion observed | Cracked at end of 144 hours. Deposit of iron oxide at top of cylinder. | 930 lbs. |
| 16 | Blue lead ground in heavy-bodied linseed oil reduced with an equal quantity of turpentine to cause paint to dry to a flat surface. Formed a thin film. | Small crack developed at end of 240 hours. No surface deposit shown, indicating good bond. Anode showed considerable corrosion | Small crack developed at end of 216 hours. Same condition as in Series I. | 1,400 lbs. |
| 27 | Chromated iron oxide in treated tung oil; 12 lbs. pigment to one gallon raw linseed oil. "Sanded surface." | Not in Series I. | No cracking shown. Passed only small amount of current. No deposit on surface. Excellent condition. | 2,000 lbs. |
| 28 | Mixture of equal parts of No 14 and No. 16. "Sanded surface." | Not in Series I. | No cracking shown. | 1,880 lbs |
| 29 | Asbestine pigment ground in No. 9 oil. "Sanded surface." | Not in Series I. | No cracking shown. Passed only very small amount of current. Passed slightly more current than No. 9. In excellent condition throughout test. | Not in Series III |
| | Oils and Varnishes | | | |
| 2 | Special heat-treated tung-oil compound thinned with turpentine. | No cracking shown. Concrete test specimen was of faulty construction, a portion of the cathode being exposed. Nevertheless the specimen passed but very small amount of current. Film was tough and elastic. | No cracking shown. Only moderate amount of current passed. No stain. | 2,665 lbs |
| 5 | Double-boiled linseed oil (lead and manganese drier). | Cracked at end of 140 hours. Passed considerable current throughout test. Heavy deposit of iron stain at surface. | Only a very fine crack developed at end of test. Passed considerable current throughout test. No stain. | 1,680 lbs. |
| 6 | Kauri gum-linseed oil varnish. | Only slight crack shown. Small amount of current passed. No stain. | No cracking shown. No stain. | 1,790 lbs. |
| 9 | Processed tung-oil compound. | No cracking shown. Passed only a very small amount of current. Gave excellent insulation value. No stain. | No cracking shown. Passed only a very small amount of current. Had a high electrical resistance. No stain. | 1,990 lbs. |
| 22 | Mixture of equal parts of No 9 and No 21 | No cracking shown. Passed less current than No. 21, but more than No. 9. No stain. | No cracking. Passed less current than No. 21, but more than No. 9. No stain. | Specimen faulty. |
| | Lacquers | | | |
| 7 | Gum sandarac in alcohol; 32-oz. solution. | No cracking shown. Only small amount of current passed. No stain at surface. | Only small amount of current passed. No stain at surface. | 990 lbs. |
| 8 | Gum shellac in alcohol; 32-oz. solution. | No cracking shown. Passed more current than No 7. No stain | Passed more current than No. 7. Slight stain at surface. | 490 lbs. |
| 18 | Soluble nitrated cotton dissolved in amyl and ethyl acetates; 8-oz. solution. | Cracked at end of 240 hours. Large amount of current passed. Some stain at surface. | Cracked at end of 192 hours. Large amount of current passed. Iron hydrate stain at surface. | 2,480 lbs. |
| 21 | Gutta-percha dissolved in benzol; 3-oz. solution. | Cracked at end of 240 hours. Passed considerable current. Stain at surface. | Cracked at end of 96 hours. Passed considerable current. Considerable stain at surface. | 2,600 lbs. |
| 26 | Condensation product of phenol and formaldehyde dissolved in alcohol. | Not in Series I | No cracking shown. Passed only small amount of current. Some iron stain at surface and a small deposit of dark cherry stain due to product of reaction between the phenolic bodies and the lime in the cement. | 1,380 lbs |

film upon the embedded iron rods was always recorded by a sharp rise in the amperage, due to the decreased resistance offered to the flow of the current between the electrodes. It was also recorded by a fizzing sound, due to the increased evolution of hydrogen gas developed by the electrolysis of the water in the damp concrete. This gas, issuing from around the iron electrode at the top of the test pieces, generally carried some water with it, and small bubbles were formed, which burst with an audible explosion when a lighted match was placed in contact with them. The hydrogen gas seemed to have a reducing or soft-

ening action upon some of the oxidized coatings and carried to the surfaces of the cylinders considerable quantities of soft, oily products, which deposited around the anode and later hardened in contact with the air. Iron oxide was also carried to the top surfaces of some of the specimens by the action of the gas fluid when formed, on account of the warmth of the cylinders at the anode where heat was developed by the electrolysis, later became solid when deposited upon the surface of the cylinders. It was in specimens showing such surface deposits that the bond between the cement and steel was the weakest.

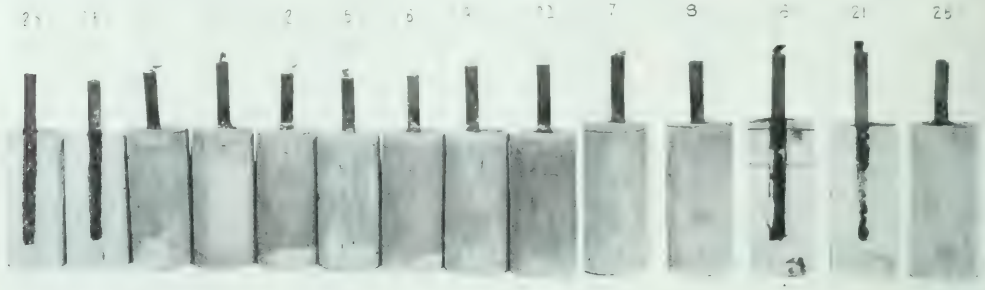



FIG. V—PART OF TEST CYLINDERS—SERIES II
Nos. 23 and 24 contained unpainted rods: cracking occurred
Nos. 1, 17, 2, 5, 6, 9 and 22 contained rods coated with lacquers, paints and special insulating oils: no cracking occurred
Nos. 18 (collodion) and 21 (gutta-percha solution) show cracking: 7 (sandarac), 8 (shellac) and 26 (condensation product) show no cracking

and water and was there deposited as a dark brown stain.

ELECTROLYTIC HYDROGENATION OF OIL FILMS—That the nature of the paint films has considerable bearing upon the action of the hydrogen gas which was found to be developed during the tests, there can be no doubt. In an investigation to determine the cause of the rapid corrosion exhibited by some grades of lacquered tin food containers, W. H. Walker[1] and Slade[2] have found linseed-oil films to act as depolarizers of hydrogen, and Walker points out that such films, if in a semi-oxidized condition, may absorb hydrogen quite as rapidly as oxygen. This may account for the appearance of the oily substances brought to the top of some of the cylinders. Electrolytic hydrogenation may have been effected by the action of the

VALUE OF WELL-DRIED AND SATURATED FILMS—Walker has also referred to the fact that paint films that have been baked, do not act as depolarizers, on account of their fully saturated condition. It would obviously be impractical to bake paint coatings upon most forms of reinforcing metal, but quite thoroughly oxidized coatings, which would probably have but slight depolarizing action, would result by allowing a period of sixty days for the drying of oil paints after application to the metal and previous to immersion in the cement. It is, moreover, possible to apply coatings which do not depend entirely upon oxygen absorption for their hardening and which contain ingredients of a fairly saturated nature. Among these could be mentioned such coatings as are composed of resins dissolved in volatile solvents, as well as some

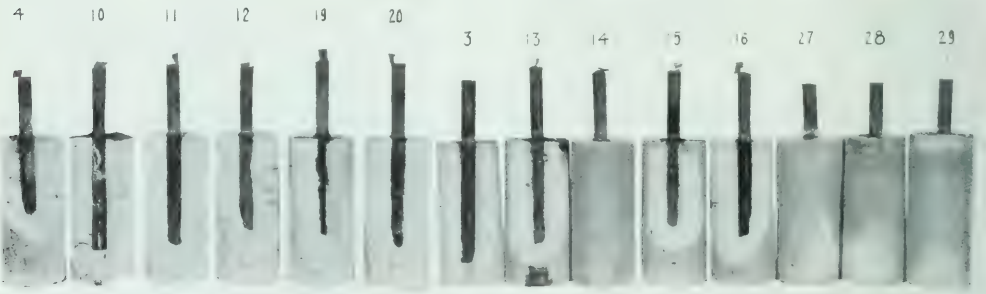



FIG. VI—PART OF TEST CYLINDERS—SERIES II
Nos. 4, 10, 11, 12, 19, 20, water paints: show cracking of cylinders with heavy corrosion and pitting of rods
Nos. 3, 13, 14, 15, 16, 27, 28, 29 contain rods coated with various oil-pigment paints
Note excellent condition of 27, 28 and 29 which contain "sanded" painted rods (see Fig. 1)

nascent hydrogen in the presence of iron oxide or other pigments which could act as catalyzers. The action was sufficient to produce a product which, although special types of oil coatings which gave good results in Series I and II.

RELATION BETWEEN FILM POROSITY AND ELECTROLYSIS—The small current flow shown by certain of the specimens in the test may in part be attributed to their impervious character. Paints which form porous

[1] "Paint and Varnish Coatings as Accelerators in the Corrosion of Metals," W. H. Walker and W. K. Lewis, THIS JOURNAL, **1** (1909), 784.
[2] "A New Method for Testing Paint Films and Preservative Coatings for Iron and Steel," W. C. Slade, THIS JOURNAL, **4** (1912), 189.

films allow the passage of water which may contain various electrolytes. Such films offer but small resistance to the passage of electrical currents. Paints which form highly impermeable films keep water away from the underlying iron and offer great resistance to the passage of electrical currents. Investigations which have determined the actual degree of porosity shown by various types of paint films have previously been made by A. M. Muckenfuss[1] and by the writer.[2] These tests have already afforded useful information to the designer of paints and might be studied with profit in the production of paints for the prevention of electrolytic corrosion.

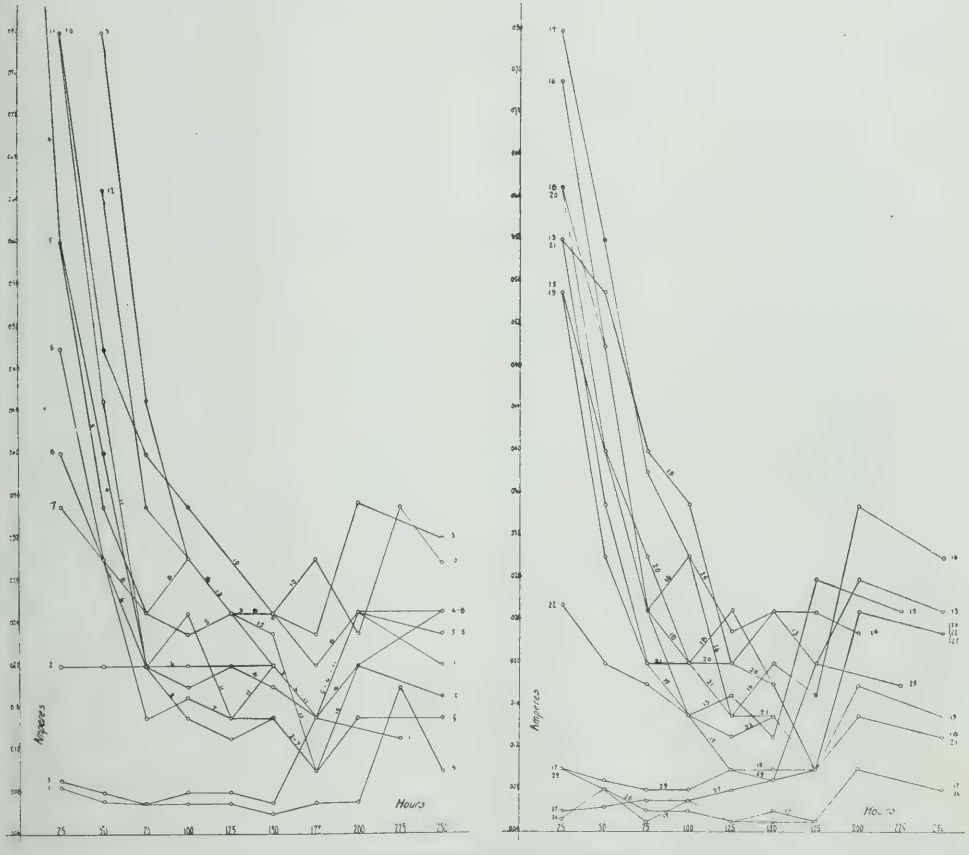



FIG. VII—AMPERE-HOUR CHARTS FOR SERIES II

BONDING TESTS—Some paints gave good bonding tests, but failed to act as insulators. Among these may be mentioned Nos. 12, 19 and 20 (water paints) and Nos. 18 and 21 (lacquers). The latter two, composed of collodion and gutta-percha, respectively, dried to a flat surface which accounts for the good bond tests shown. Among the oil paints, No. 16, which also had the property of drying to a flat surface, gave a much better bond than paints of a similar composition which dried to a gloss surface. The good bonding tests shown by several of the water paints is readily explainable, the wet concrete exerting a solvent action upon such paints, which gave opportunity for direct contact with the steel. Some paints which gave excellent results in the insulating tests gave conversely poor results in the bonding tests. Among these may be mentioned Nos. 7 and 8, composed of sandarac and shellac, respectively. Most of the oil-pigment paints made with raw linseed oil gave poor or only fair results. It is probable that the raw oil fails to dry hard, and, although apparently well dried, remains in a semi-oxidized condition. The oil films would in such cases be rather porous and therefore inefficient as insulators. Such films would be readily acted upon by the hydrogen evolved by electrolysis. Much better results were obtained with boiled linseed

[1] "Report on a Permeability Test for Paints and Varnishes," A. M. Muckenfuss, THIS JOURNAL, **5** (1913), 535; *Proc. Amer. Soc. for Test. Mater.*, **14**, II (1914), 361.

[2] "Excluding and Water-Resisting Properties of Paint Films for the Protection of Iron and Steel," H. A. Gardner, *Bull.* **18**, Scientific Section, Paint Mfrs. Assn. of U. S., p. 17.

oil, a product that dries to a harder, less porous, and more fully saturated film. The value of the "sanded surface" method is shown by comparing test No. 27 with test No. 15, the paints used being of the same composition. The sanded surface of No. 27 gave much better insulating values and its bonding strength was double that of the unsanded specimen. Another instance of the value of the "sanded surface" method is shown by a comparison of specimens Nos. 28 and 14.

USE OF PIGMENTS—It is quite likely that the nature of the pigment used in a paint designed to prevent electrolysis of embedded metal will have some bearing upon the results obtained from its use. The addition of a pigment to an oil usually increases the resistance to moisture and makes a more impermeable film. Theoretically, pigments which are of a non-conducting nature should be preferable. The inert pigments are examples of this type (asbestine, china clay, silica, etc.). There should, however, be present in a paint a sufficient quantity of rust-inhibitive pigment (basic pigments or pigments of the chromate type) to produce a passive condition of the steel, similar to the condition that is produced by the basic lime compounds in cement.

Prominent among the protective compounds that gave the best results are Nos. 2 and 9, composed of processed and heat-treated tung oil (Chinese wood oil). These compounds dried to a hard, non-porous film of a saturated nature. Had they been sanded, they undoubtedly would have given still better results. Distinction should also be accorded to Nos. 17, 27 and 28, although the good results obtained with the last two should be largely credited to the sanding of the surfaces during drying.

## CONCLUSIONS

The corrosion of metal embedded in concrete structures, by stray currents of high voltage, is often productive of serious effects. The use of properly made paints upon such metal constitutes a safeguard that should not be neglected by the engineer. Such paints may be prepared as follows:

I—The vehicle should contain:

1—Boiled or bodied oils or products which dry to fairly saturated films.

2—Oils which dry by semi-polymerization rather than by oxidation.

3—Oils which dry to a flat rather than a high gloss surface.

II—The solid portion should contain a percentage of:

1—Pigments which are coarse and which therefore tend to form films having a rough surface.

2—Pigments which are inert and which do not act as conductors of electricity.

3—Pigments which are either basic or of the chromate type.

III—The painted metal should be "sanded" if possible.

The writer wishes to acknowledge the very valuable assistance throughout these tests of Mr. Leland P. Hart.

INSTITUTE OF INDUSTRIAL RESEARCH
WASHINGTON, D. C.

## PAINT VEHICLES AS PROTECTIVE AGENTS AGAINST CORROSION[1]

By Maximilian Toch

A careful search of the literature of the past twenty years has failed to reveal anything like a systematic investigation of the relative value of different vehicles used in the manufacture of paints for structural steel and the prevention of corrosion. There are a few isolated cases in which boiled linseed oil,[2] Kauri linseed oil varnish[3] and spar varnish as protective coatings on structural steel were studied. For many years past much has been written and many investigations have been made on the protective quality of the pigments, but no one has apparently made any study of the vehicles.

It is quite obvious that without a vehicle a pigment is useless, and I know of no instance where a pigment could be used alone, with perhaps the single exception of Portland cement, if that may be classed as a pigment; even then, Portland cement would be useless unless water were used as a vehicle. I hardly need make the experiment of taking a dry pigment and using water as a vehicle to show you that when the water evaporated it would leave the pigment, and the pigment in turn would leave the metal; and yet, to the best of my knowledge, nobody has paid any attention to the very important role that is played by the vehicle itself. There is an old proverb which says, "One hand is useless, for one hand washes the other," and it strikes me that the same is true with reference to vehicle and pigment, for one is of little value without the other, and if any value is to be attached to either of them the vehicle has by far the advantage, because, as I will show you, there are some vehicles which protect for a considerable length of time.

With this end in view exposure tests were made in 1913, in which fifty-two steel plates (in duplicate) were carefully freed from grease by washing with benzol, dried, sanded, and rubbed clean with pumice, and then coated with all the paint vehicles or protective vehicles to the extent of fifty-two in number, many of which, of course, are seldom, if ever, used alone, and some of which are failures a short time after they are put on. However, I wanted to do this thing thoroughly, and for this purpose I selected the same quality of steel, known as cutlery steel, which I have been using for many years for my exposure tests. It is a steel which rusts very rapidly and of which I have several samples here.

I must eliminate those plates which have shown no rusting in the year and five months that they have been exposed. These were coated with the paraffin or machinery oil compounds, and it would be poor advice to any engineer to coat steel with paraffin compounds, for the method of cleaning before the application of any good paint would have to be very carefully followed out, since no protective paint would hold on steel that retained the least trace of a paraffin

[1] Paper presented before the New York Section of the Society of Chemical Industry, Chemists' Club, April 23, 1915.

[2] C. Von Kreybig, *Farben Ztg.*, **17**, 1766–8; J. N. Friend, Carnegie Scholarhsip Report, Iron and Steel Inst., May, 1913, pp. 1–9.

[3] Address of Prof. A. H. Sabin before American Society of Civil Engineers, Nov. 4, 1896, reported in *Engineering News*, July 28, 1898.

coat. Then the paraffin, or non-drying oils, all collect a great deal of dirt, which showed that this would have to be entirely removed before any paint could be applied.

Plate No. 41 showed excellent results, and a material of this kind would not be so very expensive where engineers demand that steel be coated with a clear liquid in the shop so that the steel may be inspected in the field. This was composed of half spar varnish and half stand oil. Stand oil is practically a polymerized linseed oil. Linseed oil when heated to 550° with a drier like Japanner's Brown or borate of manganese will produce a very thick viscous liquid, which is largely used as a patent leather finish. This can be reduced with 50 per cent of thinner and still have the fluidity or viscosity of raw linseed oil, and is, therefore, inexpensive.

Plate No. 50 was coated with a material containing 10 per cent of paraffin oil, which might be classed as an adulterated linseed oil, and while it showed up very well, it could not be recommended because, on an exposed structure like a bridge, a coat of good protective paint would not adhere very thoroughly.

Plate No. 52 has taught us a valuable lesson with regard to the use of raw China wood oil which is heated to a sufficient degree of heat to take 10 per cent of a Tungate drier, and then thinned with 15 per cent of benzine. This made a material which is hardly more expensive than good, boiled linseed oil, and left a most excellent surface for repainting. In fact, this has proved itself the equal of Plates No. 22 and No. 23, with the addition of a better surface for repainting.

Plate No. 46 was coated with kettle-boiled linseed oil, and is very good, but this material might be regarded by some engineers as too expensive for application, as it took all day to make this oil. A carefully selected linseed oil was chosen to start with, to which was added 5 per cent of litharge and no other drier. This oil dried very badly, but when it did dry produced a good flexible film which lasted. This must not be confounded with the average boiled linseed oil of commerce.

The various coatings used in these exposure tests have been divided according to their protective value into five classes:

1 and 1B—Those vehicles which have little or no value for the prevention of rusting.

(*a*) The raw and refined drying and semi-drying vegetable oils. (Plates Nos. 1, 7, 8, 13, 35, 36, 47, 48.)

(*b*) The same oils to which 10 per cent of drier has been added. (Plates Nos. 2, 3, 4, 6, 9, 10, 11, 12, 14, 34.)

INSPECTION REPORT ON STEEL PLATES EXPOSED DECEMBER 8, 1913

| No. | Nature of Coating | Corrosion April 14, 1914 | Corrosion December, 1914 | Corrosion April 15, 1915 | Value |
|---|---|---|---|---|---|
| 1 | Raw linseed oil | Complete | Complete | Complete | 1 |
| 2 | R. l. oil + 10% linoleate drier | About 1/3 | Bad along edges; partly protected in middle | Complete | 1B |
| 3 | R. l. oil + 10% Japan drier | Slight | (1) Slight along edges; fairly protected over rest of film | Complete | 1B |
| 4 | R. l. oil + 10% Japan drier | Almost complete | (2) Bad along edges; partly protected in middle<br>Almost complete | Complete | 1 |
| 5 | Japan drier | Complete | Complete | Complete | 1 |
| 6 | Menhaden oil + 10% Japan drier | Complete | Complete | Complete | 1 |
| 7 | Menhaden oil | Almost complete | Complete | Complete | 1 |
| 8 | Soya bean oil | Complete | Complete | Complete | 1 |
| 9 | S. b. oil + 10% light drier | About 1/3 | Much on upper half; none on lower half | Complete | 1B |
| 10 | S. b. oil + 10% linoleate drier | About 1/3 | Much on upper half; none on lower half | Complete | 1B |
| 11 | 1/2 Raw oil, 1/2 menhaden oil + 10% linoleate drier | About 1/2 | Much on upper half; none on lower half | Complete | 1B |
| 12 | 1/2 Raw oil, 1/2 soya bean oil + 10% linoleate drier | About 1/2 | Bad 3/4 way down; fairly good on lower fourth | Complete | 1B |
| 13 | Perilla oil | Complete | Complete | Complete | 1 |
| 14 | Perilla oil + 10% Japan drier | Almost complete | Complete | Complete | 1 |
| 15 | Petrolatum | Slight (much dirt) | Slight (collected much dirt) | Slight (very good) | 4 |
| 16 | Spar varnish | None | Slight | Slight (very good) | 5 |
| 17 | Turpentine substitute | Complete | Complete | Complete | 1 |
| 18 | Anhydrous pine oil | Complete | Complete | Complete | 1 |
| 19 | Benzine | Complete | Complete | Complete | 1 |
| 20 | Turpentine | Complete | Complete | Complete | 1 |
| 21 | Paraffin oil | Complete | Complete | Complete | 1 |
| 22 | { Bodied linseed oil + | { None | None | None (very good) | 5 |
| 23 | { Turpentine substitute thinner | { None | Very slight | Very slight (very good) | 5 |
| 24 | Pyroxylin lacquer | Complete | Complete | Complete | 1 |
| 25 | Celluloid solution | Complete | Complete | Complete | 1 |
| 26 | No. 38 China wood oil varnish | Slight | Appreciably under whole film | Rather bad | 2 |
| 27 | No. 5 copal, China wood oil varnish | None | None | Rather bad | 2 |
| 28 | No. 6 copal, wood oil varnish | Slight | Much over whole plate | Complete | 2 |
| 29 | No. 39 China wood oil varnish | Slight | Under whole film to small extent | Complete | 2 |
| 30 | Steam cylinder oil | Complete | Complete | Complete | 1 |
| 31 | Gear case oil | Slight (much dirt) | Slight (much dirt) | Slight (still protected) | 4 |
| 32 | Blown linseed oil + turpentine | Slight | Slight in few spots. Bad over all | | 2 |
| 33 | Kerosene oil | Complete | Complete | Complete | 1 |
| 34 | Raw oil + 2% cobalt drier | About 1/2 | Bad 1/2 way down | Complete | 1B |
| 35 | Raw China wood oil | About 1/2 | Almost complete | Complete | 1 |
| 36 | 1/2 Raw oil, 1/2 raw China wood oil | About 1/2 | Bad 3/4 way down | Complete | 1 |
| 37 | Blown linseed oil, turpentine substitute, 10% linoleate drier | Slight | Part in quite a few isolated spots | Complete | 2 |
| 38 | Raw oil, 10% paraffin oil, 10% Japan drier | About 1/2 | Bad 3/4 way down | Complete | 1B |
| 39 | China-wood-oil-varnish mixture | None | None (very good) | Bad | 3 |
| 40 | 1/2 heavy boiled linseed oil, 1/2 raw oil | None | None (very good) | Bad | 3 |
| 41 | 1/2 Spar varnish, 1/2 stand. oil | None | None (very good) | None (still good) | 5 |
| 42 | 80% raw oil, 15% spar varnish, 5% linoleate drier | None | A little along upper edge and in several other spots | Bad | 3 |
| 43 | 1/2 Raw oil, 1/2 No. 6 Copal wood oil varnish, 5% Japan drier | None | None (very good) | Bad | 3 |
| 44 | 1/2 Heavy boiled linseed oil, 1/2 menhaden oil, 5% Japan drier | None | Very slight | Bad | 3 |
| 45 | 1/2 Heavy boiled linseed oil, 1/2 soya bean oil, 5% Japan drier | None | None (very good) | Bad | 3 |
| 46 | Kettle-boiled oil | None | Practically none | Unchanged (very good) | 5 |
| 47 | Pale refined varnish oil | Complete | Complete | Complete | 1 |
| 48 | Pale refined linseed oil | Complete | Complete | Complete | 1 |
| 49 | 80% Wood oil, 10% No. 38 China wood oil varnish, 10% Japan drier | None | Practically none | Complete | 3 |
| 50 | 90% raw oil, 10% paraffin oil, 1% cobalt drier | None | Somewhat on top. Perfectly good at bottom | Slight (still good) | 5 |
| 51 | 95% spar varnish, 5% petrolatum in turpentine subs. | None | Slight underneath film along edges | Slight (still good) | 5 |
| 52 | China wood oil, heated with tox-tungate and thinned with benzine | None | None (very good) | None (very good) | 5 |

(*c*) The more or less volatile paint thinners. (Plates Nos. 17, 18, 19, 20, 33.)

(*d*) Solutions of celluloid and pyroxylin. (Plates Nos. 24, 25.)

(*e*) The liquid (at room temp.) paraffin oils. (Plates Nos. 21, 30.)

2—Those vehicles which showed some degree of protection, though not very much at best.

(*a*) Wood-oil varnishes containing a certain percentage of rosin. (Plates Nos. 26, 29.)

(*b*) Copal-wood-oil varnishes. (Plates Nos. 27, 28.)

(*c*) Varnishes made from linseed oil which have been thickened and oxidized by blowing with air, oxygen or ozonized air. (Plates Nos. 32, 37.)

This compared with the results obtained below with cooked-oil varnishes proves conclusively that the film yielded by a blown oil is not nearly as waterproof and resistant to severe weather conditions as that formed by a boiled or polymerized oil.

3—Varnishes or varnish mixtures which protected the steel very nicely as long as weather conditions were not severe and temperature changes not very rapid and pronounced. (Plates Nos. 39, 40, 42, 43, 44, 45, 49.)

4—The semi-solid and solid paraffin oils. These show a very high degree of protection from rusting. (Plates Nos. 15, 31.)

5—Those varnishes and vehicles which afford a high degree of protection against corrosion. To be set down in this class a material must be extremely water-proof; it must dry with a film which is very elastic and yet tough in order to be able to withstand "weathering." A film which can not remain intact against condensed moisture, snow and ice and despite comparatively wide and sometimes rapid changes in temperature (as between day and night even in rather warm climates), will of necessity afford very little protection for the steel to which it is applied. As the Table on page 511 shows, this class comprises:

(*a*) Spar varnish. (Plate No. 16.)

(*b*) Varnishes made from linseed oil, or China wood oil, which have been thickened by a heat process. (Plates Nos. 22, 23, 52.)

(*c*) Open kettle-boiled oil. (Plate No. 46.)

In Plate No. 50 we find a rather anomalous case. It seems that raw linseed oil which has been dried with a small percentage of a liquid paraffin oil proved to be an excellent coating for rust prevention.

The addition of any paraffin or non-drying oil, even in such a small quantity as is shown in Plate No. 50, is dangerous in case repainting becomes necessary. Although the matter is not settled in my mind as to whether linseed oil and paraffin oil dissolve in each other my idea at present is that, although they apparently make a clear solution, separation takes place. I have conducted several experiments, and find that a film of linseed oil which contains paraffin oil in some quantities when apparently dry shows minute globules of paraffin oil in wet condition when the film is heated over 100° C. A film of linseed oil containing ten per cent of paraffin oil after it is six months old can be extracted with naphtha and shows uncombined paraffin oil. These experiments prove conclusively that it is dangerous to mix a paraffin oil with linseed oil for any purpose, excepting where it is not necessary, or not the intention, to repaint subsequently.

NOTE: All the photographs submitted (see page 513) were taken during December, 1914.

**ABSTRACT OF DISCUSSION**

Dr. Thompson, the chairman, asked Mr. Toch whether the oil which showed up so well was a kettle-boiled oil or a commercial boiled oil, and what was its gravity. Mr. Toch replied it was a kettle-boiled oil which he had made himself, and while he did not know its exact gravity from memory he was quite sure it was over 0.980.

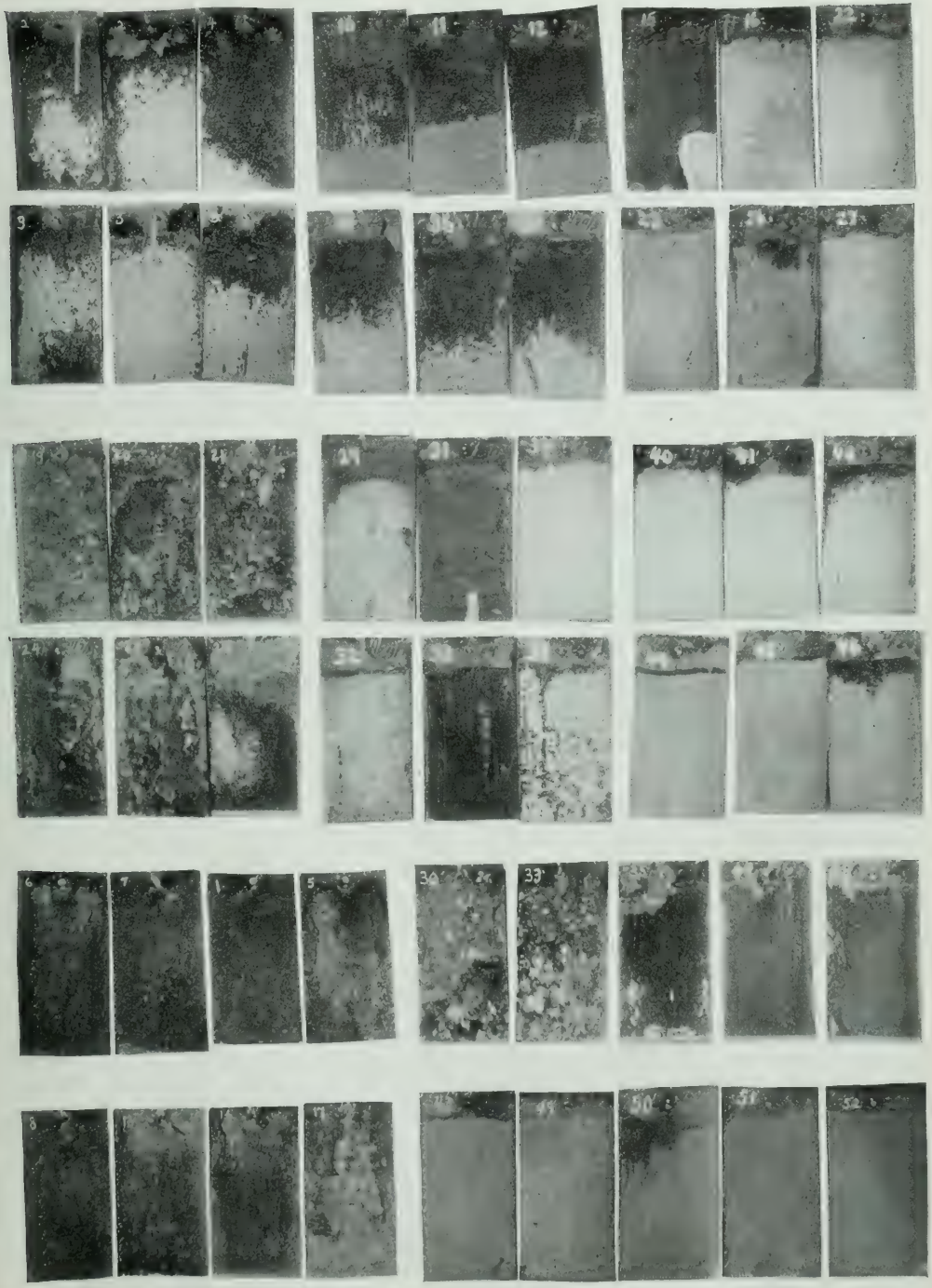
Mr. Gaines said that in his laboratory a sample of a heavy paraffin oil was submitted by the Standard Oil Company for the purpose of protecting steel against rust, and this sample while it protected against rust collected dirt and cinders in the meantime. Mr. Toch referred to sample panel 15, which he said was coated with an analogous material, which he had thoroughly cleaned off to show that a paraffin compound, if it were heavy enough, protected steel from corrosion, but it had to be completely removed before any paint would adhere to the metal.

Mr. Low asked whether Mr. Toch had any data on the viscosity of these oils previous to their being applied, for it appeared to him that the value of the oil depended upon the thickness of the coating, and that was probably why the kettle-boiled oil (panel No. 46) and the boiled China wood oil with the Tungate drier (panel No. 52) produced such good results.

Mr. Toch replied that there was no question that Mr. Low was correct in his premises. The thickness of the coating is in direct ratio to its protective quality, provided it has a protective quality to start with, and assuming, of course, that it is a drying oil. Mr. Toch stated that he had not made any measurements of the thickness of the various films, but those that stood up well showed an appreciable thickness of film.

Prof. Sabin said that a shop coat of linseed oil for bridge work had not entirely gone out of use. There are several different reasons for doing it. The structural metal, as received from the shop, is covered with mill scale. Sooner or later it will come off, carrying with it any paint that has been applied. The shop coat of linseed oil is applied, the bridge erected; the mill scale is allowed to rust off, and then the bridge is thoroughly cleaned and painted. On another road a shop coat of linseed oil is applied, the bridge erected and then honestly painted by the company's painters. Others say that a shop coat of linseed oil enables the inspector to see whether the riveting, etc., is properly done, better than when the work is painted. Most engineers believe that they can get better painting done with the railroad's own painters than can be obtained by the bridge company's painters. The question is whether it is possible to get a vehicle that will work easier than linseed oil and can be sold at a price that will pay to use it. The tests for linseed oil are so simple that almost any engineer can determine whether he is getting a pure article.

Mr. Stevenson said that in the erection of steel the



shop coat is almost always torn off in the rough handling it gets. It costs more to get on a coat of paint in the shop than it does in the field. Linseed oil gives protection for four or five months, which is as long as it is wanted, and has given very good results except in one or two cases.

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## DETERMINATION OF THE BIOCHEMICAL OXYGEN DEMAND BY THE SALTPETER METHOD IN STOCKYARDS, TANNERY AND CORN PRODUCTS WASTES[1]

By Arthur Lederer[2]

Received April 13, 1915

The saltpeter method described by me in the May (1914) issue of the *Journal of Infectious Diseases* and in a paper presented at the last December meeting of the American Public Health Association (*Am. J. Pub. Health*, April, 1915) is based upon experimental work with domestic sewage and polluted river water. Briefly, the method depends upon the denitrification of a sodium nitrate solution by the sewage bacteria present. It was found that the amount of saltpeter oxygen absorbed by the organic matter on incubation is the same as if fresh water oxygen was used.

In preparing and adding the sodium nitrate solution to the sewage it was assumed that five atoms of oxygen are available from two molecules of sodium nitrate, and the figures obtained on this basis checked very well with figures obtained by the dilution method. By the dilution method is meant the preparation of sewage-water mixtures in stoppered bottles with the addition of a definite quantity of methylene blue. The dilution may or may not be carried to the point of absolute stability. Usually the mixtures are incubated for ten days at 20° C. Ten days' incubation suffices for all practical purposes. Twenty days' incubation is preferable when the time element is not important.

The stability is expressed in terms of "relative stability." Knowing the free oxygen content of the diluting water and the time of decolorization, the biochemical oxygen demand of the sewage can easily be calculated, and expressed in milligrams of oxygen per liter of sewage or p. p. m. The principal objection to the dilution method from a scientific standpoint is the impossibility of determination of intermediate points of deoxygenation as is possible with the saltpeter method, and from the working standpoint that it is time-consuming and ill adapted for field work.

During the incubation with the saltpeter solution I observe the sediment, the odor, and the gas formation. If the sediment becomes "septic" (*i. e.*, black color) during incubation, the bottle with the next higher content of saltpeter is selected for the determination of the residual nitrate-nitrite oxygen. If the saltpeter is present in sufficient quantities there is no putrid odor. If active gas formation does not take place, the presence of either free acid or caustic alkali or other germicides may be discovered.

This brings me to the subject of trade wastes. A municipal sewage may contain a considerable quantity of trade waste without losing entirely the characteristics of a domestic sewage. In such a case the saltpeter method can be employed without any modification. However, sewage or trade wastes occur containing caustic alkali or acid, or a germicidal or antiseptic substance. These are the wastes which I want to discuss more closely. In previous publications I have warned against the indiscriminate application of the saltpeter method in the trade wastes, for the reasons already given. In trade wastes investigations carried on for The Sanitary District of Chicago under the direction of Langdon Pearse, I have had ample opportunity to study the application of the saltpeter method to such wastes, including those from the stockyards, tannery, and corn products industry. The modifications of the method required when working with some of these wastes are simple and do not complicate the application in the least.

With the packing house waste mixed with domestic sewage, the method remains the same as with domestic sewage. This waste resembles somewhat a concentrated domestic sewage, with a high organic nitrogenous and carbonaceous content. When working with such a waste of unknown strength, I have employed 500, 1,000, 1,500, and 2,000 parts per million of oxygen in the form of sodium nitrate. On the individual plant outlet higher concentrations might be required. Some concentrated effluents containing blood and other complex organic matter absorb as much as 15,000 p. p. m. of oxygen. The biologic oxygen consumption of the mixed waste obtained from the stockyards and packing town, with domestic sewage, in Chicago at Center Ave., fluctuates between 900 and 1,300 p. p. m. of oxygen during the working period of the day.

A little experience is the best guide to the quantity of sodium nitrate required. It is useless to add methylene blue to these wastes as an indicator on account of the adsorption which takes place in the presence of colloids. The appearance of a black color in the sediment or the elimination of the putrid odor after incubation are not reliable indices, as is the case with domestic sewage. Profuse gas formation takes place whether there is a sufficient quantity of sodium nitrate present or not. The bacterial content of the packing house and stockyards waste is always very high. Domestic sewage is nearly always mixed in varying proportion, roughly, about twenty-five per cent. The best index of accomplished denitrification is undoubtedly furnished by the nitrites. For instance, if nitrites are absent or present in traces in the 500 p. p. m. oxygen bottle, after incubation, discard the bottle and select the one with the higher amount of oxygen for the actual determination of the residual nitrite-nitrate. Supposing we find that on the fifth day of incubation with the highest concentration of sodium nitrate there is but a weak nitrite reaction (5 cc. of the liquid is all that is required for this test) we have then reason to assume that we shall be unable to obtain an accurate oxygen demand figure unless we add some more saltpeter oxygen This can be done probably without incurring an appreciable error. At

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[1] Chemist and Bacteriologist, The Sanitary District of Chicago.

any rate, it is advisable to obtain an approximate figure rather than to lose the result entirely. The residual nitrite is determined by the sulfanilic acid-naphthylamine method, the nitrate by the aluminum reduction method. At the conclusion of the aluminum reduction, an aliquot portion of the liquid is directly nesslerized. It is clear, of course, that a certain working error is involved in the determination of such large quantities of residual nitrite-nitrate, but the error should not exceed 10 per cent, even in the hands of the inexperienced chemist. Undoubtedly, the employment of a more rapid method and less sensitive method than the ones mentioned would be desirable, but such methods are not available.

A question arises whether the oxygen consumption increases with the excess of sodium nitrate employed. An extended series of tests with domestic sewages indicates that the oxygen consumption increases somewhat with the excess of saltpeter employed, but not to an extent sufficient to interfere with correct conclusions. I have found that the excess must be considerable before the oxygen consumption is increased by 10 per cent or thereabouts.

The excess consumption is insignificant when compared with that obtained by employing fresh water dilutions as is done in the so-called English incubation test.[1] The smaller the excess the more accurate the result: it is merely a question of adding to the number of bottles; the additional labor involved is slight. The saltpeter method on stockyards waste checks well with the dilution method, as can be noted from the following table:

TABLE I—COMPARISON OF DILUTION METHOD AND SALTPETER METHOD ON MIXED STOCKYARDS SEWAGE

| Serial No. | Biochemical Oxygen demand, p. p. m. Dilution method | Saltpeter method |
|---|---|---|
| 1 | 1130 | 1090 |
| 2 | 1200 | 1110 |
| 3 | 890 | 848 |
| 4 | 1100 | 1160 |
| 5 | 940 | 890 |
| 6 | 960 | 950 |
| Average..... | 1036 | 1009 |

The oxygen consumption during the first 24 hrs. at 20° C. amounts to approximately 20 to 30 per cent of the ultimate consumption—during the first five days, 70 to 85 per cent. In domestic sewage the oxygen consumption during the first 24 hrs. is likewise approximately 20 to 30 per cent of the ultimate. It is of interest to obtain the oxygen consumption in the first 24 hrs., as this indicates what might happen in the stream when the trade waste is discharged.

Work on the substitution of sodium nitrite for sodium nitrate as a source of oxygen gave promising results with weak domestic sewage. The substitution would simplify the method, inasmuch as the residual oxygen would be present only in the form of nitrite and not nitrate as well. Closer studies proved, however, that nitrites give results lower than the nitrate. With weak sewages the differences are negligible, but in stronger sewages and in the mixed stockyards sewage, an average of a very large number of results shows results 5 to 10 per cent lower than those obtained with the saltpeter and the dilution method. With tannery waste, nitrite results were even 25 per cent lower. Still, the analytical part of the nitrite method is so simple that in the case of the continuous control of a sewage settling plant it may seem feasible to disregard the small difference, or else add to all of the results obtained a certain percentage of oxygen. This percentage could be elicited experimentally by a comparison with the nitrate or dilution method.

[1] Lederer, THIS JOURNAL, 6 (1914), 882.

I have also applied this test to the combined waste from a large establishment producing cornstarch and glucose. There was the admixture of domestic sewage from the workmen in the plant, with consequent high bacterial content. Often the effluent would be slightly acid, on account of the presence of free sulfurous acid, but the acidity would quickly disappear on standing. Even though the effluent was distinctly alkaline to methyl orange, gas formation was not noted at first. Checks were not obtained with the dilution method. It was then found that the presence of carbohydrates resulted in a fermentation during the incubation, forming organic acids which inhibited denitrification. However, when a few cubic centimeters of a saturated sodium bicarbonate solution were added at the start, to take care of the acids of fermentation, the method worked well.

It is useless to add methylene blue as an indicator or to observe the sediment and odor. It is nearly impossible to apply the dilution method to this waste, on account of the adsorption of coloring matter even in the higher dilutions. The presence or absence of nitrites furnishes the best index. The total oxygen consumption varied between 400 and 1200 p. p. m. The oxygen consumption during the first 24 hrs. was only about 7 per cent, and during the first 5 days approximately 60 per cent of the total.

The presence of sodium bicarbonate apparently does not interfere with the results obtained. Considerable quantities were added experimentally without change in the oxygen demand figures, as can be noted from Table II.

TABLE II—BIOCHEMICAL OXYGEN DEMAND OF DOMESTIC SEWAGE CONTAINING VARYING QUANTITIES OF SATURATED SODIUM BICARBONATE SOLUTION. RESULTS IN PARTS PER MILLION

| Serial No. | Biochemical oxygen demand of sewage containing 0.0 | 1 cc. | 3 cc. | 5 cc $NaHCO_3$ |
|---|---|---|---|---|
| 1 | 134 | 140 | 146 | |
| 2 | 157 | 161 | 170 | 170 |
| 3 | 118 | — | — | 115 |
| 4 | 130 | 135 | 138 | 126 |
| 5 | 158 | 153 | 159 | 150 |
| 6 | 150 | 165 | 150 | 153 |

During the course of the incubation, tests can be made for free acid and if acid should develop, sodium bicarbonate may be added at any time. The temporary lifting of the stopper has no influence on the progress of deoxygenation. In dealing with such wastes, I have made it a rule to add a few cubic centimeters of a saturated sodium bicarbonate solution to each bottle at the start.

Caustic alkali was not noted by me, but it should be tested for with phenolphthalein, and if present neutralized with hydrochloric acid. It is particularly likely to occur in tannery waste. These vary considerably in strength from time to time. A mixed waste is frequently strong in caustic alkali. If this is the case, add dilute hydrochloric acid to neutralize the

free lime, using phenolphthalein as an indicator. Preferably the sample should stand for about 30 min. with a slight excess of acid and be tested again for free lime, inasmuch as the free lime in the sediment does not combine very rapidly with the acid.

The effluent resulting from the liming process may contain such an excessive quantity of lime sediment as to make complete initial neutralization extremely difficult. My experience with these particular effluents is that they do not lend themselves to biochemical demand determinations readily by either the saltpeter or the dilution method. When employing the dilution method adsorption of the methylene blue takes place in the majority of cases even in the higher dilutions. In a mixed tannery waste, however, suspended lime is ordinarily not present in quantities sufficient to interfere with the reliability of either mode of procedure.

As a rule, the bacterial content is high, making unnecessary the seeding of the waste with sewage after neutralization. However, in order to insure the presence of sewage bacteria, the waste may be seeded after neutralization by the addition of one cubic centimeter of domestic sewage or polluted river water for each 8-oz. bottle containing the waste.

The wash water resulting from the chemical tanning process is likely to be acid. If it is desired to test this waste separately, it becomes necessary to neutralize with sodium bicarbonate and to seed with sewage. Although the tannery wastes are often strongly colored, the dilutions required in employing the dilution method are as a rule so great that they do not interfere with the observations of the decolorization of the methylene blue. The dilution method has been found to check well with the saltpeter method when employed on combined tannery waste with the precautions mentioned. The average of 24 days' results showed the dilution method not quite 3 per cent higher. Considering the unavoidable working errors involved by either method, this is an excellent check. The total oxygen demand varied appreciably during the day, namely, from 400 to 1000 p. p. m. The oxygen consumption in the first 24 hrs. was about 7 per cent and in the first 5 days 60 per cent of the total.

As yet, I have not encountered other germicidal or antiseptic trade wastes, although such waste can undoubtedly be found in the gas works industry. Offhand, I should say that in such waste the dilution method will be preferably employed to offset the germicidal effect, and the dilution method would probably be desirable when determining the oxygen demand of a disinfected sewage. Cases are rare where a sewage or waste contains germicides other than free lime or free acid in quantities sufficient to interfere with the application of the saltpeter method. If free lime or free acid is present in any waste, the procedure to be tried should be the one which is described.

Finally, I may say a few words to clear up certain misconceptions regarding the meaning of the term oxygen demand. As determined, the oxygen is entirely supplied by the nitrate. But this does not mean that the oxygen demand so determined will have to come from the available oxygen in the stream into which the sewage is discharged. On the contrary, while most of the oxygen may be derived from the stream, the rest may come from the air by absorption or from the plankton. No definite rule can be given, for each particular case is a matter of individual study. Whether all of the oxygen must be supplied from the stream or not, the saltpeter method affords a reliable and simple comparison of the strength of a sewage or waste from the deoxygenating standpoint. This and the amount of settling suspended matter are the items most interesting to the sanitary engineer or chemist. Of less value are the routine chemical determination of the constituents usually looked for in sewage. The great advantage of the saltpeter method lies in the fact that the oxygen consumption can be determined after any desired interval in a much more reliable and comparable manner than can be accomplished by methods involving fresh water dilutions. To the sanitary engineer this is a matter of great importance. The method has also been employed by me for the past year to determine the efficiency of sewage purification devices and the degree of pollution of rivers. For the latter purpose, somewhat different technique is required,[1] the discussion of which is not within the scope of this paper.

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## THE ACIDITY AND ASH OF VANILLA EXTRACT

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In a paper entitled "The Chemical Composition of Authentic Vanilla Extracts, together with Analytical Methods and Limits of Constants,"[2] Winton and Berry tabulate analyses of 77 extracts prepared in the laboratory from different varieties, grades and lengths of vanilla beans and 18 extracts employing different menstrua. The determinations made were vanillin, normal lead number, color value of the extract and of the lead filtrate and the color insoluble in amyl alcohol. In addition to the extracts made by the direct treatment of the beans with the menstruum, second extracts were prepared from the residues and separately analyzed.

Since this paper was published it occurred to us that determinations of acidity and ash, as well as the solubility and alkalinity of the ash, would be of value in the examination of suspected samples. It is indeed surprising that such simple determinations should have been overlooked in the search for means of distinguishing genuine from imitation extracts especially when ash and ash constants have been regarded of such importance in the analysis of fruit products and various other classes of foods.

The ash values would appear to be useful on the one hand because the common ingredients of imitation extracts, namely, vanillin, coumarin, sugar, glycerine and alcohol, are practically free from ash and on the other hand because the use of alkali in the manufacture of extracts from beans would not only increase

[1] Lederer, *Am. J. Pub. Health*, May, **1915**

[2] Proceedings of the Assn. of Official Agricultural Chemists for 1911, U. S. Dept. of Agric., Bureau of Chemistry, *Bull.* **152**, 146–158.

the amount of ash but change the values for solubility and alkalinity.

A marked degree of acidity, due chiefly to organic acids dissolved from the beans and in lesser degree to natural vanillin, is a characteristic of genuine vanilla extract, whereas low total acidity or low acidity not vanillin is indicative of adulteration.

Fortunately, the extracts prepared and analyzed by Winton and Berry, excepting those made from the residues which seemed unimportant, had been preserved and opportunity was found by one of us (E. H. B.) during the present year for the supplementary determinations named. Check analyses were made by Mr. C. K. Glycart, of the Chicago laboratory. The work on the acidity of vanillin was carried out by one of us (A. R. A.) at Washington.

### THE ACIDITY OF VANILLIN

The fact that vanillin combines with alkalies has long been known and compounds with sodium, barium, magnesium, zinc, lead and other metals are described in the literature.[1]

If the acid hydrogen of vanillin were completely replaceable by metals it might be calculated from its formula that one gram of vanillin should neutralize 65.8 cc. of $N/10$ alkali; this replacement is, however, not complete as is evidenced by the analytical figures given in Table I. While one gram of vanillin is sometimes present in 100 cc. of imitation extract, the average quantity in that volume of U. S. P. vanilla extract found by Winton and Berry is from 0.11 to 0.31 gram, equivalent to from 7.2 to 20.4 cc. of $N/10$ alkali. From these figures it is evident that the acidity of genuine vanilla extract of standard strength is due in appreciable part to vanillin and that the distinction between genuine and imitation extracts is one of degree rather than the presence of acidity in one and its absence in the other.

In order to determine by actual experiment the acidity of vanillin and whether other ingredients of extracts influence the results, solutions of different amounts of vanillin with and without the addition of sugar, glycerine and caramel were dissolved in 10 cc. of 60 per cent alcohol diluted to 200 cc. with water and titrated with $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. Two different lots of vanillin were used, one made by Merck, melting at 78.4° C., and the other by the Verona Chemical Co., known as "Vera Vanillin," melting at 78.0° C. The results appear in Table I.

TABLE I—ACIDITY OF VANILLIN WITH AND WITHOUT SUGAR, GLYCERINE AND CARAMEL. RESULTS IN TERMS OF CC. $N$ 10 NaOH

| | Vanillin Mg | Substances Added: None | 2 g sugar | 2 cc. glycerine | Caramel | NaOH Theory requirement |
|---|---|---|---|---|---|---|
| Merck's | 100 | 6.3 | 6.3 | 6.3 | 6.5(a) | 6.58 |
| | 35 | 2.2 | 2.2 | 2.2 | ... | 2.30 |
| | 10 | 0.6 | 0.6 | 0.6 | ... | 0.66 |
| "Vera" | 100 | 6.3 | 6.3 | 6.3 | ... | 6.58 |
| | 35 | 2.2 | 2.2 | 2.2 | | 2.30 |

(a) Indistinct end point.

From the figures obtained, it appears that the acidity of commercial vanillin by actual titration, using phenolphthalein, is slightly lower than the theoretical, being for one gram 63 instead of 65.8 cc. of $N/10$ alkali; furthermore, that it is not influenced by sugar, glycerine and caramel. It should be noted that while the natural color present in 10 cc. of genuine vanilla extract does not interfere with the titration after dilution to 200 cc., the caramel in imitations may be present in sufficient amount to render the end point indistinct. This fact is more of an advantage than a disadvantage as it furnishes evidence of the presence of caramel in addition to that obtained by the usual tests.

We have found that the vanillin in an imitation extract may be fairly accurately determined by the titration of the ether solution of vanillin and coumarin obtained by shaking out the lead filtrate as in the Hess and Prescott method; furthermore, that the supernatant ether solution after this titration may be evaporated for the determination of coumarin. When, however, the extract contains organic acids, as is true of genuine vanilla extract, the titration gives high results due to the solubility in ether of the acetic acid liberated from the lead acetate in the precipitation of the organic acids of the extract. Experiments are now in progress with the view of overcoming this error.

### METHODS OF DETERMINING ACIDITY AND ASH

TOTAL ACIDITY—Dilute 10 cc. of the extract to 200 cc. and titrate with $N/10$ alkali, using phenolphthalein as indicator. Calculate to 100 cc. of extract by multiplying the number of cc. obtained in the titration by ten.

VANILLIN ACIDITY—Multiply the percentage of vanillin by 65.8, thus obtaining the cc. of $N/10$ alkali corresponding to the vanillin in 100 cc. of the extract.

ACIDITY OTHER THAN VANILLIN—Subtract the vanillin acidity from the total acidity.

TOTAL ASH—Evaporate 10 cc. of the extract in a platinum dish and burn below redness.

SOLUBILITY AND ALKALINITY OF ASH—Follow the method of the A. O. A. C. for saccharine products,[1] except that all the results should be calculated to grams per 100 cc. of the extract.

### ACIDITY AND ASH IN U. S. P. VANILLA EXTRACT

The results of determinations of acidity and ash, also of solubility and alkalinity of ash appear in Table II. These supplement the data previously reported by Winton and Berry[2] who determined vanillin, normal lead number and color values. For reasons explained by these authors the abnormal figures obtained on the extracts of Ceylon beans are not included in the maximum, minimum and average of all varieties.

ACIDITY—It is remarkable that the range in total acidity (30 to 52 cc. $N/10$ NaOH per 100 cc.) is less than of the acidity corrected for vanillin (14 to 42 cc.). Extracts having a high acidity usually have low vanillin content and *vice versa*, suggesting a physiological relation between the two. Notwithstanding the wider range of the acidity other than vanillin, this figure will doubtless be of the greater value in judging imitation extracts in which the acidity is largely or entirely due to synthetic vanillin.

The acidity other than vanillin, as a rule, bears a

[1] Tiemann and Haarmann, *Ber.*, **7** (1874), 614.

[1] U. S. Dept. of Agr., Bur. of Chem., *Bull.* **107**, rev., 68 and 69.

[2] *Loc. cit.*

TABLE II—ACIDITY, ASH AND ALKALINITY OF ASH OF VANILLA EXTRACT (TINCTURE OF VANILLA, U. S. P.) MADE IN THE LABORATORY

| Serial No. | Kind and quality of bean | Acidity of extract Cc. N/10 alkali per 100 cc. Total | Equivalent to vanillin | Other than vanillin | Ash Gram per 100 cc. Total | Water soluble | Water insoluble | Alkalinity of ash Cc. N/10 acid per 100 cc. Total | Water soluble | Water insoluble |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Mexican 1st | 43 | 11 | 32 | 0.338 | 0.279 | 0.059 | 42 | 33 | 9 |
| 2 | | 37 | 10 | 27 | 0.297 | 0.246 | 0.051 | 37 | 29 | 8 |
| 3 | 2nd | 42 | 11 | 31 | 0.326 | 0.283 | 0.043 | 40 | 32 | 8 |
| 4 | | 42 | 11 | 31 | 0.297 | 0.260 | 0.037 | 36 | 29 | 7 |
| 5 | | 48 | 11 | 37 | 0.354 | 0.299 | 0.055 | 42 | 34 | 8 |
| 6 | 3rd | 45 | 12 | 33 | 0.347 | 0.290 | 0.057 | 42 | 33 | 9 |
| 7 | | 50 | 12 | 38 | 0.378 | 0.317 | 0.061 | 46 | 36 | 10 |
| 8 | | 47 | 13 | 34 | 0.346 | 0.285 | 0.061 | 46 | 34 | 12 |
| 9 | 3rd (splits) | 50 | 12 | 38 | 0.392 | 0.321 | 0.071 | 48 | 36 | 12 |
| 10 | 4th | 49 | 12 | 37 | 0.387 | 0.323 | 0.064 | 49 | 38 | 11 |
| 11 | 5th | 48 | 10 | 38 | 0.398 | 0.332 | 0.066 | 50 | 38 | 12 |
| 12 | | 52 | 10 | 42 | 0.422 | 0.349 | 0.073 | 53 | 40 | 13 |
| 13 | Cuts | 46 | 10 | 36 | 0.385 | 0.327 | 0.058 | 47 | 38 | 9 |
| | Maximum | 52 | 13 | 42 | 0.422 | 0.349 | 0.073 | 53 | 40 | 13 |
| | Minimum | 42 | 10 | 27 | 0.297 | 0.246 | 0.037 | 36 | 29 | 7 |
| | AVERAGE | **46** | **11** | **35** | **0.369** | **0.301** | **0.058** | **46** | **35** | **10** |
| 14 | Bourbon: 1st | 38 | 13 | 25 | 0.263 | 0.220 | 0.043 | 35 | 26 | 9 |
| 15 | | 41 | 13 | 28 | 0.274 | 0.227 | 0.047 | 37 | 28 | 9 |
| 16 | | 41 | 12 | 29 | 0.265 | 0.221 | 0.044 | 35 | 26 | 9 |
| 17 | 2nd | 42 | 10 | 32 | 0.335 | 0.275 | 0.060 | 43 | 32 | 11 |
| 18 | | 46 | 13 | 33 | 0.348 | 0.291 | 0.057 | 42 | 31 | 11 |
| 19 | | 51 | 14 | 37 | 0.373 | 0.319 | 0.054 | 47 | 34 | 13 |
| 20 | 3rd | 36 | 14 | 22 | 0.329 | 0.282 | 0.047 | 40 | 29 | 11 |
| 21 | | 39 | 13 | 26 | 0.287 | 0.232 | 0.055 | 36 | 25 | 11 |
| 22 | | 48 | 13 | 35 | 0.336 | 0.263 | 0.073 | 44 | 28 | 16 |
| 23 | 3rd (splits) | 40 | 12 | 28 | 0.314 | 0.256 | 0.058 | 36 | 25 | 11 |
| 24 | 4th | 38 | 10 | 28 | 0.328 | 0.263 | 0.065 | 39 | 25 | 14 |
| 25 | | 37 | 9 | 28 | 0.317 | 0.248 | 0.069 | 42 | 25 | 17 |
| 26 | | 38 | 8 | 30 | 0.333 | 0.253 | 0.080 | 44 | 26 | 18 |
| 27 | 5th | 37 | 9 | 28 | 0.351 | 0.298 | 0.053 | 38 | 28 | 10 |
| 28 | | 35 | 10 | 25 | 0.310 | 0.252 | 0.058 | 38 | 25 | 13 |
| 29 | | 35 | 8 | 27 | 0.313 | 0.248 | 0.065 | 40 | 33 | 7 |
| | Maximum | 51 | 14 | 38 | 0.373 | 0.319 | 0.080 | 47 | 34 | 18 |
| | Minimum | 35 | 8 | 22 | 0.263 | 0.220 | 0.043 | 35 | 25 | 9 |
| | AVERAGE | **40** | **11** | **29** | **0.317** | **0.259** | **0.058** | **40** | **27** | **13** |
| 30 | Seychelles: 1st | 39 | 12 | 27 | 0.258 | 0.214 | 0.044 | 34 | 25 | 9 |
| 31 | | 35 | 12 | 23 | 0.251 | 0.213 | 0.038 | 35 | 26 | 9 |
| 32 | | 35 | 13 | 22 | 0.316 | 0.261 | 0.055 | 43 | 28 | 15 |
| 33 | 3rd | 40 | 13 | 27 | 0.309 | 0.256 | 0.053 | 39 | 25 | 14 |
| 34 | | 41 | 12 | 29 | 0.299 | 0.241 | 0.058 | 40 | 29 | 11 |
| 35 | | 42 | 12 | 30 | 0.301 | 0.244 | 0.057 | 41 | 29 | 12 |
| 36 | 4th | 41 | 13 | 28 | 0.307 | 0.262 | 0.045 | 40 | 30 | 10 |
| 37 | | 38 | 11 | 27 | 0.293 | 0.249 | 0.044 | 35 | 24 | 11 |
| 38 | | 39 | 10 | 29 | 0.305 | 0.249 | 0.056 | 47 | 30 | 17 |
| | Maximum | 42 | 13 | 30 | 0.316 | 0.262 | 0.058 | 47 | 30 | 17 |
| | Minimum | 35 | 10 | 27 | 0.251 | 0.213 | 0.038 | 34 | 24 | 9 |
| | AVERAGE | **39** | **12** | **27** | **0.293** | **0.243** | **0.050** | **39** | **27** | **12** |
| 39 | Madagascar: 2nd | 42 | 15 | 27 | 0.220 | 0.193 | 0.027 | 34 | 26 | 8 |
| 40 | | 44 | 15 | 29 | 0.242 | 0.206 | 0.036 | 34 | 26 | 8 |
| 41 | | 46 | 12 | 34 | 0.264 | 0.219 | 0.045 | 37 | 26 | 11 |
| 42 | 3rd | 45 | 13 | 32 | 0.300 | 0.264 | 0.036 | 39 | 29 | 10 |
| 43 | | 47 | 13 | 34 | 0.326 | 0.266 | 0.060 | 46 | 32 | 14 |
| 44 | | 48 | 13 | 35 | 0.325 | 0.271 | 0.054 | 46 | 33 | 13 |
| 45 | 4th | 45 | 20 | 25 | 0.313 | 0.262 | 0.051 | 41 | 29 | 12 |
| 46 | | 44 | 16 | 28 | 0.253 | 0.208 | 0.045 | 38 | 27 | 11 |
| 47 | | 44 | 16 | 28 | 0.313 | 0.268 | 0.045 | 40 | 29 | 11 |
| | Maximum | 47 | 20 | 35 | 0.326 | 0.271 | 0.060 | 46 | 33 | 14 |
| | Minimum | 42 | 10 | 26 | 0.220 | 0.193 | 0.027 | 34 | 26 | 8 |
| | AVERAGE | **45** | **14** | **31** | **0.284** | **0.239** | **0.045** | **39** | **28** | **11** |
| 48 | Comores: 1st(*a*) | 41 | 12 | 29 | 0.310 | 0.251 | 0.059 | 42 | 31 | 11 |
| 49 | | 39 | 11 | 28 | 0.302 | 0.248 | 0.054 | 42 | 30 | 12 |
| 50 | | 41 | 11 | 30 | 0.337 | 0.274 | 0.063 | 46 | 33 | 13 |
| 51 | 3rd(*a*) | 41 | 12 | 29 | 0.348 | 0.289 | 0.059 | 46 | 33 | 13 |
| 52 | | 41 | 11 | 30 | 0.347 | 0.279 | 0.068 | 49 | 33 | 16 |
| 53 | | 41 | 10 | 31 | 0.366 | 0.285 | 0.081 | 51 | 34 | 17 |
| 54 | 4th(*a*) | 41 | 8 | 33 | 0.432 | 0.357 | 0.075 | 53 | 38 | 15 |
| 55 | | 40 | 8 | 32 | 0.411 | 0.332 | 0.079 | 54 | 38 | 16 |
| 56 | | 39 | 10 | 29 | 0.374 | 0.299 | 0.075 | 51 | 34 | 17 |
| 57 | 1st(*b*) | 34 | 20 | 14 | 0.235 | 0.198 | 0.037 | 33 | 24 | 9 |
| 58 | | 42 | 14 | 28 | 0.280 | 0.232 | 0.048 | 40 | 28 | 12 |
| 59 | 2nd(*b*) | 43 | 16 | 27 | 0.229 | 0.182 | 0.047 | 35 | 22 | 13 |
| 60 | 4th(*b*) | 47 | 8 | 39 | 0.400 | 0.326 | 0.074 | 54 | 38 | 16 |
| 61 | 1st(*c*) | 36 | 13 | 23 | 0.265 | 0.217 | 0.048 | 33 | 23 | 10 |
| 62 | 3rd(*c*) | 37 | 13 | 24 | 0.315 | 0.270 | 0.045 | 40 | 28 | 12 |
| 63 | 4th(*c*) | 40 | 10 | 30 | 0.379 | 0.320 | 0.059 | 46 | 33 | 13 |
| | Maximum | 47 | 20 | 39 | 0.432 | 0.357 | 0.081 | 54 | 38 | 17 |
| | Minimum | 34 | 8 | 14 | 0.229 | 0.182 | 0.037 | 33 | 22 | 9 |
| | AVERAGE | **40** | **12** | **28** | **0.333** | **0.272** | **0.061** | **45** | **31** | **14** |
| 64 | S. Amer.: 1st | 52 | 15 | 37 | 0.305 | 0.261 | 0.044 | 38 | 26 | 12 |
| 65 | 2nd | 44 | 12 | 32 | 0.344 | 0.295 | 0.049 | 39 | 27 | 12 |
| 66 | Splits | 50 | 14 | 36 | 0.327 | 0.273 | 0.054 | 42 | 30 | 12 |
| | Maximum | 52 | 15 | 37 | 0.344 | 0.295 | 0.054 | 42 | 30 | 12 |
| | Minimum | 44 | 12 | 32 | 0.305 | 0.261 | 0.044 | 38 | 26 | 12 |
| | AVERAGE | **49** | **14** | **35** | **0.325** | **0.276** | **0.049** | **40** | **28** | **12** |
| 67 | Ceylon: 1st | 34 | 5 | 29 | 0.424 | 0.364 | 0.060 | 49 | 37 | 12 |
| 68 | | 33 | 5 | 28 | 0.361 | 0.313 | 0.048 | 43 | 33 | 10 |
| 69 | | 49 | 4 | 45 | 0.443 | 0.386 | 0.057 | 56 | 44 | 12 |
| | Maximum | 49 | 5 | 45 | 0.443 | 0.386 | 0.060 | 56 | 44 | 12 |
| | Minimum | 33 | 4 | 28 | 0.361 | 0.313 | 0.048 | 43 | 33 | 10 |
| | AVERAGE | **39** | **5** | **34** | **0.409** | **0.354** | **0.055** | **49** | **38** | **11** |
| 70 | Java: 4th | 45 | 15 | 30 | 0.349 | 0.299 | 0.050 | 49 | 38 | 11 |
| 71 | | 52 | 16 | 36 | 0.294 | 0.250 | 0.044 | 40 | 33 | 7 |
| 72 | | 48 | 14 | 34 | 0.290 | 0.246 | 0.044 | 38 | 31 | 7 |
| | Maximum | 52 | 15 | 37 | 0.349 | 0.299 | 0.050 | 49 | 38 | 11 |
| | Minimum | 45 | 14 | 30 | 0.290 | 0.246 | 0.044 | 38 | 31 | 7 |
| | AVERAGE | **48** | **15** | **33** | **0.311** | **0.266** | **0.046** | **42** | **34** | **8** |
| 73 | Tahiti | 33 | 7 | 26 | 0.288 | 0.249 | 0.039 | 37 | 29 | 8 |
| 74 | | 30 | 7 | 23 | 0.221 | 0.179 | 0.042 | 30 | 23 | 7 |
| | AVERAGE | **31** | **7** | **24** | **0.254** | **0.214** | **0.040** | **33** | **26** | **7** |
| 75 | Vanillons | 38 | 4 | 34 | 0.263 | 0.214 | 0.048 | 38 | 30 | 7 |
| | Tonka beans: | | | | | | | | | |
| 76 | Angostura: Prime | 5 | 0 | 5 | 0.132 | 0.122 | 0.010 | 15 | 12 | 3 |
| 77 | Bloaters | 5 | 0 | 5 | 0.163 | 0.156 | 0.007 | 16 | 14 | 2 |
| | AVERAGE | **5** | **0** | **5** | **0.147** | **0.139** | **0.008** | **15** | **13** | **2** |
| | ALL ANALYSES (*d*) | | | | | | | | | |
| | Maximum | 52 | 20 | 42 | 0.432 | 0.357 | 0.081 | 54 | 40 | 18 |
| | Minimum | 30 | 7 | 14 | 0.220 | 0.179 | 0.027 | 30 | 22 | 7 |
| | AVERAGE | **42** | **12** | **30** | **0.319** | **0.265** | **0.054** | **42** | **30** | **12** |

(*a*) Pomoni, Anjouan. (*b*) Comoro. (*c*) Mayotte. (*d*) Excluding Ceylon vanilla, Vanillons, and Tonka beans.

closer relation to both the normal lead number and the amount of total ash. For example, the highest acidity was obtained in sample No. 12 which was one of the highest in normal lead number and total ash, while the lowest acidity was obtained in sample No. 57 which was the lowest in normal lead number and one of the lowest in ash.

ASH—The range of total ash (0.220 to 0.432 gram per 100 cc.) is greater than that of the total acidity but less than that of the acidity other than vanillin. The relation between ash and normal lead number is more striking than between either of these and the acidity. The highest ash and normal lead number were obtained in the same sample (No. 54), while the lowest was found in sample No. 39 with a lead number only a trifle above the minimum.

SOLUBILITY OF ASH—As a rule over 80 per cent of the tota. ash was soluble in water.

ALKALINITY OF ASH—The figures for the total ash ranged from 30 to 54 cc. and for the soluble ash from 22 to 40 cc. of *N*/10 NaOH per 100 cc. of extract. It is a remarkable coincidence that the ranges of alkalinity of total ash and of total acidity of the extract are practically identical.

ACIDITY AND ASH IN EXTRACTS MADE WITH DIFFERENT MENSTRUA

The results are given in Table III and like those in

TABLE III—ACIDITY, ASH AND ALKALINITY OF ASH OF VANILLA EXTRACT PREPARED WITH DIFFERENT MENSTRUA IN THE LABORATORY

| Per cent alcohol used | Addition | Acidity of extract Cc. N/10 alkali per 100 cc. Total | Equivalent to vanillin | Other than vanillin | Ash Gram per 100 cc. Total | Water soluble | Water insoluble | Alkalinity of ash Cc. N/10 acid per 100 cc. Total | Water soluble | Water insoluble |
|---|---|---|---|---|---|---|---|---|---|---|
| | MEXICAN BEANS: | | | | | | | | | |
| 60 | None | 54 | 12 | 42 | 0.409 | 0.363 | 0.046 | 49 | 39 | 10 |
| 60 | Sugar—U. S. P. | 54 | 12 | 42 | 0.391 | 0.330 | 0.061 | 47 | 37 | 10 |
| 60 | Glycerin | 53 | 10 | 43 | 0.386 | 0.323 | 0.063 | 50 | 39 | 11 |
| 35 | None | 54 | 11 | 43 | 0.507 | 0.409 | 0.098 | 65 | 47 | 18 |
| 35 | Sugar | 53 | 11 | 42 | 0.481 | 0.381 | 0.100 | 63 | 45 | 18 |
| 35 | Glycerin | 52 | 11 | 41 | 0.508 | 0.402 | 0.106 | 66 | 47 | 19 |
| | BOURBON BEANS: | | | | | | | | | |
| 60 | None | 47 | 12 | 35 | 0.355 | 0.294 | 0.061 | 42 | 28 | 14 |
| 60 | Sugar—U. S. P. | 46 | 12 | 34 | 0.341 | 0.282 | 0.059 | 45 | 32 | 13 |
| 60 | Glycerin | 45 | 13 | 32 | 0.348 | 0.282 | 0.066 | 43 | 27 | 16 |
| 35 | None | 45 | 11 | 34 | 0.414 | 0.319 | 0.095 | 52 | 30 | 22 |
| 35 | Sugar | 45 | 11 | 34 | 0.388 | 0.303 | 0.085 | 51 | 34 | 17 |
| 35 | Glycerin | 44 | 12 | 32 | 0.405 | 0.310 | 0.095 | 49 | 29 | 20 |
| | TAHITI BEANS: | | | | | | | | | |
| 60 | None | 29 | 7 | 22 | 0.225 | 0.198 | 0.027 | 30 | 24 | 6 |
| 60 | Sugar—U. S. P. | 30 | 7 | 23 | 0.221 | 0.178 | 0.043 | 30 | 23 | 7 |
| 60 | Glycerin | 27 | 7 | 20 | 0.226 | 0.182 | 0.044 | 30 | 22 | 8 |
| 35 | None | 22 | 6 | 16 | 0.234 | 0.189 | 0.045 | 31 | 22 | 9 |
| 35 | Sugar | 24 | 6 | 18 | 0.227 | 0.173 | 0.054 | 32 | 22 | 10 |
| 35 | Glycerin | 23 | 6 | 17 | 0.244 | 0.190 | 0.054 | 33 | 23 | 10 |

Table II should be compared with the analyses reported by Winton and Berry.[1]

The influence of sugar or glycerine in the menstruum on the amount of acidity and ash extracted was hardly appreciable. Decreasing the strength of the alcohol increased the amount of ash and diminished the acidity.

SUMMARY

I—The following ranges in acidity and in ash values were found in 77 U. S. P. extracts made in the laboratory from different varieties, grades and lengths of vanilla beans:

TOTAL ACIDITY: 30 to 52 cc. $N/10$ alkali per 100 cc.
ACIDITY OTHER THAN VANILLIN: 14 to 42 cc. $N/10$ alkali per 100 cc.
TOTAL ASH: 0.220 to 0.432 gram per 100 cc.
SOLUBLE ASH: 0.179 to 0.357 gram per 100 cc.
ALKALINITY OF TOTAL ASH: 30 to 54 cc. $N/10$ acid per 100 cc.
ALKALINITY OF SOLUBLE ASH: 22 to 40 cc. $N/10$ acid per 100 cc.

II—Practically the same values were obtained with and without the use of sugar or glycerine in the menstruum.

III—Diminishing the strength of alcohol in the menstruum tended to increase the ash values and diminish the acidity.

IV—The possibility of developing a method of determining vanillin based on the acidity is suggested.

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## A MODIFICATION OF WICHMANN'S METHOD FOR THE DETECTION OF SMALL AMOUNTS OF COUMARIN, PARTICULARLY IN FACTITIOUS VANILLA EXTRACTS

By J. R. DEAN

Received April 9, 1915

The essential part of the Wichmann method for the detection of coumarin in vanilla extracts is the conversion of the coumarin, in the residue obtained by evaporating the distillate from a vanilla extract to dryness, into salicylic acid by fusion with potassium hydroxide and testing for salicylic acid with ferric chloride. Saccharin and salicylic acid interfere completely with this test.

The following modification of Wichmann's method has been found to be as useful as the original, is much less troublesome and is not interfered with by either salicylic acid or saccharin.

Render a de-alcoholized portion of the extract alkaline with 5 cc. of ammonia (use of the residue after an alcohol determination is recommended) and extract with 15 cc. of ether.[3] Vanillin, salicylic acid and saccharin are insoluble in ether in the presence of ammonia while coumarin is readily dissolved. Transfer the ether to a nickel or porcelain crucible and evaporate on the steam bath or hot plate. Add five drops of a 50 per cent solution of potassium hydroxide and, after carefully drying, fuse at the lowest possible temperature, care being taken to avoid any blackening. Dissolve the mass in a few cc. of water, render acid with dilute sulfuric acid and transfer to a test tube. Add 5 cc. of chloroform to dissolve out the salicylic acid produced in the fusion and shake the tube vigorously. Allow the chloroform to separate and remove it with a small pipette extended to the bottom of the tube. Transfer the chloroform to a second test tube, filtering through a small plug of cotton. Add 1 or 2 cc. of water, containing a drop or two of ferric chloride solution, to the chloroform and shake as before. The presence of coumarin is indicated by the formation of the purple color of ferric salicylate.

TABLE OF RESULTS

| SAMPLES Extract of vanilla plus | No. of samples | Results | Depth of purple color |
|---|---|---|---|
| Nothing | 4 | Negative | |
| 25 mg. salicylic acid | 4 | Negative | |
| 25 mg. saccharin | 4 | Negative | |
| 1 mg. coumarin | 4 | Positive | Light purple |
| 2.5 mg. coumarin | 4 | Positive | Strong purple |
| 5 mg. coumarin | 4 | Positive | Deep purple |
| 5 mg. coumarin 25 mg. salicylic acid | 4 | Positive | Deep purple |
| 25 mg. saccharin 25 mg. coumarin | 4 | Positive | Very deep purple |

It does not seem possible to employ the above reaction in an accurate quantitative method for coumarin that would be any shorter or better than the extraction method now employed. By experience, however, one can learn to form a very good idea of the amount of coumarin present by the depth of color obtained.

Attention is called to the fact that coumarin would interfere with Durand's[1] test for saccharin as both coumarin and saccharin yield salicylic acid when fused with either potassium or sodium hydroxide. It is possible to eliminate the saccharin, as stated above, but as coumarin is of such an inert nature chemically, its removal is far less easy—an extraction by means of an immiscible solvent in the presence of an alkali being the method generally used. Coumarin and saccharin are very likely to be found together in food products, especially in soft drinks of a cheap nature where coumarin has been used in place of, or with, vanilla or vanillin. In using Durand's test for saccharin it would be necessary to remove the coumarin by rendering the substance alkaline and extracting as above. After the complete removal of the coumarin, the sample under examination could be rendered acid and tested for saccharin as in Durand's method.

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## STUDIES IN SYNTHETIC DRUG ANALYSIS III—ESTIMATION OF CAFFEINE AND ANTIPYRIN IN ADMIXTURE

By W. O. EMERY AND S. PALKIN

Received March 20, 1915

The first recorded attempts looking to the quantitative separation of these two drugs were apparently made by J. J. Hofman,[2] who, taking advantage of the tendency of antipyrin to yield with mercury salts difficultly soluble products, subjected the caffeine-antipyrin mixture to the action of mercuric nitrate, thereby precipitating the antipyrin as the molecular compound $C_{11}H_{12}N_2O.Hg(NO_3)_2$. After separating the precipitate by filtration, the caffeine was isolated from an aliquot of the filtrate by extraction with chloroform and estimated as pure caffeine. The weight of the

[1] *Loc. cit.*

[2] "A Method for the Detection of Small Amounts of Coumarin, Particularly in Factitious Vanilla Extracts," by H. J. Wichmann. *Circular* 95, U. S. Dept of Agr., Bureau of Chemistry.

[3] Hess and Prescott, *J. A. C. S.*, **25** (1899), 256.

[1] Halsey Durand, THIS JOURNAL, **5** (1913), 987.

[2] *Pharm. Weekblad*, No. **43** (1894)

original mixture having been previously ascertained, that of antipyrin could of course be readily calculated. As already pointed out by Zernik,[1] the method is faulty in that the precipitation of antipyrin with mercuric nitrate is not quantitative, a portion of the molecular compound remaining dissolved in the liquid as shown by the isonitroso reaction. The result is that caffeine separated in this manner is never quite pure but is contaminated with an appreciable quantity of antipyrin in the form of its combination with mercuric nitrate. Zernik[2] effected an improvement in the method by carrying out the precipitation in a saturated solution of potassium nitrate, but even so allowance had to be made for traces of antipyrin-mercuric nitrate, which still persisted in the recovered caffeine.

The procedure on which our experimental work is based had its inception in a study of the behavior of antipyrin toward iodin,[3] its preliminary formulation having been dictated by the following considerations. Like many basic substances, antipyrin yields in aqueous-acid media with iodized potassium iodide one or several iodin addition products or periodides, according to the conditions of the experiment.[4] In the presence of a substance like sodium acetate, however, or better sodium bicarbonate, the additive tendency of the halogen is immediately followed by one of substitution, the final result being that the antipyrin is quantitatively converted into its monoiodo derivative. On discharging the iodin excess with thiosulfate, we have in the resulting menstruum monoiodoantipyrin, which can be readily isolated and weighed. In the event that caffeine also is present during such treatment it will be found unchanged and in admixture with the recovered iodoantipyrin. Determination of iodin in the composite residue thus obtained supplements all the data required for the calculation of both caffeine and antipyrin. The procedure as finally adopted for the separation proper is embodied in the following essential operations:

METHOD

Transfer to a 150 cc. separatory funnel (Squibb type), by means of two 5 cc. portions alcohol-free chloroform followed by 10 cc. water, about 0.25 g. of the caffeine-antipyrin mixture, add 1 g. sodium bicarbonate and 10–15 cc. 0.2 *N* iodin (or double the quantity of 0.1 *N* iodin), the latter reagent being added in successive small portions and the liquid mixture vigorously shaken 15–20 seconds after each addition. When all the iodin has been thus added, a decided excess of this reagent should be apparent in the liquid after a final vigorous shaking of 1 minute, in which event all the antipyrin will have been converted into the monoiodo derivative. If, however, all the iodin previously applied should appear to have been expended, a little more must be added to insure excess and the mixture again shaken. Now discharge the uncombined iodin by means of a small crystal of sodium thiosulfate, add 15 cc. redistilled U. S. P. chloroform, then shake vigorously 1 minute. After clearing, draw off the solvent into a second separator containing 5 cc. water, shake and after clearing pass the chloroform through a small, dry filter into a tared 50 cc. beaker and evaporate to apparent dryness on the steam bath, accelerating the operation by means of an air blast. Repeat the extraction with two (three, in case 0.1 *N* iodin is used) 25 cc. portions of chloroform, washing, filtering and evaporating each portion in rotation substantially as directed in the first instance. Recover all crystalline products separating about the tips of separator, funnel and edge of filter by judicious washing with chloroform. Dry the nearly colorless crystalline residue of caffeine and iodoantipyrin one-half hour at 105°, then cool and weigh. Designate this weight "A".

Dissolve the composite residue of caffeine and iodoantipyrin in 5 cc. glacial acetic acid, add 10 cc. saturated aqueous solution of sulfur dioxide, then transfer the resultant liquid by diluting, pouring and rinsing with hot water to a 400–500 cc. beaker until the final volume amounts to about 200 cc. Add aqueous silver nitrate solution (about 0.3 g. silver nitrate), sufficient at least to precipitate all the halogen, and follow with a few drops of nitric acid, then heat nearly to boiling, stirring the while in order to agglomerate the silver iodide. Add about 15 cc. concentrated nitric acid, cover the beaker with a watch glass and boil gently 5 or 6 minutes. Filter by decantation through a tared Gooch, washing the precipitate once with a little alcohol, then with two 100 cc. portions boiling water, finally transferring the silver iodide completely to the crucible. Wash several times with hot water and then with alcohol to remove all traces of organic matter. Dry one-half hour in the air bath at 110°, cool and weigh. The weight of silver iodide multiplied by the factor 0.8012 yields the quantity of antipyrin present in the sample taken.

The quantity of caffeine is ascertained by subtracting the product obtained by multiplying the weight of silver iodide by the factor 1.3374, from the weight of the composite residue "A".

In practice, the preliminary or gross separation of the caffeine-antipyrin mixture from the usual excipients of tablet and pill combinations is most conveniently effected by extraction of the finely powdered mass on a tared filter with chloroform, this solvent together with its attendant alcohol being subsequently completely expelled first by gentle distillation and finally by evaporation on the steam bath, prior to proceeding with the separation proper. Likewise in the case of alcoholic preparations containing caffeine and antipyrin as essential ingredients, the recovery of these two substances is best carried out after evaporation of the alcohol on the steam bath. The residual menstruum is thereupon exhausted with chloroform in the usual way, the resulting solution of caffeine and antipyrin being treated precisely like the one obtained from tablet or pill combinations.

The use of alcohol-free chloroform in connection with the halogenation of antipyrin is necessary in order to preclude the possible formation of iodoform, the pres-

[1] *Z. anal. Chem.* **21** (1906), 674.
[2] *Ibid.*, **21** (1906), 686.
[3] Cf. THIS JOURNAL **6** (1914), 51.
[4] A paper on the periodides of antipyrin is in course of preparation.

SERIES 1

| IODOANTIPYRIN | SILVER IODIDE | IODIN (per cent) | |
|---|---|---|---|
| Gram | Gram | Recovery | Theory |
| 0.2000 | 0.1498 | 40.47 | 40.40 |
| 0.3000 | 0.2240 | 40.34 | 40.40 |

SERIES 2

| ANTIPYRIN | SILVER IODIDE | ANTIPYRIN RECOVERY | |
|---|---|---|---|
| Gram | Gram | Gram | Per cent |
| 0.2500 | 0.3115 | 0.2496 | 99.84 |
| 0.2500 | 0.3111 | 0.2493 | 99.72 |
| 0.2500 | 0.3124 | 0.2503 | 100.12 |
| 0.3000 | 0.3731 | 0.2989 | 99.63 |

SERIES 3

| | | | | RECOVERY | | | |
|---|---|---|---|---|---|---|---|
| | | | | Caffeine | | Antipyrin | |
| Caffeine | Antipyrin | Residue "A" | AgI | | | | |
| Gram | Gram | Gram | Gram | Gram | Per cent | Gram | Per cent |
| 0.0500 | 0.2000 | 0.3836 | 0.2495 | 0.0499 | 99.8 | 0.1999 | 99.9 |
| 0.0500 | 0.2000 | 0.3837 | 0.2490 | 0.0507 | 101.4 | 0.1995 | 99.7 |
| 0.0500 | 0.2000 | 0.3837 | 0.2494 | 0.0501 | 100.2 | 0.1999 | 99.9 |
| 0.0500 | 0.2000 | 0.3845 | 0.2492 | 0.0512 | 102.4 | 0.1997 | 99.8 |
| 0.0500 | 0.2000 | 0.3844 | 0.2490 | 0.0514 | 102.8 | 0.1995 | 99.7 |
| 0.0500 | 0.2000 | 0.3834 | 0.2494 | 0.0499 | 99.8 | 0.1998 | 99.9 |
| 0.0500 | 0.2000 | 0.3835 | 0.2489 | 0.0506 | 101.2 | 0.1994 | 99.7 |
| 0.0500 | 0.2000 | 0.3837 | 0.2500 | 0.0497 | 99.4 | 0.2003 | 100.1 |
| 0.0500 | 0.2000 | 0.3839 | 0.2486 | 0.0514 | 102.8 | 0.1994 | 99.7 |
| 0.0500 | 0.2500 | 0.4658 | 0.3107 | 0.0503 | 100.6 | 0.2489 | 99.5 |
| 0.0500 | 0.2500 | 0.4672 | 0.3118 | 0.0502 | 100.4 | 0.2498 | 99.9 |
| 0.0500 | 0.2500 | 0.4686 | 0.3120 | 0.0513 | 102.6 | 0.2500 | 100.0 |
| 0.0500 | 0.2500 | 0.4674 | 0.3114 | 0.0509 | 101.8 | 0.2495 | 99.8 |
| 0.0500 | 0.2500 | 0.4657 | 0.3116 | 0.0493 | 98.6 | 0.2497 | 99.9 |
| 0.0500 | 0.2500 | 0.4661 | 0.3115 | 0.0498 | 99.6 | 0.2496 | 99.8 |
| 0.0648 | 0.2592 | 0.4976 | 0.3237 | 0.0649 | 100.2 | 0.2593 | 100.0 |
| 0.0648 | 0.2592 | 0.4976 | 0.3236 | 0.0648 | 100.0 | 0.2593 | 100.0 |
| 0.1000 | 0.1000 | 0.2654 | 0.1238 | 0.0998 | 99.8 | 0.0992 | 99.2 |
| 0.1667 | 0.2500 | 0.5864 | 0.3138 | 0.1666 | 99.9 | 0.2514 | 100.5 |
| 0.1667 | 0.2500 | 0.5824 | 0.3124 | 0.1648 | 98.8 | 0.2503 | 100.1 |
| 0.1667 | 0.2500 | 0.5831 | 0.3107 | 0.1677 | 100.6 | 0.2489 | 99.5 |

ence of which in the composite residue "A" would naturally vitiate the analytical findings.

The application of iodin in small portions appears to favor the production of a purer iodoantipyrin than is the case when this reagent is all added at one time, as evidenced by the color of the caffeine-antipyrin residue. In order to free the latter from all contaminating volatile products under the conditions outlined in the method, particular attention should be given to the actual working conditions of the drying oven,[1] since incomplete or improper desiccation must necessarily lead to widely divergent caffeine values, while heating at temperatures materially higher than 105° is found to exert an unfavorable influence on the recovery of both caffeine and antipyrin.

The color changes following the addition of strong nitric acid are quite characteristic, passing from colorless through deep red to pale yellow in the course of 5 minutes' boiling. In view of this somewhat radical treatment to which the caffeine is likewise subjected, any direct determination of this substance becomes impractical. The quantity of caffeine is therefore ascertained indirectly with a reasonable degree of accuracy by subtracting the weight of iodoantipyrin (calculated) from that of the composite residue "A".

As already indicated, the determination of antipyrin is effected by estimating the halogen contained in the iodo derivative and calculating to the parent substance. Considerable experimentation was required before a suitable procedure could be found for the quantitative withdrawal of iodin from the pyrazolon complex. Treatment by Carius naturally gave very accurate returns but in point of facility was far from satisfactory. The well-known methods depending on the action on the one hand of alcoholic potash and on the other of metallic sodium and alcohol both failed completely in the object sought. Even direct and continued boiling with an aqueous acid solution of silver nitrate gave little better results. Thus, in two determinations carried out under slightly varying conditions, only 35.28 and 37.82 per cent iodin could be recovered as silver iodide, the theory demanding 40.40 per cent. A very effective and convenient reagent was finally discovered in sulfur dioxide, which rather unexpectedly perhaps yet none the less completely removes the substituted iodin, as evidenced by numerous controls.

[1] Cf. Lorin H. Bailey, THIS JOURNAL, **6** (1914), 585.

EXPERIMENTAL

The data given for Series 1, 2 and 3 are representative of results obtained by the authors in operations carried out substantially in accordance with the procedure outlined above.

Experiments bearing directly on the behavior of caffeine and iodoantipyrin, when heated alone and in admixture at 105° and under conditions comparable with those followed in the regular method, indicate that loss by volatilization is mainly chargeable to caffeine, as will appear from an examination of the following results. The several charges were first dissolved in 25 cc. chloroform and the solvent then blasted off at a moderate heat prior to treatment in the drying oven.

| | | WEIGHT AFTER HEATING ALONE | | | |
|---|---|---|---|---|---|
| Initial wt | | 30 min. | 30 min. | 1 hr. | Total loss |
| Caffeine | 0.1000 | 0.0993 | 0.0990 | 0.0980 | 0.0020 |
| Iodoantipyrin | 0.4000 | 0.4005 | 0.4003 | 0.4001 | - - - |

| Caffeine | Iodoantipyrin | WEIGHTS AFTER SUCCESSIVE HEATINGS IN ADMIXTURE | | | | | | Total loss |
|---|---|---|---|---|---|---|---|---|
| 0.0500 | 0.4000 | 0.4494 | 0.4491 | 0.4478 | 0.4464 | 0.4454 | 0.4431 | 0.0069 |
| 0.1000 | 0.4000 | 0.4995 | 0.4992 | 0.4981 | 0.4963 | 0.4951 | 0.4926 | 0.0074 |
| 0.2000 | 0.4000 | 0.5996 | 0.5991 | 0.5978 | 0.5963 | 0.5954 | 0.5922 | 0.0078 |

Iodin determinations in the three composite residues were made with the following results:

| RESIDUE | AgI | IODOANTIPYRIN | |
|---|---|---|---|
| Gram | Gram | Gram | Per cent |
| 0.4431 | 0.2989 | 0.3997 | 99.92 |
| 0.4926 | 0.2986 | 0.3993 | 99.82 |
| 0.5922 | 0.2985 | 0.3992 | 99.80 |

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## THE DETERMINATION OF NITRIC NITROGEN IN SOILS

By E. R. ALLEN

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OBJECT OF THE RESEARCH—The determination of nitric nitrogen has been the subject of a very large amount of experimentation, discussion and controversy. In spite of the array of methods that have been proposed, more or less uncertainty exists in the use of any one of them, as is shown, for instance, by the following statements: "No single method appears to be applicable to the determination of nitrogen in nitrates in all classes of water, sewages and sewage effluents, and there is no method which is not subject to considerable error;"[1] and, "The accurate determination of nitric acid in combination presents great difficulties, and can be made only by indirect means; the methods here given are sufficient for most purposes. Very few of them can be said to be simple, but it is to be feared that no simple process can ever be obtained for the determination of nitric acid in many of its combinations."[2]

[1] "Standard Methods of Water Analysis," Amer. Pub. Health Assoc., p. 23 (1912).

[2] Sutton, "Volumetric Analysis," 10th Ed., p. 271 (1910).

In our investigations on the physiology of the process of nitrification in soils, we have been confronted at the outset with the uncertainty of the methods, and the paucity of information regarding the probable errors of the same. In reading the literature quite extensively we have been impressed by the non-uniformity of methods employed by physiologists; and in many cases it is impossible to decide how many of the differences reported are due to differences in physiology and how many to analytical errors.

Another source of error contributing to the confusion of the existing data on the nitric nitrogen problem is that it is not certain that the prevailing methods of extracting the soil actually recover all the nitric nitrogen. The object of the present research will be, however, to develop a method suitable for the study of the physiology of nitrification. A second paper will be devoted to the separation of ammonia, nitric and organic nitrogen, and a third to the extraction of nitric nitrogen from soils.

REQUIREMENTS TO BE MET—A method to meet the requirements of the physiological study of nitrification should be applicable to amounts of nitrate nitrogen varying from 0.1 to 25.0 mg. contained in each case in 250 cc. of soil extract—therefore, in the presence of organic matter. The error should be of the order of magnitude of 2 per cent or less. One-hundred-gram portions of soils are convenient amounts with which to work in nitrification studies. If this amount is extracted with five times its weight of water, for instance, and an aliquot, usually 250 cc., taken for analysis, then with samples containing 2, 100, and 500 parts nitric nitrogen per million of soil, and intermediate values, as may be met in nitrification studies, an error of 2 per cent would require an analytical procedure, the probable error of which would be ±0.002, ±0.10, and ±0.5 of a milligram for the amounts named. The method should also permit the determination of ammonia nitrogen in the same sample.

## HISTORICAL—REDUCTION METHODS

A review of all the literature on methods of nitric nitrogen determination would be scarcely possible or desirable. It is obvious that reduction methods —provided they proceed rapidly and quantitatively— are the most desirable since nitrogen is more easily and more accurately measured as ammonia than in any other form: small amounts may be accurately determined colorimetrically, while larger amounts may be very satisfactorily determined by titration. However, the fact that reduction methods have by no means been adopted to the exclusion of other procedures indicates that they do not give uniformly reliable results. Indeed many instances are recorded in the literature in which chemists have failed to agree on reduction procedures. The careful and thorough work of Mitscherlich and Herz[1] clears up much in this connection: they conclude that most reduction methods are burdened with errors; that, however, reduction with Devarda's alloy does give quantitative results, and that by proper refinement of the distillation apparatus and of the titrimetric procedures a very high degree of accuracy may be attained.

THE DEVARDA METHOD[1] consists of reducing nitric nitrogen in strongly alkaline solution with a finely divided alloy composed of 50 per cent copper, 45 per cent aluminum, and 5 per cent zinc. It is the only method, so far as we are aware, that has escaped serious criticism in the literature. While its *superiority* over other methods has been questioned by some, we have not found a case in which the *reliability of the method itself* has been questioned. According to W. S. Allen,[2] it gives reliable results, and Cahen[3] regards it as satisfactory and vastly superior to Pozzi-Escot's[4] method. After trying different reduction methods Valmari[5] concluded that a finely powdered copper-aluminum alloy, to which a small amount of zinc had been added to produce brittleness—to which class, therefore, Devarda's alloy belongs—is the best reducing agent for nitric nitrogen. Mitscherlich and Herz[6] conducted an extended investigation on the perfection of an accurate Kjeldahl method which would include all forms of nitrogen, in course of which they studied, among other sources of error, the question of the reduction of nitric nitrogen. Using phenolsulfonic acid and zinc dust, sodium hydroxide and zinc-iron dust, Jodlbauer's method, and Forster's method, they were unable to obtain the theoretical amount of ammonia from nitrate. Because they were unable to recover the deficiency of nitrogen by digesting the residues, according to Kjeldahl, for total nitrogen, and because the use of larger amounts of reducing materials did not lessen the losses, they concluded that the "nitrogen loss is not to be attributed to an unfinished and, therefore, incomplete reduction but is much more likely due to the fact that gaseous nitrogen is evolved during the procedure. This loss can be avoided only through other reduction media. As such a one we have chosen Devarda's alloy."[7]

Besides pointing out that the Devarda procedure is the best for effecting reduction of nitric nitrogen, Mitscherlich and Herz, and also Valmari, proposed modifications of the original procedure.

THE MITSCHERLICH-DEVARDA METHOD differs from the original Devarda method in the apparatus used, which effectively prevents the carrying over of alkaline spray into the receiver and still retains the advantage of ease of transfer of the ammonia from distilling flask into receiver, while avoiding the error due to the solubility of the alkali of a glass distillation tube and to the slight absorbing action on ammonia of block-tin condenser tubes. Using this

[1] *Landw. Jahrb.*, **38** (1909), 279–318.

[1] *Zeit. anal. Chem.*, **33** (1894), 113; Treadwell-Hall, "Analytical Chemistry," 3rd Ed., Vol. II, p. 454 (1913).

[2] Orig. Comm. VIII, Int. Cong. App. Chem., Vol. I, p. 19–31, New York (1913).

[3] *Analyst*, **35** (1910), 307.

[4] Reduction with aluminum-mercury couple.

[5] "Unter. ü. d. Lösbarkeit u. Zersetzbarkeit d. Stickstoff im Boden," Dissertation, Helsingfors, **1912**, p. 43.

[6] *Loc. cit.*

[7] *Loc. cit.*, p. 317.

apparatus Mitschlerich and Herz obtained excellent results. From 10 determinations on each of four known amounts of nitrogen they obtained these results:[1]

| No. | Cubic Centimeters $N/50$ $H_2SO_4$ | | Milligrams Nitrogen | | |
|---|---|---|---|---|---|
| | Average | Probable error | True value | True value | Probable error | Deviation from true value |
| I | 24.335 | ±0.070 | 24.40 | 6.84 | ±0.02 | —0 018 |
| II | 12.15 | ±0.044 | 12.20 | 3.42 | ±0.012 | —0.014 |
| III | 6.095 | ±0.025 | 6.10 | 1.71 | ±0.007 | —0.001 |
| IV | 2.44 | ±0.021 | 2.44 | 0.68 | ±0.006 | —0.000 |

They conclude: "these results show better than any words that in our hands the reduction of the nitrate nitrogen is complete, and that the error of this analysis has not become greater than that of the ammonia distillation." The source of the nitrate nitrogen in these analyses was potassium nitrate which gave the theoretical amount of potassium sulfate. Mitscherlich and Herz conclude their paper by saying, "from the preceding work it is worthy of note that hitherto performed nitrate nitrogen analyses are burdened with *very* great errors, because great losses occur in the reduction processes.[2]

THE VALMARI-DEVARDA METHOD possesses the distinctive feature that reduction is carried out in *dilute* alkaline solution, whereas *strong* alkali is required by the original directions of Devarda. According to Valmari, the reaction of a copper-aluminum-zinc alloy is electrolytic, innumerable small cells being formed with aluminum as anode and copper as cathode. The potential difference is, however, not enough to decompose water at room temperature. Boiling produces an evolution of hydrogen, and this evolution is much increased if the conductivity of the water is increased by the presence of neutral electrolytes, and a very low concentration of alkali—even that imparted to the solution by magnesium oxide—hastens the actions sufficiently to reduce nitrate rapidly and quantitatively to ammonia. The nitrogen of a nitrate solution may be distilled off with magnesium oxide and a finely divided copper-aluminum-zinc alloy in a 30-minute distillation period, just as if it were a solution of an ammonium salt.

Valmari found that in solutions high in organic matter the reaction is retarded so that the evolution of hydrogen is not sufficient to effect quantitative reduction. Satisfactory results are obtained by the addition of 5 cc. of the sodium hydroxide solution used in Kjeldahl determinations, which makes the solution about $N/10$ in NaOH. Valmari also recommends the altering of the composition of Devarda's alloy, pointing out that the percentage of aluminum should be higher, but that the brittleness of the mixture sets a certain limit that must not be overstepped. The proportions of 60 per cent aluminum, 37 per cent copper, and 3 per cent zinc give an alloy still capable of being pulverized.

THE ALUMINUM REDUCTION METHOD, which has been used with varying success in water analysis, has recently been recommended by Burgess for the determination of nitrates in soil extracts.[3] The procedure used is described on p. 525. The fact that the somewhat extravagant conclusions are drawn that "the aluminum reduction method for the determination of nitrates in soils yields the most accurate results of all methods now commonly in vogue," and that "the presence of extraordinarily large amounts of soluble organic materials (soluble humus and dextrose) have little effect on the method," and also the fact that the Associate Referee of the Association of Official Agricultural Chemists on nitrogenous materials in soils[1] recommends the adoption of this as an official method, caused us to include some tests of it in this work.

DISCUSSION—Although the power of Devarda's alloy to reduce nitric nitrogen to ammonia quickly and quantitatively is apparently agreed upon, the original Devarda method possesses two sources of error: (1) Owing to the rapid evolution of hydrogen, some fine alkaline spray is likely to be carried over into the receiver, necessitating the redistillation of the receiver contents over MgO. (2) In solutions high in organic matter—as are frequently encountered in soil extracts—the action of the strong alkali on the organic matter is so marked that a sharp separation of the nitric from the organic nitrogen is not possible. The Mitscherlich-Devarda method eliminates the first of these errors and retains the second,[2] while the Valmari-Devarda procedure reduces both, but, except in the case of reduction in MgO solutions, when there is no danger of spray going over, completely eliminates neither. The aluminum reduction method also used a much more dilute alkaline solution for reduction than that employed in the Mitscherlich-Devarda method. However, neither Valmari nor Burgess gave the extended attention to the refinement of the methods they recommended that Mitscherlich and Herz gave to theirs. Before, therefore, these methods employing more dilute alkaline solutions could be accepted they had to be as rigidly examined as the Mitscherlich-Devarda method had been. If a method applicable in the presence of organic matter, in which the reduction is carried out in *weakly* alkaline solutions could be developed to a point where its probable error was of the order of magnitude obtained by Mitscherlich and Herz, it would surpass any that has yet appeared, and we could hope to later perfect the separation of the nitric from the organic nitrogen and thus attain our original object. The comparison of the reduction procedures used in the aluminum reduction, Mitscherlich-Devarda, and Valmari-Devarda methods, the determination of conditions affecting quantitative reduction, and the determination of the probable error of the method furnishes the basis of the experimental part of this work.

## EXPERIMENTAL

CHOICE OF INDICATOR FOR THE TITRATION OF AMMONIA—Since a reduction method for nitric nitrogen involves the titrimetric determination of am-

[1] *Loc. cit.*, p. 289.

[2] *Loc. cit.*, p. 318.

[3] University of California Publications in Agr. Sci., Vol. I, No. 4 (1913).

[1] *The American Fertilizer*, **41** (1914), 33.

[2] It should be stated, however, that Mitscherlich and Herz were not concerned with the separation of organic and nitric nitrogen but only in the question of *complete* reduction, so that their method for *total* nitrogen would certainly include all nitric nitrogen.

monia, an indicator suitable for the titration of weak bases had to be chosen. Preliminary tests convinced us that methyl red, *p*-dimethyl-amino-azobenzene-*o*-carboxylic acid,[1] is easily the best indicator that has yet appeared for the titration of weak bases as ammonia. It is possible to titrate with ease $N/50$ solutions of ammonia against strong acids, provided no $CO_2$ is present. We have observed also that the end point is more distinct if the solution to be titrated is cooled to 10–15° C. This is doubtless due to cutting down of hydrolysis of the ammonia salt of the complex organic acid indicator at this temperature. The end point is more certain than with either Congo red or alizarin red, and vastly more distinct than with methyl orange, lacmoid, or cochineal. Another advantage is that its color change takes place at a lower concentration of hydrogen as ion than does that of methyl orange. According to Tizard[2] the visible color change, red to yellow, takes place between $10^{-5.7}$ and $10^{-7}$, while A. A. Noyes[3] reports that the transition color of methyl red is most marked at $(H^+) = 10^{-6}$ as compared with $(H^+) = 10^{-4}$ for methyl orange. Throughout this work we have adhered to the first faint appearance of brown—free from pink—in the pale lemon-yellow alkaline solution as our end point.

PREPARATION OF MATERIALS AND SOLUTIONS: TITRIMETRIC STANDARDS—Tenth- and fiftieth-normal solutions of sulfuric acid and of sodium hydroxide were prepared free from $CO_2$, and were standardized by the sodium carbonate method which Mitscherlich and Meeres[4] found the most accurate. Fifty-cc. burettes[5] provided with three-way stopcocks, connected with the reservoir bottle, essentially as recommended by Treadwell,[6] were used. The white topped titrating shelf was directly in front of a south window, and the entering light was diffused by passage through a sheet of white paper. The method of reading the burettes was that specified by the Bureau of Standards.[7] When portions of the solutions had stood in the burettes 24 hours or more they were discarded. Temperature corrections were made when necessary.

ANALYTICAL STANDARDS—The sources of nitric and ammonia nitrogen used in the testing of methods reported in this paper were solutions of nitric acid and of ammonium hydroxide. These were prepared from carefully neutralized,[8] ammonia-free water and C. P. $HNO_3$ or $NH_4OH$. They were accurately standardized against the titrimetric standards by series of titrations.

[1] Rupp and Loose, *Ber. d. chem. Ges.*, **41** (1908), 3905, see also Treadwell-Hall, "Analytical Chemistry," Vol. II, p. 543, 3rd Ed. (1913). This indicator can now be purchased from Merck & Co.

[2] *J. Chem. Soc. Trans.*, **97** (1910), 2477–90.

[3] *J. Am. Chem. Soc.*, **32** (1910), 824.

[4] *Landw. Jahrbücher*, **39** (1910), 345.

[5] All burettes used in this work were made according to the specifications of the U. S. Bureau of Standards, but did not bear the control stamp. Calibration curves by means of a 2 cc. Ostwald pipette showed, however, that the limits of error did not exceed the tolerances permitted by the Bureau of Standards *Circ.* **9** (1913), 16.

[6] Treadwell-Hall, "Analytical Chemistry," Vol. II, 3rd Ed., p. 556 (1910).

[7] *Loc. cit.*, p. 17.

[8] The term "neutral water" as used in this paper refers to water neutral to the indicator used, *i. e.*, to methyl red. Strictly neutral water, *i. e.*, in which $(H^+) = 10^{-7}$, would of course be alkaline to methyl red.

AMMONIA-FREE WATER—The regular laboratory-distilled water was treated with bromine water till the tint was distinctly yellowish, allowed to stand at least four hours, transferred to a 5-liter Jena balloon flask, sufficient alkali added to destroy the color, distilled through an ordinary glass condenser, and stored in glass stoppered bottles. Of course, water so prepared reacted slightly alkaline. Whenever used in titrimetric operations it was carefully neutralized beforehand with $N/50$ $H_2SO_4$. When $CO_2$-free water was desired, the receiver was protected with a soda-lime tube. This water was used in all operations reported in this paper.

AMMONIA-FREE MAGNESIA—J. T. Baker's C. P. magnesium oxide was heated in an electric furnace one hour or more at a temperature of 700 to 800° C.

SOIL EXTRACTS HIGH IN ORGANIC MATTER BUT FREE FROM NITRIC NITROGEN—One kilogram of air-dried greenhouse soil, which had been heavily manured for several years and had recently received a liberal application of barnyard manure, was well shaken with two liters of water containing 20 g. of dextrose and allowed to stand over night. It then showed not the slightest trace of nitrate by the diphenylamine test. Three hundred and fifty cc. gave, on distillation with magnesium oxide, 0.32 and 0.37 mg. of ammonium nitrogen and after Kjeldahl digestion 2.27 mg. of organic nitrogen.

The solution was very highly colored, appearing decidedly reddish in the deeper layers. It represents an extreme, though not an impossible case. Its reducing power was tested by titration with Fehling's solution. Ten cc. portions of the extract reduced 8.66, 8.48 and 8.56 cc. of Fehling's solution.

ALUMINUM-COPPER-ZINC ALLOY—The regular Devarda alloy (Cu 50 : Al 45 : Zn 5) was used and not that recommended by Valmari. The Devarda alloy is purchasable on the market and met the requirements of our work. J. T. Baker's product was used, which was found to be absolutely free from nitrogen. A product purchased from another dealer contained, oddly enough, an appreciable amount of nitrogen. The J. T. Baker product was obtained in the form of a powder, much of which would not pass a 20 mesh sieve. Before use it was all pulverized to pass a 60 mesh sieve.

DIPHENYLAMINE REAGENT—In an investigation of this sort it is, of course, necessary to have a means of determining qualitatively minute amounts of nitric nitrogen. The diphenylamine-sulfuric acid method as modified by Withers and Ray[1] meets this requirement. We followed their directions except that as a rule the solutions were tested at room temperature instead of at 40°. By actual tests the reagent we used gave, under these conditions, a faint but distinct reaction in a solution containing 1 part of nitric nitrogen in 25,000,000. The responses to this reaction are classified in the accompanying tables as strong, faint, and none.

INDICATOR SOLUTION—Two-hundredths of a gram (0.02) of methyl red, *i. e.*, the free acid, was dis-

[1] *J. Am. Chem. Soc.*, **33** (1911), 708.

solved in 100 cc. redistilled alcohol.[1] Four drops of this solution were used per titration.

CHOICE OF REDUCTION PROCEDURE—Three methods were tested for their applicability to our conditions:

1—THE ALUMINUM REDUCTION METHOD—The procedure was that employed by Burgess,[2] except that one-half the amount of soil extract, containing only 12.5 mg. nitric nitrogen was used. The soil extracts plus 25 cc. $N/28$ $HNO_3$ and 2 cc. of 50 per cent NaOH were concentrated to about 40 cc. by gentle boiling. The volume of the reducing solutions was 60–70 cc. It was observed that the action on the aluminum was much slower in the presence of organic matter than in the checks. In the latter the aluminum strips completely dissolved over night, while in the former they had been but slightly attacked, and were coated with a thin gelatinous layer of organic matter. In obtaining the data of Table I these strips were left in the flasks during distillation in Nos. 2*c* and *d*, and 3*c* and *d*, while in the cases of Nos. 2*a* and *b*, 3*a* and *b*, and all of Set 4, they were washed off and discarded.

TABLE I—RECOVERY OF 12.5 MG. OF NITRIC NITROGEN BY THE ALUMINUM REDUCTION METHOD

| Set No. | Material | No. hrs. reduction | | Mg. N found | $Ph_2NH$ reaction (*a*) |
|---|---|---|---|---|---|
| 1 | Check | 16 at 20–22° C | *a* | 12.26 | Faint |
| | | | *b* | 12.29 | None |
| | | | *c* | 11.95 | None |
| | | | *d* | 12.32 | Faint |
| 2 | Soil extract | 16 at 20–22° C. | *a* | 8.11 | Strong |
| | | | *b* | 8.25 | |
| | | | *c* | 10.60 | |
| | | | *d* | 7.50 | |
| 3 | Soil extract, clarified with lime | 16 at 20–22° C | *a* | 3.81 | Strong |
| | | | *b* | 4.82 | |
| | | | *c* | 5.91 | |
| | | | *d* | 8.10 | |
| 4 | Soil extract, clarified with lime | 40 hrs. at 20–22° | *a* | 12.60 | Strong |
| | | | *b* | 12.15 | |
| | | | *c* | 10.16 | |
| | | | *d* | 12.38 | |

(*a*) **The diphenylamine reactions reported in this and subsequent tables are the results of tests made on 1 cc. portions of the solutions after reduction.**

It is believed that the production of ammonia from organic matter entered somewhat into the determinations of Set 4. This action would, of course, be greater in the longer reduction periods. This would explain why No. 4*a* gave high values for nitrate and still by the diphenylamine method showed considerable nitrate unreduced.

The data in Table I indicate that the claims made for this method by Burgess are too broad. Organic matter evidently *does* retard the reduction. It should be noted here also that the aluminum reduction method has been prescribed for the determination of nitric nitrogen in waters, "if the quantity of organic nitrogen is less than 0.1 part in 100,000.[3] The organic materials used by Burgess, *i. e.*, soluble humus and dextrose, do not contain the type of colloidal matter that is encountered in extraction of soils containing decaying organic matter. Furthermore, it is doubtful if a method which involves the transfer of a solution containing ammonia in the presence of a fixed alkali will yield highly satisfactory results. At any rate the procedures described below involved less time and gave promise of greater accuracy.

2 THE VALMARI-DEVARDA METHOD of reducing in the presence of MgO was first studied. The nitric nitrogen was introduced as $N/28$ $HNO_3$ into Kjeldahl flasks, diluted to 300 cc., and 1 g. MgO and 3 mg. alloy added. The flask was then connected with the regular Kjeldahl distilling rack, and distillation carried on for 30 minutes, rinsing out the condenser with steam at the end of this period, as has been recommended by Benedict.[1] The results, given in Table II. show that the method gives promising results with

TABLE II—REDUCTION AND DISTILLATION OF NITRIC NITROGEN IN THE PRESENCE OF MAGNESIUM OXIDE

| 5 MG. NITROGEN TAKEN | | | 25 MG. NITROGEN TAKEN | | |
|---|---|---|---|---|---|
| No. | Mg. N found | $Ph_2NH$ reaction | No. | Mg. N found | $Ph_2NH$ reaction |
| 1 | 4.956 | Faint | 1 | 23.21 | Faint |
| 2 | 4.962 | Faint | 2 | 23.58 | Faint |
| 3 | 5.091 | Faint | 3 | 23.75 | Faint |
| 4 | 4.990 | Faint | 4 | 22.85 | Faint |
| 5 | 5.013 | Faint | 5 | 23.94 | Faint |
| AVERAGE | 5.002 | | | 23.46 | |

5 mg. nitric nitrogen but fails in the presence of 25 mg. Since Valmari obtained satisfactory results for 17.5 mg. of nitric nitrogen it was surprising that our results were low for 25 mg. It at once occurred to us that the alkalinity of the magnesia itself is not sufficient for rapid reduction of this amount of nitric nitrogen and expulsion of the ammonia, but that the increased alkalinity resulting from the reduction of the alkali nitrate, used by Valmari, might be sufficient to produce quantitative results. In obtaining the data in Table II the nitric acid added was converted into magnesium nitrate, which on reduction gave rise to insoluble magnesium hydroxide, thus not increasing the alkalinity. The importance of this point was shown in the following experiment in which the 12.5 cc. $N/7$ nitric acid added were just neutralized with $N/10$ alkali, the magnesium oxide and alloy then added, and the reduction and distillation carried out as before. In five determinations, 25.09, 24.81, 25.05, 24.91 and 24.80 (av. 24.93) mg. nitrogen were recovered.

These results show that, while the alkalinity produced by MgO alone is not sufficient to effect quantitative reduction and distillation of a 25-mg. portion of nitric nitrogen in a 30-minute period, the alkalinity produced as a result of the reduction of an alkali nitrate added to that produced by MgO is sufficient to effect the reduction in this time. In all subsequent operations the standard nitric acid added was neutralized with standard alkali, regardless of whether the reducing solution was made alkaline with MgO or NaOH.

The behavior of the method in the presence of organic matter was next studied: 300 cc. of the soil extract high in organic matter were measured into Kjeldahl flasks, then 10 cc. of a previously analyzed potassium nitrate solution (3.96 mg. nitric nitrogen) and 5 cc. of an analyzed ammonium sulfate solution (4.98 mg. ammonia nitrogen) were added. One gram of magnesium oxide was added, the ammonia distilled off (30 minutes), and flask and contents

[1] **The directions given in Treadwell-Hall (Vol. II, 3rd Ed., p. 543 (1913)) are to dissolve 0.02 g. of free acid in 100 cc. of hot water. This recommendation is certainly incorrect, as the above amount of free acid will not dissolve in 100 cc. of water. The free acid is almost insoluble in water, its saturated solution at the ordinary temperature being only about $N/100,000$, while its alkali salts are very soluble (Tizard, *Loc. cit.*, 2485).**

[2] **University of California Publications in Agr. Sci., Vol. I, No. 4 (1913).**

[3] **Sutton's "Volumetric Analysis," 10th Ed., p. 465 (1911).**

[1] *J. Am. Chem. Soc.*, **22** (1900), 259. **This procedure was used in all distillations reported in this paper, which were performed with the regular Kjeldahl distilling apparatus.**

cooled; the water distilled off was replaced with ammonia-free water, 3 grams Devarda's alloy were added and the reduction and distillation proceeded with. The analyses gave 5.05 and 5.16 mg. ammonium nitrogen, and 0.32 and 0.36 mg. nitric nitrogen. After reduction the solutions gave intense diphenylamine reactions. The very low results for nitric nitrogen confirm Valmari's statement that the method fails in the presence of large amounts of organic matter. Clarification of the extracts with lime and other precipitants, the addition of electrolytes, increasing the amount of magnesia, all effected some improvement, but did not bring the method up to where it could be recommended as a quantitative procedure. An additional difficulty with the magnesia method is the fact that in the presence of organic matter the foaming was very bad and could not be avoided by the addition of such substances as paraffin or crude oil.

The other procedure of the Valmari-Devarda method, *i. e.*, reduction in approximately $N/10$ NaOH was next tested in pure solutions and in the presence of organic matter. Two cc. of our Kjeldahl alkali (50 per cent) added to 300 cc. of water produced an alkalinity slightly above 0.1 normal (10 cc. of this neutralized 11.92 cc. of $N/10$ $H_2SO_4$). The procedure was the same as used before except that on account of foaming, even in pure solutions, distillation could be carried on less rapidly and 45 minutes were required to distill over 100–125 cc. The solutions high in organic matter were boiled for 30 minutes after the addition of the alkali and standard nitric acid, in order to expel ammonia. Since there is always danger of some of the fine alkaline spray, produced by the rapid evolution of hydrogen, being carried over, the contents of the receivers were redistilled over magnesium oxide. In order to show the magnitude of the error so introduced, the results of both distillations are reported. Twenty-five mg. of nitric nitrogen were added in all cases as $N/28$ $HNO_3$.

TABLE III—REDUCTION OF 25 MG. NITRIC NITROGEN IN APPROXIMATELY N/10 SODIUM HYDROXIDE

| | In Pure Solution | | | | With High Organic Matter | | | |
|---|---|---|---|---|---|---|---|---|
| | Mg. N found | | | | Mg. N found | | | |
| No. | First dist. | Second dist. | $Ph_2NH$ reaction | No. | First dist. | Second dist. | $Ph_2NH$ reaction |
| 1 | 24.99 | 24.73 | Faint | 6 | 24.98 | 25.06 | None |
| 2 | 25.02 | 24.90 | Faint | 7 | 24.91 | 24.90 | None |
| 3 | 25.12 | 25.01 | Faint | 8 | 24.39 | 24.73 | None |
| 4 | 25.07 | 24.77 | Faint | 9 | 24.45 | 24.49 | None |
| 5 | 25.22 | 24.94 | Faint | 10 | 24.65 | 24.63 | None |
| Av. | 25.08 | 24.87 | | Av. | 24.68 | 24.76 | |

Reduction is evidently more complete in the presence of organic matter. The tendency of the results to be lower under these conditions is no doubt due to the slight reducing action of the organic matter during the preliminary distillation period. That there is less alkali carried over in Nos. 6–10 than in 1–5, is to be attributed to the fact that, on account of foaming, the solutions containing organic matter were distilled more slowly.

The magnesia method of Valmari appears to be reliable if organic matter is absent. The fact, however, that the alkalinity of the magnesia itself is not sufficient to effect complete reduction would suggest that, although very rapid and convenient, the method had best not be indorsed too stongly as yet. It is unreliable in the presence of any considerable amount of organic matter. The Valmari-Devarda method, reducing in approximately $N/10$ alkali, appears to be the more reliable procedure and is evidently applicable in the presence of organic matter.

3—MITSCHERLICH-DEVARDA METHOD—The procedure proposed by Mitscherlich and Herz for the reduction of nitric nitrogen differs from the original Devarda method in that a different distillation apparatus is used. It differs from Valmari's method in this particular and also in the fact that strongly alkaline solutions are used for reduction and distillation. It is shown below that for reduction a dilute alkaline solution is preferable to the concentrated one used by Mitscherlich, although Mitscherlich has shown beyond a doubt that his method gives reliable results. Furthermore, as mentioned above, reduction in a strongly alkaline solution renders the separation of the nitric and organic nitrogen almost impossible.

Of the procedures tested, then, reduction with Devarda's alloy in dilute sodium hydroxide solution is to be preferred.

FACTORS AFFECTING REDUCTION—The factors studied were: (1) Concentration of alkali; (2) amount of alloy; (3) time. Since MgO solutions are too weak to effect quantitative reduction in the presence of organic matter and solutions $N/10$ in NaOH are sufficiently strong, and since it is advantageous to keep the concentration of the alkali to a minimum, determinations were made in solutions high in organic matter which had been made approximately $N/20$ in NaOH. The conditions were otherwise the same as in the set of determinations reported above, in which $N/10$ NaOH in presence of high organic matter was studied. Only 6.78 and 11.03 mg. of nitrogen were recovered from the 25 mg. nitric nitrogen added and the solutions after reduction gave intense reactions for nitrites with Griess' reagent. Hence $N/20$ NaOH is not sufficiently strong to effect a rapid and complete reduction, while according to Table III $N/10$ is sufficiently concentrated. The concentrations between $N/10$ and $N/20$ were not studied.

The directions in the literature vary somewhat in regard to the amount of alloy required. Sutton[1] states that 5 times the weight of the nitrate should be used. Valmari uses 1 to 2 grams, while Mitscherlich and Herz obtained with 2 grams the nitrogen equivalent of 23.48 cc. $N/50$ acid as against a true value of 24.40, while their results quoted above were obtained by the application of 3 g.; *i. e.*, the amount of alloy which Valmari recommends, Mitscherlich and Herz found insufficient. In order to obtain more information on this point the experiments as shown in Table IV were carried out. The reduction of 25 mg. nitric nitrogen was performed in the regular manner in 300 cc. portions of pure solutions.

Nos. 22, 23 and 34 are the values obtained after redistillation over MgO, while the other data were obtained from a single distillation.

The results in Table IV show that the recommendation to use an amount of alloy equal to five times the weight of nitrate is unsound. The concentration of the alkali is apparently of more importance than

[1] "Volumetric Analysis," 10th Ed., p. 285, 1910).

the amount of nitrate. The data also clear up the contradictions in the recommendations of Mitscherlich and Herz as compared with those of Valmari. Two grams of alloy are insufficient in strong alkali, while this amount is sufficient in MgO solutions

TABLE IV—AMOUNT OF ALLOY REQUIRED TO REDUCE 25 MG. NITRIC NITROGEN IN PRESENCE OF DIFFERENT AMOUNTS OF ALKALI

| | MgO | | | N/10 alkali | | | Strong alkali(a) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Grams | Mg. N | $Ph_2NH$ | Mg. N | $Ph_2NH$ | | Mg. N | $Ph_2NH$ | |
| No. | alloy | found | reac. | No. found | reac. | | No. found | reac. | |
| 1 | 0.50 | *a* 21.54 | Strong | 21 *a* 19.03 | Strong | | 31 ... | ... | |
| | | *b* 18.07 | Strong | *b* 22.34 | Strong | | | ... | |
| 2 | 0.75 | *a* 24.91 | Strong | 22 *a* 24.84 | Faint | | 32 *a* 16.48 | Strong | |
| | | *b* 23.38 | Strong | *b* 24.62 | Strong | | *b* 15.94 | Strong | |
| | | *c* 23.42 | Strong | *c* 25.05 | Faint | | ... | ... | |
| | | *d* 24.56 | Strong | *d* 24.27 | Strong | | ... | ... | |
| 3 | 1.00 | *a* 22.42 | Strong | 23 *a* 24.78 | Faint | | 33 *a* 21.35 | Strong | |
| | | *b* 23.45 | Strong | *b* 25.01 | None | | *b* 22.02 | Strong | |
| | | *c* 23.52 | Strong | *c* 24.78 | Faint | | ... | ... | |
| | | *d* 24.91 | Strong | *d* 24.81 | None | | ... | ... | |
| 4 | 2.00 | *a* 25.00 | Faint | ... | | | 34 *a* 24.39 | Faint | |
| | | *b* 25.00 | Faint | ... | | | *b* 24.94 | Faint | |
| | | *c* 25.15 | Faint | ... | | | ... | ... | |
| | | *d* 25.15 | Faint | ... | | | ... | ... | |

(*a*) 25 cc. of 50 per cent NaOH in 300 cc. Mitscherlich and Herz used 50 cc. of concentrated alkali per 200 cc.

and one gram is sufficient in $N/10$ solutions. The superiority of $N/10$ NaOH solutions over more concentrated ones in the matter of the alloy used is apparently due to the fact that in the former case practically all the hydrogen is evolved at 100°, while in the latter case much of it is evolved at lower temperatures. The fact that MgO solutions, in which practically all the hydrogen is evolved at 100°, require more alloy than solutions $N/10$ in NaOH is perhaps due to the fact that in these extremely weak alkaline solutions more hydrogen is evolved from the larger surface of the larger amount of alloy. At any rate, in view of the data on $N/10$ NaOH and on strongly alkaline solutions, the former solutions were heated during the reduction as strongly as foaming would permit.

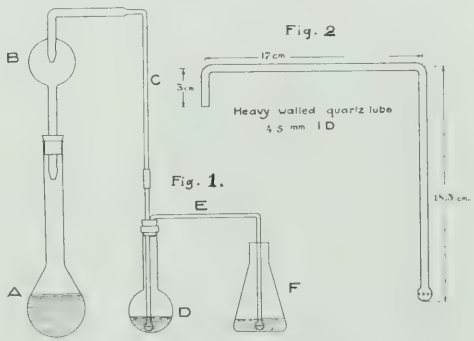
The time required for quantitative reduction of 25 mg. of nitric nitrogen was next determined. The 300 cc. of solution contained in a Kjeldahl flask was heated to boiling in minimum time, which in each case was 8 minutes. The boiling was continued for the lengths of time indicated below, the seething solution quickly filtered with suction and the filtrate tested with diphenylamine.

| No. | I | II | III | IV |
|---|---|---|---|---|
| Minutes boiled..... | 0 | 2.5 | 5.0 | 10.0 |
| $Ph_2NH$ reaction..... | Strong | Strong | Faint | Faint |

The data show that reduction had proceeded sufficiently at the end of five minutes. Optimum conditions for quantitative reduction are, therefore, $N/10$ NaOH and one gram of alloy, the time required for the expulsion of the ammonia being ample to allow quantitative reduction.

CHOICE OF DISTILLATION APPARATUS—The almost endless number of devices that have been proposed for the distillation and quantitative determination of ammonia may be divided into two general classes. In the first of these the condenser, usually block tin, is cooled with water, and in the second the water cooling is dispensed with, and the ammonia is transferred and absorbed by passing the steam directly into the standard acid of the receiver. Those of the first type are preferable for the carrying out of routine determinations in large numbers where a convenient amount of nitrogen may be taken for analysis, while those of the second type are better suited for refined procedures on small amounts of nitrogen. Obviously then a device of the second class is to be preferred for use in determinations of nitric nitrogen in soils in which the amounts of nitrogen dealt with are very limited indeed and in which every possibility of refinement must be taken advantage of. The most desirable apparatus of this second class is evidently that of Mitscherlich.[1] The Pannertz[2] modification of the original Devarda, and that more recently devised by W. S. Allen[3] are both inferior to Mitscherlich's apparatus, because (1) the scrubbing of the vapors is less complete, and (2) the solubility of the alkali contained in the glass distillation tubes vitiates titrations with $N/50$ solutions. We, therefore, adopted for subsequent[4] work the apparatus shown in Fig. 1, which is essentially that of Mitscherlich, and which constitutes Mitscherlich's modification of the original Devarda method.

A few slight modifications have been made in the apparatus. The Hugerschoff distillation bulb used by Mitscherlich is replaced by the Hopkins tube *B;* the 250 cc. Kjeldahl scrubbing flask is replaced by the 200 cc. round-bottomed ring-necked Jena




flask *D;* and the delivery ends of the distillation tubes *C* and *E* are provided with slight bulb-like enlargements perforated with 1 mm. holes. This last improvement not only insures better scrubbing in flask *D* and better absorption in flask *F*, but by producing more even ebullition reduces the danger of spattering. Flask *F* is a 300-cc. seasoned Jena Erlenmeyer. Mitscherlich and Herz call special attention to the necessity of the distillation tube *E* being made of quartz. Trials with such substances as Jena glass, borate silica Jena glass, and porcelain, failed to give satisfactory results. Only when quartz was used were the probable error of distillation and titration kept sufficiently low. Since Mitscherlich and Herz report 366 determinations[5] conducted to ascertain the suitability of substances other than quartz and failed to get a satisfactorily low probable error of

[1] *Landw. Jahr.*, **38** (1909), 780.

[2] Treadwell-Hall, "Analytical Chemistry," Vol. II, 3rd Ed., p. 454 (1913).

[3] Orig. Comm. 8th Int. Cong. App. Chem., Vol. I, pp. 19–31, New York (1912).

[4] All distillations up to this point had been carried out with the ordinary Kjeldahl distilling rack.

[5] *Landw. Jahrb.*, **38** (1909), 302.

the blank distillation with any other material, we accepted their conclusions on this point without further experimentation.[1]

Approximately 40 cc. of water are placed in flask *D*, together with a pinch of magnesium oxide and one of magnesium sulfate. The former facilitates the expulsion of ammonia, although Mitscherlich and Herz found it unnecessary,[2] while, when magnesium sulfate is present and spray containing sodium hydroxide is carried over from flask *A* to *D*, the hydroxyl ions are at once precipitated as magnesium hydroxide, and the probability of alkali being carried into flask *F* is reduced.

The time required to completely reduce the nitric nitrogen and drive it quantitatively into flask *F* was determined on 25-mg. portions of nitric nitrogen, which were reduced with 1 g. alloy in *N*/10 NaOH. The reduction and distillation were carried on for varying periods. The distillation was controlled so as to avoid any danger from loss due to spattering from flask *F*. Extraneous heat was not applied to flask *D*.

| No | I | II | III | IV |
|---|---|---|---|---|
| Minutes reduction and distillation | 20 | 30 | 40 | 40 |
| Milligram nitrogen recovered | 24.38 | 24.74 | 25.05 | 25.05 |

The above data show incomplete recovery in a 20 min. period, doubtful in 30 min., while satisfactory results are obtained in 40 minutes' reduction and distillation. A period of 40 minutes was, therefore, adopted for all subsequent work.

Blank reductions and distillations, using N-free reagents, showed very small amounts of acid neutralized. In ten runs the average was equal to 0.09 cc. of *N*/50 $H_2SO_4$, with maximum and minimum values of 0.18 and 0.01 cc., respectively. This shows that no appreciable amount of spray is carried over nor alkali dissolved out of the glass parts of the apparatus.

PROBABLE ERROR OF THE METHOD—No description or development of a method is complete without some consideration of the accuracy attainable with it, which property of a method is best expressed as its probable error calculated by the method of least squares. The choice of a method for a particular line of investigations is made somewhat at random unless there is some knowledge at hand relative to the accuracy attainable with the different methods applicable. We have, therefore, devoted some attention to the matter of probable errors, and, although our values are calculated from only 10 determinations, they serve to show the order of magnitude of the error of the results yielded by the method.

The probable error of the complete method was determined in pure solutions on 5- and 25-mg. portions of nitric nitrogen, using *N*/10 alkali in the reducing solution, 1 gram alloy, and distilling for 40 minutes in the Mitscherlich apparatus.

These probable errors are certainly to be regarded as quite small. That obtained with *N*/50 solutions is of practically the same magnitude as that reported by Mitscherlich and Herz who used *N*/50 solutions altogether. Since the reduction is effected in weakly alkaline solutions and will proceed quantitatively in the presence of high organic matter, the method

TABLE V—PROBABLE ERROR OF NITRIC NITROGEN DETERMINATION

| No | cc. *N*/50 $H_2SO_4$ | Mg. nitrogen | cc. *N*/10 $H_2SO_4$ | Mg. nitrogen |
|---|---|---|---|---|
| 1 | 17.76 | 4.976 | 17.80 | 24.94 |
| 2 | 17.76 | 4.976 | 17.79 | 24.92 |
| 3 | 17.76 | 4.976 | 17.83 | 24.98 |
| 4 | 17.67 | 4.951 | 17.81 | 24.95 |
| 5 | 17.83 | 4.996 | 17.73 | 24.84 |
| 6 | 17.73 | 4.968 | 17.79 | 24.92 |
| 7 | 17.75 | 4.976 | 17.78 | 24.91 |
| 8 | 17.70 | 4.960 | 17.81 | 24.95 |
| 9 | 17.70 | 4.960 | 17.76 | 24.88 |
| 10 | 17.67 | 4.951 | 17.82 | 24.97 |
| Av. | 17.733 | 4.969 | 17.79 | 24.93 |
| Theoretical value | | 5.000 | | 25.00 |
| Probable error | | ±0.009 | | ±0.028 |
| Deviation from theoretical value | | —0.031 | | —0.07 |

is to be regarded as having attained the aim of this work, and, it is believed, can later be perfected to a point where it will meet the requirements of a physiological study of nitrification.

## DISCUSSION

GENERAL CONSIDERATIONS—A few additional points deserve attention in regard to the above results. Apparently too much has been claimed for the aluminum reduction method. Aside from the objection to it that it involves transfer of alkaline solutions containing ammonia, it is certainly more sensitive to some forms of organic matter than is the reduction with Devarda's in solutions *N*/10 or stronger in NaOH. Reduction in solutions made alkaline with MgO has much to commend it, since the error due to carrying over of spray is avoided, in pure solutions at least; it is very rapid, since the amount of hydrogen evolved is too small to produce foaming, and, therefore, the reduction and distillation may be performed in 30 minutes. A very large amount of effort was spent in this work in an attempt to obtain a reliable and accurate method by the reduction in the presence of MgO, and distillation with an ordinary Kjeldahl rack, a method which would be extremely simple and rapid. The quest was finally abandoned, however, partly because the reduction in presence of MgO is of doubtful value and partly because the Kjeldahl rack itself is less suited for refined work than the apparatus proposed by Mitscherlich and Herz. Of course, the MgO reduction might be employed in ordinary soil extracts and the *N*/10 solutions in those high in organic matter, as originally recommended by Valmari, yet the fact that solutions *N*/20 in NaOH are unreliable for the reduction in the presence of high organic matter indicates that a very low amount of organic matter would prevent quantitative reduction of nitric nitrogen in MgO solutions which are less than *N*/1000, and justifies, in our judgment, the rejection of this procedure for the determination of nitric nitrogen in soil extracts, where varying and uncertain amounts of organic matter are always present.

Solutions approximately *N*/10 in NaOH are apparently the lowest alkalinity that can be safely used in reductions with Devarda's alloy in soil extracts. It is superior to reduction in the more concentrated solutions not only in the points mentioned above but because there is less danger of the flask contents

[1] The tubes which we used were obtained from Hanovia Chemical Co., Newark, N. J., and were made according to specifications shown in Fig. 2, at a cost of $7.80 each. Thin-walled tubes can be purchased at a much lower cost, but because of their fragility are not to be recommended.

[2] *Landw. Jahrb.* **38** (1909), 306.

boiling over as a result of violent action, and such devices as a water bath[1] under the generating flasks may be dispensed with. Using $N/10$ solutions for reduction and the Mitscherlich apparatus, extremely accurate results are obtained quite easily.

PROCEDURE RECOMMENDED—The procedure finally recommended for the determination of nitric nitrogen in soil extracts, which is to be designated as the Valmari-Mitscherlich-Devarda method, and which is regarded as the most reliable that has yet appeared, in that it combines the strong and eliminates the weak features of each, is as follows: Forty cc. of water, a small pinch of magnesia and one of magnesium sulfate are added to flask *D* of the Mitscherlich apparatus (Fig. 1). Twenty-five cc. of standard acid and 60 cc. of neutral redistilled water are placed in flask *F*. Two hundred and fifty or 300 cc. of aqueous soil extract are placed in a 500 cc. Kjeldahl flask, 2 cc. of 50 per cent sodium hydroxide added, the mouth of the flask closed with a small funnel to prevent spattering, and the contents of the flask boiled for 30 minutes. The water which has boiled off is replaced, and, after cooling, 1 g. of Devarda's alloy (60 mesh), and a small piece of paraffin are added and the flask connected with the apparatus; reduction and distillation are carried on for 40 minutes. The receiver contents are then cooled, 4 drops of 0.02 per cent solution of methyl red added, the excess acid is nearly neutralized, the liquid boiled to expel $CO_2$, cooled to 10–15° and the titration completed.

SUMMARY

I—A reduction method is considered to be preferable for the determination of nitric nitrogen in soil extracts. Of such procedures only the modified Devarda and aluminum reduction methods gave promise of meeting our requirements.

II—Reduction with Devarda's alloy in MgO solutions, and the aluminum reduction method, did not give reliable results in the presence of high organic matter.

III—Reduction with Devarda's alloy in strongly alkaline solutions renders separation of the organic and nitric forms of nitrogen almost impossible, requires a larger amount of alloy than does reduction in solutions $N/10$ in NaOH, and the reaction is so violent that care must be continually exercised to prevent a loss of the determination.

IV—Reduction with Devarda's alloy in solutions $N/10$ in NaOH gave reliable results in the presence of high organic matter. It requires a small amount of alloy, the reaction proceeds quietly, and the action of such dilute alkaline solutions on organic matter is very slight. Reduction in solutions $N/20$ in NaOH is unreliable in the presence of high organic matter.

V—The Mitscherlich apparatus is superior to the other distillation devices for the manipulation of the Devarda method.

VI—The method proposed, which combines the desirable features of the Valmari-Devarda and of the Mitscherlich-Devarda procedures, and which is to be designated as the Valmari-Mitscherlich-Devarda method, is the most accurate and reliable that has yet appeared for the determination of nitric nitrogen in soil extracts.

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[1] Used by W. S. Allen, *Loc. cit.*

## THE LOSS OF NITROGEN AND ORGANIC MATTER IN CULTIVATED KANSAS SOILS AND THE EFFECT OF THIS LOSS ON THE CROP-PRODUCING POWER OF THE SOIL[1]

By C. O. SWANSON

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The decrease in the crop-producing power of the soil is a fact familiar to all students of agricultural problems. The larger productiveness of virgin soils as compared with the productiveness of these same soils after they have been under cultivation for several decades is well known by the men who broke up the virgin prairie sod and have continued to cultivate that soil for half a lifetime or more. If we make a study of the figures compiled by the State Board of Agriculture for the forty-year period, 1872–1911, we shall find that the leading crops show an average decrease in crop production. In Brown County the average corn production for the first twenty-year period, 1872–1891, was 36 bu., and for the second twenty-year period, 1892–1911, was 30 bu. Riley County produced an average of 33 bu. in the first period, and 25 bu. in the second. In Sedgwick County, the first period shows an average of 32 bu., and the second 21 bu. "More live stock" is mentioned by some people as the panacea for this soil. If that by *itself* were the cure, then a typical live stock county, where more grain is fed than raised, should not show this decrease in crop production. Butler is such a county. In the period between 1872 and 1891, the average corn production was 32 bu. per acre, and in the second period, 1892–1911, the average was 26 bu. It is not necessary to give more figures to prove this fact. Any one who makes a study of the figures compiled by the State Board of Agriculture will find that there is an average decrease in crop production and that this is true in Butler, Greenwood and Chase, typical live stock counties, as well as Brown, Sedgwick and Russell, where the type is called grain farming.

Seeds adapted to climate and soil is an important factor in crop production. Seed improvement may not have made all the progress promoters of agriculture desire, but that the seed used by farmers in general is more adapted to the climate and soil than the seed used thirty or forty years ago no student of agriculture will deny. Instruments of tillage have also been improved. The better the soil is cultivated, other things being equal, the greater its crop-producing power. In spite of these two factors which should have increased the average crop production per acre, we have a decrease.

The Chemical Department of the Agricultural Experiment Station has made a chemical analysis of about 250 samples of Kansas soil taken from thirteen different counties. These samples are analyzed for total nitrogen, phosphorus, potassium, calcium, or-

[1] Read before the Kansas Academy of Science, December 22, 1914.

ganic and inorganic carbon. Studies in physiological botany have shown that plants also require iron, magnesium and sulfur from the soil. But agricultural experience as well as chemical analysis of soils has shown that soils are well supplied with these elements and for that reason they are not included in our chemical analysis.

A study of the figures obtained in the chemical analysis of these Kansas soils shows that the elements nitrogen and carbon have disappeared from cultivated soils in proportionately larger quantities than the other essential elements. The opportunity for making this comparison does not always present itself. Generally a sample is taken to represent a soil type. If the field which best represents this type is in cultivation, it may not be possible to get a sample of the same soil type from a native meadow or pasture. A few such opportunities have presented themselves, and the data obtained in the analysis of such samples form the basis of the discussion in this paper.

The soil sample is taken in three strata: surface (0–7 in.), subsurface (7–20 in.), and subsoil (20–40 in.). Both nitrogen and carbon occur to a greater per cent in the surface stratum. They are a part of the organic matter or that portion of the soil which has come from decomposed plant substances. The carbon is assumed to constitute half of the organic matter. The ratio of nitrogen to carbon is about 1 to 11. An acre of soil 7 in. deep is assumed to weigh 2,000,000 lbs. If the percentage composition is known, the amount of any element per acre can be computed. The amount of carbon is multiplied by two to represent the organic matter.

In the accompanying table are given the pounds of nitrogen and organic matter per acre in the surface soil. These data are obtained from figures published in *Bull.* **199,** Kansas Experiment Station, and from unpublished data on file in the Department of Chemistry. Data for samples of the same type taken as close together as possible have been selected for comparison. In several cases, the sample of the cultivated soil and the uncultivated soil were taken only a few rods apart. In cases where no sample of the cultivated soil is directly comparable with the uncultivated soil on account of location and known history, the average of several cultivated soils is used. This makes a fair comparison.

It is true that occasionally a sample from a cultivated field shows a higher percentage of nitrogen and organic matter than a sample from the same type in a virgin field. Such cases are noticed in the report of the soils of Shawnee County, published in *Bull.* **200,** Kansas Experiment Station. In these cases the cultivated soil has received special care and the uncultivated soil represents a very poor phase of the type.

From the original data presented in Table I, the figures in Table II are calculated. "The pounds loss of nitrogen" is the difference between the amount of nitrogen in the virgin soil and that in the cultivated soil. This difference varies from 1200 to 1800 lbs. per acre. Soil sample 1032 from Greenwood County was taken from a field which had been cultivated to

TABLE I

| County | Soil Type | Soil No. | Description | Lbs per Acre N | Org. matter |
|---|---|---|---|---|---|
| Riley | Oswego silt loam | 1024 | Native meadow | 4980 | 122,400 |
| | | 1023 | Continuous grain cropping about 30 years (wheat and corn) | 3700 | 85,600 |
| Brown | Marshall silt loam | 1052 | Native meadow | 5480 | 139,200 |
| | | .... | Average of 6 cultivated soils, the highest nitrogen 4560, and organic matter 111,600 | | |
| | | | Rotation of corn, oats, clover and wheat | 4240 | 106,800 |
| Russell | Sedgwick clay loam | 1037 | Native buffalo grass, in pasture | 4260 | 98,400 |
| | | 1036 | 30 yrs. continuous wheat growing | 2960 | 64,400 |
| Allen | Oswego fine sandy loam | 1093 | Native meadow | 3760 | 83,600 |
| | | 1094 | Cultivated (corn and broom corn) | 2440 | 46,400 |
| Butler | Sedgwick clay loam | 1127 | Native pasture | 4280 | 106,400 |
| | | 1128 | Cultivated (corn and forage crops) | 2800 | 66,800 |
| Greenwood | Osage silty clay loam | 1031 | Native meadow | 4600 | 113,600 |
| | | 1032 | Corn 30 years | 3400 | 73,200 |
| | | 1219 | Old timber land, 12 years in corn | 4800 | 112,400 |
| Greenwood | Osage silty clay loam | 1258 | Corn and forage crops | 3600 | 76,400 |
| | | 1034 | Catalpa grove | 5200 | 126,000 |
| Greenwood | Summit silty clay loam | | Average of 5 cultivated samples, the highest nitrogen 4200, and organic matter 90,000. Corn and forage crops | 3400 | 76,400 |
| Reno | Reno loam | 1071 | Native pasture | 3400 | 74,800 |
| | | | Average of 3 cultivated soils cultivated mostly to wheat | 1920 | 36,400 |

corn for thirty years. The comparison sample of uncultivated soil was taken from a native meadow, a few rods away. Sample 1034, Greenwood County, taken in a catalpa grove, shows a higher content of nitrogen and organic matter than any of the virgin soils, except soil sample 1052, taken in a native meadow in Brown County. That indicates that as far as this comparison goes, the soil in the catalpa grove shows no tendency towards depletion of nitrogen or organic matter. The sample of soil taken in a field cultivated to corn and forage crops next to the catalpa grove, showed a nitrogen content of 3700 and organic matter to the extent of 89,200 lbs. per acre in the surface soil, or a difference of 1,500 lbs. nitrogen and 36,800 lbs. organic matter in favor of the soil in the catalpa grove.

TABLE II

| County | Soil | Pounds Loss Per Cent Loss: N | Org. matter | N | Org. matter | Per cent N in org. matter | Ratio of N and C in organic matter |
|---|---|---|---|---|---|---|---|
| Riley | Native | | | | | 4.07 | 1 : 12.2 |
| Riley | Cultivated | 1280 | 36800 | 25.7 | 30.7 | 4.32 | 1 : 11.6 |
| Brown | Native | | | | | 3.93 | 1 : 12.7 |
| Brown | Cultivated | 1240 | 32400 | 22.6 | 23.3 | 3.97 | 1 : 12.6 |
| Russell | Native | | | | | 4.33 | 1 : 11.5 |
| Russell | Cultivated | 1300 | 34000 | 30.5 | 34.5 | 4.60 | 1 : 10.7 |
| Allen | Native | | | | | 4.50 | 1 : 11.0 |
| Allen | Cultivated | 1320 | 37200 | 35.1 | 44.5 | 5.26 | 1 : 9.5 |
| Butler | Native | | | | | 4.02 | 1 : 12.7 |
| Butler | Cultivated | 1480 | 39600 | 34.5 | 37.2 | 4.19 | 1 : 11.9 |
| Greenwood | Native | | | | | 4.05 | 1 : 12.3 |
| Greenwood | Cultivated | 1200 | 40400 | 26.1 | 35.6 | 4.64 | 1 : 10.8 |
| Greenwood | Native | | | | | 4.27 | 1 : 11.7 |
| Greenwood | Cultivated | 1200 | 36000 | 25.0 | 32.0 | 4.71 | 1 : 10.6 |
| Greenwood | Native | | | | | 4.13 | 1 : 12.1 |
| Greenwood | Cultivated | 1800 | 49600 | 34.6 | 40.0 | 4.48 | 1 : 11.2 |
| Reno | Native | | | | | 4.55 | 1 : 11 |
| Reno | Cultivated | 1480 | 38400 | 43.5 | 51.3 | 5.28 | 1 : 9.5 |

What does the loss of 1200 lbs. of nitrogen from the surface soil of an acre of land mean? To produce one bushel of corn the soil must furnish 1 lb. of nitrogen for the grain and $^1/_2$ lb. for the stalks and cobs. The 1200 lbs. of nitrogen represent the amount needed to produce 800 bu. of corn, stalks and grain, or $26^2/_3$ bu. per acre for 30 years, assuming that everything is removed from the land and that no nitrogen is lost in the drainage water. Such farming practice would be possible only with virgin soils well stocked with nitrogen and organic matter. Crops use a certain per cent of the nitrogen in the soil and for that reason

complete soil exhaustion is impossible. But soils are considered exhausted when the total amount of plant food possible for the crop to obtain is less than is required to produce a profitable crop. If a soil has been cultivated for thirty years to corn and has produced an average of 26 bu. per acre during this time, it will not be possible to produce this amount of corn in the next thirty years with the same method of farming practice. It is a common observation of farmers that it takes more work than formerly to produce crops. Cultivation is one of the means of producing usable plant food. In new soils that plant food which is most easily made usable is transformed first. When this has been used up the first flush of abundant crop production passes and more work is required by the farmer.

In the third and fourth columns of Table II are shown the percentage losses of nitrogen and organic matter. The per cent loss of nitrogen varies from 22.6 per cent in sample from Brown County to 43.5 per cent in the samples from Reno County. The next greatest losses are found in the samples from Butler and Greenwood Counties, where according to the popular conception the farmers have the means of conserving soil fertility. Brown County shows the smallest loss and in this part of the state proper systems of crop rotations have been used more. The per cent loss of organic matter varies from 23.3 in the Brown County samples to 51.3 in the Reno County samples. In every case the percentage loss of organic matter is greater than the percentage loss of nitrogen. These figures show that the cultivated soils of Kansas have lost on the average more than one-third of their original stock of organic matter. The seriousness of this situation cannot be overemphasized. While these figures show the percentage of total loss, they do not tell anything about the quality of organic matter lost. This fact will be discussed later.

In the fifth column of Table II is found the per cent of nitrogen in organic matter. In every case the per cent of nitrogen is greater in the cultivated soils than in the virgin soils. Chemically, carbon is the more active element. As organic matter becomes old it becomes more inert. The chemical changes are slower and the response of the soil is more sluggish.

Column six gives the ratio of nitrogen to carbon in organic matter. The widest ratio is found in virgin soils and the narrowest in the cultivated soils. The average of the native soils is 1 : 12 and of the cultivated soils, 1 : 11.1. What is the significance of this ratio?

E. J. Russel states in his book "Soil Conditions and Plant Growth," that the ratio between nitrogen and carbon in stubble is 1 : 40 and in legumes 1 : 25. Most of the organic matter in Kansas soils has come from the prairie grass. A number of samples of prairie hay analyzed at the Chemical Department of the Experiment Station have shown an average nitrogen content of 0.85 per cent. This is a very low nitrogen content and would compare very well with the stubble to which Russel refers. As there are some native legumes this would influence the ratio. Taking the ratio of nitrogen to carbon in the native vegetation as 1 : 36 would not be an unfair assumption. If the ratio of nitrogen to carbon in virgin soil is 1 : 12, it means that it would have taken three pounds of native vegetation for each pound of organic matter found in the soil, provided there had been no loss of nitrogen in the process of transforming the native vegetation into such organic matter as is found in the soil. But it does not require any extensive study of the organic chemical changes which go on in the soil to know that great losses do occur.

This discussion is made for the purpose of showing the enormous amount of native vegetation required to produce the organic matter in the soil, and in this discussion we leave out that present below the surface soil and this in the aggregate would amount to about twice that in the surface soil. Most of the native prairie soils in Kansas contain over 100,000 lbs., or 50 tons of organic matter in the surface soil of one acre 7 in. deep. On the basis of the above discussion, which is founded on chemical facts with the estimate less than what is known to actually take place, it has taken more than 150 tons of native vegetation to produce the organic matter found in our native prairie soils. If, then, over one-third of this organic matter had been lost from our soils after less than fifty years of cultivation, it makes the thoughtful man stop and consider.

Organic matter is the life of the soil. Organic matter is of very little value in the soil unless it is undergoing chemical changes. This chemical change cannot take place without loss in the amount of organic matter. When organic matter decays it forms a number of substances and many of these are indispensable for the proper functioning of the soil. It is these chemical changes which narrow the ratio between nitrogen and carbon and cause the consequent loss of the amount of organic matter. The loss of organic matter is not of itself an evil. Unless it does take place, the soil will not be fertile. In nature the raw materials for these transformations are supplied. The evil consequences follow when man upsets the order of nature and fails to supply the raw materials which are used up.

There are seven of nature's essentials for profitable crop production; namely, good seed, proper amount of light, suitable temperature, proper physical and biological conditions of the soil, an adequate amount of moisture, and plant food. The organic matter of the soil is directly connected with and influences all these conditions except seed and light.

The dark color of the soil is due to organic matter, and dark-colored soils warm up faster than those of lighter color. Soils well stocked with humus drain better, and well drained soils are warmer than wet soils. The organic matter increases the water-holding capacity of sandy soils and prevents the sand from washing and blowing. The organic matter gives clay and silt soils a better structure resulting in better tillage and drainage properties. Organic matter furnishes food for the countless microörganisms in the soil; without these, plant food cannot be prepared. The chemical

reactions directly associated with and due to organic matter are the greatest agencies in the soil for making usable plant food from the materials stored up in the rock powder which makes up the great portion of the soil.

Farmers in many parts of the state are complaining of the development of gumbo spots in their fields. The majority of such spots, observed by the writer, are due to the loss of the original surface soil, either through soil blowing or soil washing. Where listing is done up and down the slopes it does not take many years to remove the original surface soil. In the drier parts of the state, blowing will accomplish the same result. The evil of soil blowing increases with the disappearance of organic matter in the soil. The organic matter causes the fine soil particles to adhere together in larger aggregates called soil grains, and these are not moved by the wind. When the organic matter is used up, these soil grains are reduced to dust which blows easily. Soil washing does not take place where the soil is open so that the water is soaked up by the soil. Organic matter gives clay and silt soils an open structure which enables the water to enter the soil; besides, it binds the fine clay particles together so that they are less easily moved by water in motion.

Agricultural writers and speakers have a great deal to say about the evil of depleting soil fertility by the system of grain farming, and more live stock is urged as a remedy. As a matter of fact, one system is not to blame altogether and the other system will not necessarily offer the remedy. If the farmers of Barton County deplete their soil fertility and particularly organic matter by exclusive wheat farming and straw burning, and the farmers of Butler County continually harvest forage crops from their cultivated fields and feed these forage crops as well as imported grain on the banks of a ravine, there is no difference between these systems as far as they affect soil fertility.

The ultimate purpose of farming is to produce substances which can be used for human food, clothing and shelter. Forestry rightly practiced does not deplete soil fertility. The cotton lint does not deplete the organic matter and soil fertility. The depletion is due to the removal of the cottonseed together with the rest of the plant. The amount of fertility removed in the animal carcass used as human food is comparatively small and can be easily restored. Four-fifths of the element phosphorus, one of the limiting elements in soil fertility, goes into the bran and shorts when flour is manufactured for human food. The small amount removed in flour can easily be restored to the soil. Wheat farming depletes soil fertility because straw is burned or wasted and bran and shorts are exported. Because dairy farming exports only such substances as can be used directly as human food, it keeps up the organic matter of the soil better than many other systems of farming.

The discussion in this paper has shown that it has taken more than 150 tons of native vegetation to produce the organic matter in the surface soil. If we accept this very conservative assumption and also know that one-third of the organic matter present in the virgin soils has been lost in less than fifty years of farming, it means that the least amount of organic matter necessary to return to the soil every year is one ton per acre in addition to what is now returned in stubble and cornstalks.

In addition to returning such substances as straw and farm manures, some substance must be added which restores the nitrogen removed in grain. A bushel of corn takes 1 lb. of nitrogen, and a bushel of wheat $1^1/_3$ lbs. The best means of obtaining this nitrogen is by growing legumes such as alfalfa. But this nitrogen will not be restored to the soil if all the hay is exported from the farms. Some of the best agricultural investigators are of the opinion, based on scientific experimentation, that legumes on the average take only as much nitrogen from the air as is found in the hay. The growing of alfalfa, if grown for export, will not solve the problem of soil fertility any more than live stock farming when the fertility is wasted on the banks of a ravine.

In all our discussions of problems of soil fertility we must not forget the peculiarity of the Kansas climate. We shall never be able to practice such a hand to mouth system as is possible in a climate of greater and more even rainfall. The soils must have a greater resistance against both excessive wet weather and dry weather. This resistance depends more on the content of organic matter than on any other factor. We have seen the enormous amount of native vegetation it has taken to produce this organic matter, and the very large loss in less than fifty years of farming. This enormous loss of organic matter is the most serious problem in soil fertility in the state of Kansas.

## SUMMARY

1—The soils of Kansas show an average decrease in crop-producing power in spite of the fact that farmers use seed which is better adapted to climate and soil, and improved methods of tillage.

2—Results based on chemical analysis of cultivated and uncultivated soils in seven representative counties show that the elements carbon and nitrogen have disappeared from the cultivated soils to the largest extent. These cultivated soils have lost from 1200 to 1800 pounds of nitrogen, and from 32,400 to 49,600 pounds of organic matter per acre in the surface soil. On a percentage basis this amounts to from 22.6 to 43.5 per cent of the nitrogen, and from 23.3 to 51.3 per cent of the organic matter. It means that these soils have lost in round numbers from one-fifth to two-fifths of the nitrogen, and from nearly one-fourth to one-half of the organic matter.

3—Decay of organic matter is the life of the soil. A comparison between the ratio of nitrogen and carbon in vegetable matter and in the organic matter of the soil shows the enormous amount of vegetable matter it has required to produce the organic matter in the soil. The loss of one-third of this organic matter together with the accompanying nitrogen loss is the most important cause of the decreased crop-producing power of the soil.

KANSAS STATE AGRICULTURAL COLLEGE, MANHATTAN

# LABORATORY AND PLANT

## PROTEIN CHARTS

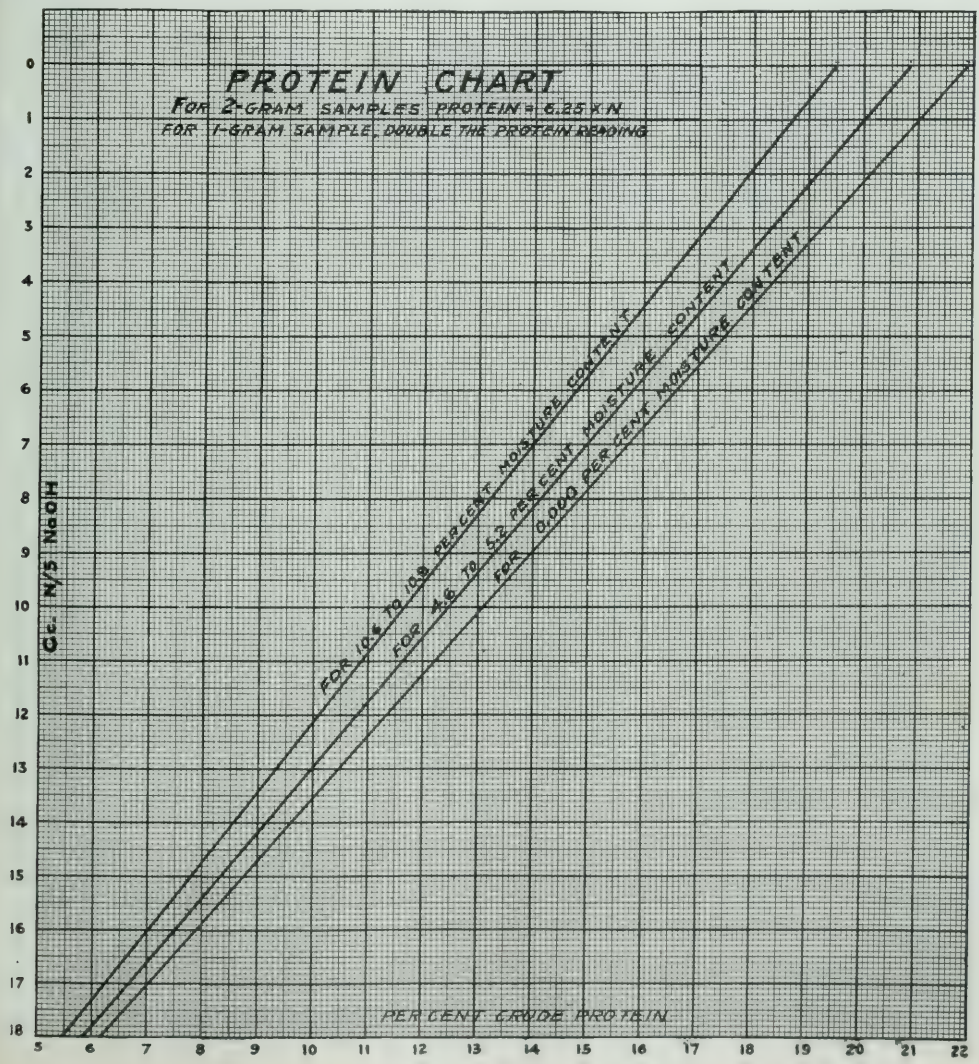
By Alexander Silverman

Received February 26, 1915

Thousands of crude protein determinations have been made in the writer's laboratory during the past four or five years, so it is natural that every possible effort should have been made to economize time. Assistants who coöperated with the writer made suggestions from time to time but the first charts were prepared by Mr. Frank D. Shumaker, who plotted the acid readings as ordinates. Subsequently, Mr. William G. Haynes revised the charts, using alkali values as ordinates and preparing curves for all moisture percentages encountered in the cattle feeds analyzed.

Some twelve to fifteen charts are in use but the writer has had only three of the curves plotted; these have been put on one sheet, owing to the limited space here available. Of substances having a protein content up to 20 per cent. a 2 g. sample is taken for analysis; for higher values, a 1 g. sample. The maximum encountered in feeds and raw materials used therein was about 43 per cent.

Ammonia is distilled over into 25 cc. $N/5$ acid and



the excess titrated with equivalent alkali. The alkali reading is then looked up on the ordinate of the chart prepared for the feed of the particular moisture content found, and the crude protein reading made on the abscissa.

The charts are presented for the purpose of lightening the labors of other chemists doing similar work, and to suggest this simple method for calculating results, as an entire set of charts can be prepared in a very short time.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH

## GAS-WASHING APPARATUS WITH ENCLOSED FILTER[1]

By E. R. WEAVER AND J. D. EDWARDS

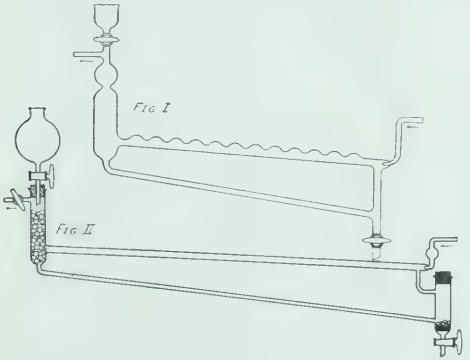
Received February 15, 1915

The three forms of gas-washing apparatus illustrated, although involving no new principles, are believed to be somewhat novel in form and they have given such satisfactory service that a description of them may be of interest to other chemists, especially as showing the arrangement of the parts for various uses.[2]

Two of the forms permit a filter to be placed within the apparatus by means of which a precipitate may be separated and washed without exposure to the air. This feature, in a simple and efficient gas wash bottle, is believed to be new and has been found useful for various purposes.

All of the forms illustrated possess the following advantages:

1—They give thorough washing by keeping the gas in contact with the liquid for a long time and yet they require but a comparatively small pressure for their operation.

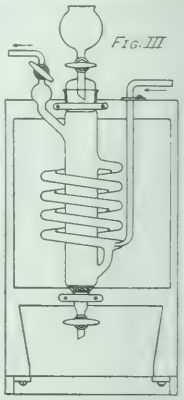



2—They provide very efficient circulation of the absorbing liquid, which prevents the saturation of one portion of the liquid while another portion remains unsaturated.

3—They can be filled or emptied without disconnecting, and, indeed while in use if the tube for introducing the reagent is arranged as shown in Figs. II and III.

The apparatus illustrated in Fig. I is designed to thoroughly wash a stream of gas with a minimum amount of liquid and with the lowest possible operating pressure. The series of bulbs blown along the top of the absorption tube aid the absorption by prolonging the time of contact between gas and reagent, but do not prevent the apparatus from draining completely. The construction is so simple that the apparatus may be readily made up from glass tubing.

Fig. II illustrates a simple washing apparatus designed for the precipitation and determination of acetylene or carbon dioxide, the precipitate being filtered off and washed without exposure to the air. A Witt plate and asbestos filter at the drain cock are covered with a layer of glass beads or another Witt plate to prevent the filter being loosened by the circulation of the liquid. The beads near the outlet serve to break up the gas bubbles and prevent loss of liquid, as well as furnish additional surface. When the absorption is complete, the stopcock on the outlet is closed, the stopcock below the filter opened, and the filtration allowed to proceed under the pressure of the inflowing gas; suction can be used if desired. Washing is accomplished by introducing wash water through the funnel tube near the gas outlet, the liquid being forced through the filter by gas pressure as before. A straight absorption tube is used instead of the bulb tube shown in Fig. I because of the difficulty of washing a precipitate clinging to the bulbs.




A helical wash bottle, Fig. III, is the same in principle and operation as No. II but has been designed with a view to economy of space. This apparatus is very compact and efficient, giving as complete absorption as several ordinary wash bottles in series, while requiring only a small fraction of the pressure necessary to operate the latter. With gas flowing at the rate of 100 cc. per minute the bubbles remain in the helix about seven seconds. Bubbles passing at the rate of one or two per second remain in the tube nearly twenty seconds. Gas passed at the rate of 500 cc. per minute is still broken into fairly small bubbles and receives a very thorough washing, but if the gas is to be passed at a more rapid rate than this the helix should be made of tubing of larger diameter. This form of apparatus is much easier to make than, and quite as efficient as some of the more elaborate apparatus on the market in which the gas bubbles follow a helical path. It possesses the additional advantage of permitting the filtration and washing of a precipitate within the apparatus without exposure to the air.

For satisfactory operation, it is necessary that the diameter of the absorption tube in all three forms be properly proportioned to the rate of gas passage. This tube should not be made too small. A tube

[1] Published by permission of the Director, Bureau of Standards.

[2] See also Cumming, *Chem. News*, **101** (1910), 39; J. D. Edwards, THIS JOURNAL, **6** (1914), 468; Purves (Gray's apparatus), *Gas World*, **60** (1914), 897.

with an internal diameter of 8 to 10 mm. was found to work very satisfactorily at rates of less than 500 cc. per minute. The tip of the inlet tube has an internal diameter of 1 to 2 mm. The size of the other parts of the apparatus will depend primarily on the amount of reagent, and the duration of contact between gas and reagent, which is desired.

BUREAU OF STANDARDS, WASHINGTON, D. C

# ADDRESSES

## SOME PROBLEMS OF CHEMICAL INDUSTRY[1]

By RAYMOND F. BACON[2]

The industrial researcher, who deals with the processes of manufacture and the phenomena of reactions involved, is becoming less and less regarded as a burden unwarranted by returns. The aim of every industrial operation is toward perfection, both in process and the necessary mechanical equipment, and every new development in manufacturing creates new problems. It follows, then, that the greater the number of researches, the greater is the progress in a given field, and the greater becomes the number of new problems. Moreover, one can only conclude that, since perfection is but, after all, an ideal, no industrial field has been sufficiently investigated.

The thirst for distinction and wealth kindles the lamp of invention, and the light of the knowledge resulting from discoveries and improvements in manufacturing operations has so emboldened us that some industries now consider themselves capable of solving any problem. This has been shown in innumerable instances, but is particularly true of the great chemical industry, which, while its achievements have been stupendous, is nevertheless confronted with many problems of importance. With your permission, I shall restrict myself to recounting some of the problems which engage the attention of the present-day chemical industrialist—problems which he is capable of clearing up, provided the service of research is called to his aid, but which have so far remained unsolved. In collating these I have drawn from all available resources of information and from my own experience.

### SOME METALLURGICAL PROBLEMS OF TODAY

While there may not be at the present time room for such abnormal discoveries in siderurgy as in the past, investigators are quietly and steadily augmenting our knowledge of iron and its alloys, and the value of such research work is generally recognized. Elaborate investigations are constantly being conducted by several manufacturers, especially by the United States Steel Corporation, which has to date expended over $800,000 in studies on the electrothermic production of steel alone. However, metallurgical research laboratories are still comparatively uncommon. Very few iron furnaces or smelting plants are without a control laboratory, which has come about notwithstanding the opposition of "practical men," and the research laboratory will eventually win a similar victory. Such problems as the working-up of blast furnace slags by an economic process could probably be solved by systematic research.

The great problems at present in the metallurgy of zinc are in concentration of the ore and in the treatment of flotation concentrate. The latter produces the troubles that fine ore always does; it is difficult to roast, and the distillation of it is attended with troubles. Viewing the present status of the practice in zinc smelting, one is impressed by the high extraction results, the low fuel consumption made possible by regenerative gas-firing, and the reduction of labor involved in the art.

In copper metallurgy, the leaching of copper ores and electrolytic deposition for precipitating are receiving increased attention. With regard to chemical precipitation, it is desirable that this process be conducted in such a way as to regenerate the solution. In electrolytic copper refining, promising progress has been made in the treatment of anode slimes, and increasing attention is being paid to the recovery of by-products. Then, too, the progress in the development of flotation processes has been phenomenal, but still our knowledge regarding flotation is meager.

The search for platinum substitutes continues, and an economic method for rapidly separating the metals of the platinum group is also desired.

The brass industry has been carried on for more than a century in Connecticut and considerable study has been given the matter of zinc loss, but so far ones engaged in the industry have been unable to find any economic and entirely satisfactory method to overcome such loss. Moreover, no entirely satisfactory gas furnace has been designed for general brass rolling mill practice.

The development in engineering construction has arrived at a point where the use of special alloys for specific requirements requires more thorough investigation. The matter of corrosion has been one of a more or less mysterious nature; confusion has arisen on account of the names of alloys; the ideal alloy for condenser tubes has not been found; the failures of screens made from brass wire are well known, and we have yet to find an aluminum alloy that will resist alkalies. It is true that there is beginning to be a well-defined literature on the subject of alloys and that now one can sometimes very closely predict the properties of combinations of the more commonly known metals; but we have not begun to open up the possibilities of usefulness in the exploration of the alloy field, in which I include the so-called "dilute alloys"—cases wherein a very small amount of a metal alloyed with, say, iron or steel confers upon it some new or unusual properties.

### SOME PROBLEMS OF INDUSTRIAL INORGANIC CHEMISTRY

Nitrous oxide is being successfully used in combination with oxygen for the production of anesthesia; but while there is a material available for the production of oxygen upon treatment with water ("oxone"), no substance which will yield nitrous oxide upon similar treatment is known. On account of the present large consumption of nitrous oxide, considerable study has been devoted to this problem.

New uses, ones such as would increase the demand, for the following products are required: Potassium hydroxide, chlorine, bleaching powder, bromine and bromides, calcium, silicon, selenium, tellurium, cobalt, uranium and molybdenum. Since sodium metantimonate is undesirable in enamels placed on cooking utensils, new uses for this and other antimony compounds are needed; attention may be directed to the fact that antimony lithopones, made by treating barium carbonate and antimony sulfite, offer, perhaps, a partial solution of this problem. It may be noted here that a large production of arsenic would follow a demand.

In the domain of ceramics, the subject of binders presents a field for research; to cite a simple instance, a binder for infusorial earth that is cheap and will stand a temperature of about 3,000° F. is being sought for by ones interested in the production of metallurgical brick.

Efforts to improve the quality of all varieties of clay goods, from ordinary brick to the highest-grade pottery, are constantly in progress by American clay-workers; this is evinced by the new

[1] Author's abstract of an address delivered before the Chicago Section of the American Chemical Society on May 14, 1915. In Dr. Bacon's absence, this address was presented by Dr. S. R. Scholes, Assistant Director of the Mellon Institute.

[2] Director of the Mellon Institute of Industrial Research and School of Specific Industries of the University of Pittsburgh

shades and texture of building brick, the new forms of hollow building tile or block, and the new effects in terra cotta that are being put on the market, and by a general improvement in the higher grades of pottery. Of interest in this connection is the realization of the value of American clays in glass-pot manufacture. Earthenware kilns designed in such a manner as to reduce the carrying of heavy weights, to do away with working in hot kilns, and to diminish the handling of dipped ware, would be very desirable, and some progress in tunnel kilns of this general type has been made in England.

It has been said that the technology of common earthenware, Rockingham ware, majolica, faience, and stoneware is comparatively simple; this is undoubtedly correct, viewing the pottery industry as it exists today, but it is also true that less advantage has been taken of scientific research in earthenware manufacture than in many other industries. A familiar problem is the nature of clay plasticity, which is quite open for study; the flowage behavior under pressure promises to be of value in this work.

There are many problems to be found in the glass industry; for example, the available results relating to the problem of strains in glass merely represent a beginning of the work necessary to a complete solution. However, the troubles of the glass manufacturer would vanish if the chemical constitution of glass were definitely determined, and if the ideal non-contaminating container (pot and tank) were found. A great problem in the glass industry is the better utilization of heat; only 5 per cent is actually utilized in making glass.

In the tinning industry electro-tinning has recently made important progress, although as yet no marked commercial success has been attained; and a beginning has been made toward coating black plates with aluminum by a cold, wet, electric process. Among the problems worthy of investigation in connection with the tinplate industry are the following:

1—Over and under black pickling, the influence of strength and temperature of the acid solution, and of time. Mention may be made here that the utilization of spent ferrous liquor obtained in pickling iron or steel, is receiving more and more attention.[1] Perhaps the acid and a paint pigment could be recovered from waste hydrochloric acid pickle liquor by a simple heat treatment in a suitable apparatus.

2—Effect of varying temperatures and time of annealing.

3—Light and heavy cold rolling.

4—Temperature effects in the tinning operations.

5—Differences from the tinplate-trade point of view between acid Bessemer steel, basic Bessemer steel, acid open-hearth steel, and basic open-hearth steel, and the comparative tin consumption of each kind.

Since the mantle industry cannot absorb more thorium (about 300 tons of thorium nitrate are consumed annually), and much larger quantities of mesothorium than 6 grams (present available supply, under normal conditions, from 3300 tons of monazite sand) will probably be required for therapeutic purposes, the extraction of larger quantities of mesothorium depends upon profitable utilization of cerium (over 1,000 tons of ceria are obtained annually in the mantle industry, and only 3 tons are required in the manufacture of mantles). Of 1,000 tons of ceria, 200 tons are normally used in the manufacture of pyrophoric alloys, 300 tons are used in the form of fluoride for impregnating arc-light carbons, and the dyeing and photographic industries take small amounts. New uses are consequently wanted for cerium compounds, which might be used, for instance, in the weighting of silk.

Chemistry is a very important factor, indeed, in the fertilizer industry, and it will, of course, carry out the work ahead. Some of the problems are:

1—Rendering available the phosphoric acid in refractory minerals by, say, electrochemical means of a suitable nature.

2—Recovery by economical processes of potash from feldspar, alunite, leucite, and beet-sugar molasses. In the case of the production from minerals, the cost of treating feldspars has so far been prohibitive; electrothermic processes will undoubtedly be eventually used. It may also be possible to recover thus the potash contained in the raw materials used in the cement industry, and some progress has, in fact, been made in the solution of this problem. My own opinion is that the successful potash recovery process will be one in which the principal product will be one other than potash and the latter will be a by-product.

### SOME PROBLEMS OF INDUSTRIAL ORGANIC CHEMISTRY

In the wood distillation industry, new uses, immune from the competition of denatured alcohol, are anxiously desired for methyl alcohol. A more rational utilization of wood-tar is also essential for the future of this industry; there is no reason why valuable by-products other than creosote and shingle stains might not be obtained from hardwood tar. In this connection an economic (direct, if possible) process for manufacturing acetaldehyde (for use as an acetylene solvent) from acetate of lime, would undoubtedly attract the producers of the latter, as would also important new uses for acetone. It is rather surprising that the manufacture of acetic acid from acetate of lime has been neglected in the United States. Hardwoods abound on the Pacific coast and can be distilled with profit, providing markets for the charcoal and calcium acetate can be created.

Commercially operable processes for the manufacture of charcoal, cellulose, gas, glucose, or ethyl alcohol from wood waste, are occasionally inquired for. A number of methods have been devised, but economies must be developed.

It may be mentioned in this place that pinene has been shown to be the chief source of isoprene in turpentine. A process for economically increasing the yield of pinene in the distillation of long-leaf pine, would possess commercial value, both from a synthetic rubber and from a turpentine standpoint.

There are many chemical problems in paper making. What, for instance, is the influence of chemicals on the "beating" process? The bleaching problem has also been very little studied; it is unknown, for example, what is the exact nature of the substances removed from the pulp by bleaching or in what form they are eliminated. Then, too, the problem of sizing is full of unsolved points; the fixation of the loading materials is a physico-chemical problem which should repay systematic investigation, and the question of new sizing agents awaits solution. Other of the many problems are the following: What are the chemical causes of the loss of resistance to ink after storage, particularly in the case of engine-sized paper? What are the chemical relations of the dyestuff towards the mineral loading materials in pulp-dyeing?[1] And then there is the problem of the clarification of the machine waste waters and the recovery of by-products therefrom. In spite of the fact that a tremendous amount of work has been done on the problem of the waste liquor from sulfite pulp mills, it still remains for the most part unsolved.

On account of the war, now would be a most opportune time to lay the foundation for an artificial silk industry in this country.

The manufacturers of the chlorides of carbon would be interested in new commercial uses for carbon tetrachloride, dichlormethane, and hexachlorethane. An economic commercial process for chlorinating natural gas rich in methane would be

[1] Of a similar nature is the problem of the economic utilization of mine water, which resolves itself into the ascertainment of either (1) a cheap process of precipitating the dissolved matter, including any free acid, or (2) a suitable process for purifying the water.

[1] Three theories have been advanced to account for the fixing of dyes by fillers. Results favor the absorption theories of Feiet and Rohland rather than the chemical combination theory of Suida, but discrepancies have been observed in all cases

attractive; a number of such processes have been worked out, but apparently these leave something to be desired.

Among other problems awaiting technical solution are: the production of oxalic acid by the electrolytic oxidation of cellulose; the production of acetaldehyde and acetic acid from acetylene; the device of ways and means to use the lower grades of gasoline in internal combustion motors; an economic process for removing resin from fir and other wood in pulp making; the production of permanent light shades on glove leather; more efficient processes for depilating, disinfecting, deliming, softening, and waterproofing skins and hides, and for brightening tanned skins; and the utilization of the fibrous wastes in several industries, especially the million bushels of envelopes decorticated from buckwheat annually. Novel processes for the refining or bleaching of vegetable oils, especially of cottonseed and soy-bean oils, always interest the refiners of these. And finally it may be mentioned here that the wine growers of California and New York now have the opportunity to produce argol, and thus begin the manufacture of tartaric acid.

As instances of some desirable commercial syntheses, mention may be made of the fact that processes are wanted for the synthesis of acetylene, formaldehyde, amyl alcohol, tartaric and citric acids, sanguinarine, hydrastine, and nicotine.

In the explosives industry, the manufacturers of nitroglycerine hope that in synthetic glycol may be found the solution of their bondage to the fluctuation of the corn and cottonseed crops. The production of glycerine depends considerably on the abundance or otherwise of pork and of cottonseed oil, and the former depends largely on the corn supply.

In depolymerizing heavy hydrocarbon oils, hydrogenation with platinum black could be accomplished if an antidote could be found for the poisonous effect of sulfur compounds. Oil refiners are endeavoring to find methods to convert every pound of gas oil into more valuable products, especially motor fuel.[1] Through the application of physicochemical principles to the "cracking" of oil, a better control of and greater flexibility in the resultant end products can be expected. This means that if gas manufacturers are to continue the use of petroleum in carbureting water gas, they must resort to one of two alternatives:

1—Greatly increase the yield of gaseous hydrocarbons from a given amount of oil; or

2—Perfect methods of using the millions of barrels of fuel oil which are at present considered unfit for carbureting water gas.

Much also remains to be done in the field of concentration, pressure and contact-surface changes with respect to illuminating and heating gas.

Sugar manufacturers do not work up their by-products; for example, they do not can molasses or manufacture alcohol from it. Molasses is a suitable source of alcohol; the by-products are yeast, fusel oil, and carbon dioxide. There is little coöperation among sugar manufacturers to improve methods. No limits have been scientifically set for moisture content and degree of infection of sugar, the two greatest points in grading sugars for storage, and the cause and prevention of infection require study along broad lines. Then, too, much remains to be learned concerning bone-black. A satisfactory drying process must be found to render the mud from sugar refineries available for use as a fertilizer; and sugar-beet wastes could furnish about 15,000 tons of potash annually.

In the rubber industry there are four leading groups of problems: quality of natural raw rubber; synthetic rubber; vulcanization; and regeneration. The viscosity of Hevea latex diminishes upon dilution with water in such a manner as to suggest that it is an emulsion rather than a suspension. Since, however, rubber is an emulsoid colloid, and consequently always a liquid, we are not able, in this way, to draw any conclusion as to the state of polymerization in the latex. The nature of coagulation has not been fully explained, although it is of absolutely vital importance as regards the quality of the rubber produced. No chemical explanation can at present be given to account for the differences in quality between Para and Plantation rubber. Research is also required to determine the nature of the factors affecting the quality of raw rubber and its velocity of vulcanization. It is important to have a raw rubber which shall vulcanize at a constant speed, and, if possible, of guaranteeing this by careful tests before buying. Rubber from which the resins or proteins have been removed will not vulcanize as readily as ordinary technically pure rubber, and the conclusion has been drawn that synthetic rubber will be bad on the ground of its being too pure. The rubber manufacturer will not, however, be in any way embarrassed on that account and will be able to add as much resin as is needed, consistent, of course, with specific work. With regard to the regeneration of waste vulcanized rubber, so far it has not proved possible to obtain from waste vulcanized rubber a product like new rubber and containing no sulfur. The combined sulfur is bound with extraordinary strength. What can be accomplished is to remove the free sulfur, some or all of the mineral fillers, and the fibrous materials, and the reclaimed rubber thus obtained by many processes is a valuable adjunct in cheap mixings.

Certain problems connected with the coal-tar industry are as follows:

1—The devising of a practical distillation method for increasing the yield of coal tar light oil (at present the yield is never over 4 per cent and averages about 2 per cent).

2—New uses for hard coal tar pitch—ones other than as a briquette binder. This investigation would have for its object the extension of the demand for this constituent of tar.

3—A commercially successful, economic method of dehydrating tar. While the water may be reduced to less than 0.5 per cent by heating the tar continuously in thin films under a partial vacuum (this plan is most in favor), it is said that any improvement in this troublesome and expensive step would be welcome.

4—An investigation to find special fields for the use of water gas tar and its products, especially the pitch (which shows, to a much higher degree than coal tar pitch, the properties of brittleness and susceptibility to temperature changes) and oils (which have not given the great value for timber preservation characteristic of the coal tar oils).

5—New uses for anthracene (other than as a basis for alizarine, etc.) in this country. The object would be the finding of such uses as would make the production of anthracene profitable.

6—The chlorination of naphthalene. The wax products obtainable thereby possess dielectric properties and promise to develop an important field. An investigation of the methods of preparing these, their properties and commercial values, along broad lines, would undoubtedly lead to important technical results.

Owing to the great number of existing technochemical problems, I have restricted myself in the choice of the ones cited and in general have refrained from even a cursory discussion thereof. I have endeavored, however, within the brief period of thirty minutes, to show that many various problems await solution and that a number of branches of chemical industry invite research.

It was for the purpose of aiding manufacturers in solving just such problems as have been mentioned that the Mellon Institute of Industrial Research was founded. I now invite you to make a visit of inspection to the new home of this representation of an alliance between industry and learning which has been gratifyingly successful, in order that you may see what we are accomplishing in obviating difficulties in manufacture, in utilizing wastes, in improving and cheapening manufactured

[1] The success which has attended scientific progress in refining petroleum is the cause of the high cost of gas oil. It must soon render necessary extensive scientific research in the gas industry.

products, in finding new uses for products, and in searching for new and useful products, for twenty-five American industrialists.

[Dr. Scholes gave here a brief discourse on the work of the Mellon Institute of Industrial Research (see THIS JOURNAL, 7, 343–7), illustrating its activities by means of sixty lantern slides.]

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
PITTSBURGH

## THE BRITISH NATIONAL DYE SCHEME

By D. GEDDES ANDERSON

Received April 6, 1915

Towards the end of the first month of the war, the British Board of Trade appointed a committee, with Lord Moulton as president, to consider and advise as to the best means of obtaining for the use of British industry sufficient supplies of chemical products, colors and dyestuffs of kinds hitherto imported from countries with which at present a state of war existed. It was brought out that British industries use annually dyes to the value of nearly $13,000,000, and of this total about $10,000,000 came from Germany, about $850,000 from Switzerland, and only about $1,000,000 were of British home production. It was further estimated that an adequate supply of dyestuffs was essential to an industry with a turnover of $10,000,000 per annum, and that 1,500,000 employees were directly or indirectly interested.

The first proposal of the Government was to subsidize the establishment of a British dye industry by the creation of a new joint stock company to increase the output of existing dye works. The company was to have a working capital of $26,000,000, of which $15,000,000 was to have been subscribed by the public (principally the dye-users), and $11,000,000 by the Government in the shape of a loan bearing interest at 4 per cent, repayable in 25 years. The Government was to have two nominees on the Board of the company with a right of veto on three points: (1) That the concern should remain permanently under British control; (2) that no arrangement should be made with any foreign producers as to keeping up the price or delimiting the area of activity; (3) a right by veto over all contracts so that no large consumers should be given an advantage in price over the small consumer.

Users of dyes were also asked to bind themselves to take their requirements from this company for a period of five years after the war.

This scheme did not prove acceptable to those interested. The directors of the influential Bradford Dyers' Association in a letter to the Board of Trade summarized the main objections as follows:

"(1) The failure of the Government to take their fair share of responsibility, and merely subscribing for debentures, wholly or mainly secured.

"(2) The stipulation by the Government, extraordinary and novel on the part of debenture holders, that they should not only nominate two directors, but that in these nominees should be vested impracticable and dangerous rights of veto.

"(3) The stringency and impracticability of the agreement for the supply of colors, the agreement being also exclusive in regard to existing makers and effectively preventing the establishment of new ventures.

"(4) The lack of advantages to the investing consumer.

"(5) The power of veto by the Government nominees and encroachment on the businesses of manufacturers of produce other than dyes and colors, by which proviso the 'working up' of by-products would be restricted and the most economic production of the staple articles rendered impossible.

"(6) The lack of information as to the intended acquisition by the proposed company and the basis as well as apprehension of the type of director possibly constituting the Board."

This letter went on to state what in the opinion of the directors were the main objects in any movement for procuring and maintaining supplies of aniline colors, namely:

"(1) The immediate increase of the British production.

"(2) The immediate increase of supplies from Switzerland.

"(3) The establishment in this country of the color-making industry on an adequate scale and on permanent and progressive lines. The attainment of the first and second of these essentials should be governed wholly by urgency. The third should be approached with the least disturbance to ordinary business procedure and conditions. It must be borne in mind that existing plants, supplemented by the maximum supplies which can be reasonably expected from Switzerland, fall woefully short of the requirements of the dependent trades. Consequently even at otherwise unreasonable cost, every possible and immediate step should be taken to increase production—by temporary extensions, by emergency production, by rapid installation of equipment for the production of intermediaries without consideration, if it means delay of the possibility of subsequent removal or concentration of equipment so provided.

"These objects can be attained only by liberal and continued outlay. If the requisite funds are to be either wholly or partly provided from private sources the invitation to subscribe must carry with it some of the assurances usually required by investors. Here we may concede a difference between the interested and the ordinary subscriber. To the former an indirect inducement may appeal; to the latter a direct attraction is essential. To the one the depreciation or loss of his investment may not mean so much if in the process he has obtained all necessary supplies on competitive terms. To the other, direct inducements must be offered by way of security of capital and prospective returns, or by reasonable security and relatively higher returns. But, owing to the inevitable losses on establishment, especially under emergency conditions, owing to the possible initial mistakes in staffing and organization, owing to the likelihood of the re-entrance of German competition in all its ruthlessness before the new conditions have been successfully established and organized, the British efforts must contemplate and prepare for initial losses probably heavy in the earliest years. It is, therefore, difficult to believe that, without special inducements, capital would be attracted.

"The circumstances, the urgency, and the magnitude of the situation call for Government aid, and in some other and more effective form than that merely of lenders on first charge security. Such aid may be applied by any of the following means:

"(1) Protective tariffs; (2) grants in aid; (3) lending schemes. Although aware that, owing to the exceptional circumstances, many who have hitherto resolutely opposed any system of protection are convinced that this form of assistance is the likeliest to be effective and to attract capital, we feel and recognize the obvious objections to advancing it. As between the remaining two courses we prefer a system of grants in aid, and beg to submit for consideration a suggested method by which such a system may be established and worked, namely: (I) That a Commission should be established to administer a fund for the objects as stated hereafter, and raised on the lines indicated. The number of the Commission should be small, and the members certainly active and experienced. (II) That the Government should make an immediate grant in aid up to, say, $2,500,000, to be administered by the Commission on the lines of the suggestions in clause 4, more particularly to objects *a* to *c* inclusive. (III) That the Government should for ten years make an annual grant of equal amount to that voluntarily raised by the trades interested, such sums to be administered by the Commission, with more particular regard to objects *d* and *e* of clause IV. (IV) That the objects of the Commission should be (*a*) immediately to stimulate the maximum of effort by the British color-makers to increase their production of colors by way (1) of plant extensions; (2) coördination of production and

by mutual supply and exchange of intermediary products; (*b*) to assist any color-making concern or concerns, either independently or through any company which may be formed, to acquire or establish such concerns by means of conditional contributions towards equipment, by guarantee of interest on prior charges, or by such other means as may be effective; (*c*) to make such arrangements, financial or otherwise, as would ensure effective coöperation by the Swiss makers; (*d*) to encourage and develop the industry on progressive and extended lines by grants on production, and for enterprise and initiative; (*e*) to establish and maintain, or to assist in establishing and maintaining research laboratories, and to encourage by grants scientific work and study.

"We respectfully submit that the very necessary assistance of the Government would be much more effective and much more rapid in attaining the desired objects if in such a form as we have here indicated than by a state-controlled company, with its unavoidable concomitants. It may be well to reiterate that in the consideration of any schemes for the relief of the situation in the color-producing industry it is understood as essential that the existing Patent Acts should be amended to ensure that the patented article shall be produced in this country from the raw material, and that any existing restrictions on the use of alcohol or other restrictions bearing unfavorably on British, in contrast with German, producers be removed. Incidentally we would respectfully remind you that the immediate position would be considerably ameliorated by the coöperation of the Government department whose assistance is necessary to facilitate the export of raw materials to Switzerland essential to the receipt of larger supplies of colors from that country."

The criticisms directed against the Government scheme by the various committees appointed to consider the question, and by the different Chambers of Commerce follows somewhat along the same lines as those taken by the directors of the Bradford Dyers' Association, but it is interesting to note that the Chambers of Commerce of London, Leeds and Bristol each advocated adequate tariff protection for some time after the war.

A second Government scheme was propounded, and on February 8th the President of the Board of Trade went into the details as follows:

"The original scheme for the development of the dye-making industry in this country on a larger scale, which was framed by a representative committee of users of dye in consultation with the Board of Trade, has now been modified, as it appeared that, owing to difficulties arising in connection with some details of the proposal, it was improbable that the amount of capital contemplated would be raised.

"The new scheme which has the approval of the enlarged committee of users, provides for an original share capital of $10,000,000, of which, in the first instance, $5,000,000 would be issued. The amount of capital to be subscribed at the outset is thus smaller than in the earlier scheme, but power is taken to extend the operations of the company as occasion may justify. The Government is prepared to advance $1 for every $1 of share capital raised, up to a maximum of $5,000,000; should it subsequently be found necessary, the Government will further contribute $1 (up to a maximum sum of $2,500,000) for every $20 further share capital subscribed. The effect of this arrangement will be that, if full advantage is taken of the Government offer, the company will ultimately have a share capital of $15,000,000 and a loan capital of $7,500,000 as in the original scheme. In the meantime, however, the new financial arrangements will, it is believed, be more manageable, and make subscription by those interested much easier.

"The Government advance will bear interest at the rate of 4 per cent and be repayable within 25 years. But whereas under the original scheme, the interest on the advance and the requisite sinking fund for repayment were to be cumulative, though payable only out of net profits, under the new arrangement the payment of interest will be non-cumulative for the first five years, and there will be no compulsory sinking fund. On the other hand, the interest on the ordinary shares will be limited to six per cent per annum so long as any part of the Government's advance is outstanding.

"Further, with a view to the promotion of research, the Government have undertaken to make a grant to the company during a period of 10 years of a sum not exceeding in the aggregate $500,000 to be devoted exclusively to experimental and laboratory work. The company will be required to show, to the satisfaction of the Treasury, that the amounts granted from time to time have been expended solely for the prescribed purposes. This is a new feature of the scheme.

"The agreement proposed to be made between consumers of dyes and the company has been modified in some respects and will, it is believed, be more acceptable to consumers than that originally proposed.

"An option has already been obtained for the acquisition by the company, when formed, of important dye-making works, and negotiations for other options of the kind are in progress, and there is reason to believe that satisfactory arrangements can be made with important producers in Switzerland. The new company will be able immediately on its formation to take advantage of these arrangements, should the directors think it expedient to do so, and to take such other steps as may be thought expedient to develop the supply of dyes both by the enlargement of the plants of the undertakings acquired, and in other ways.

"The scheme, like the original scheme, provides for the nomination by the Government so long as any part of the Government advance is outstanding, of two directors who will have the ordinary powers of directors and also certain special powers to prevent undue preference or encroachment on the business of undertakings non-concerned with the making of dyes and colors, but there is not, nor has there ever been, any intention to utilize these powers so as to hamper the business management of the company in such matters as the working-up of by-products or the giving of priority in supply to shareholders in the company.

"I share in the belief of the committee that the new scheme, and the subsidiary arrangements which I have mentioned, will provide both for the immediate and effective utilization of existing sources of supply and for their expansion with as much rapidity as is compatible with sound development."

The agreement referred to by the president of the Board of Trade is as follows:

"Memorandum of Agreement made this.....day of..... 191.. between British Dyes Ltd. whose registered offer is at .....in the.....of.....(hereinafter called 'the Company') of the one part and.....of.....in the.....of .....(hereinafter called 'the Customer') of the other part.

"WHEREAS the Company has been incorporated since the commencement of the present war for the purpose among other things of producing, manufacturing and selling dyes, colors and other chemical substances (hereinafter collectively referred to as dyes) which previously to the war were exclusively or principally manufactured in Germany and sold by Germans and German companies and firms. And whereas under the provisions of the contracts at which particulars are set out in the schedule hereto the customer is or may be bound after the war to take delivery of the goods specified in the third column of the said schedule. And whereas the company has supplied and (or) agreed to supply the customer with certain of the dyes required by the customer for the purposes of the customer's business but it was stipulated by the company and accepted by the customer as one of the terms and conditions upon which

such supply would be made that this agreement between the parties hereto should be executed.

"Now it is hereby agreed and declared by and between the company and the customer as follows; that is to say:

"1—The consideration for this agreement is the supply by the company to the customer of certain of the dyes required by the customer and the mutual accommodation of the parties hereto by the sale and purchase of such dyes during the continuance of the present war.

"2—The customer undertakes with the company that as from the conclusion of the present war and for a period of five years thereafter or until five years have elapsed from the last delivery to the customer pursuant to the terms of the contracts set out in the schedule hereto or until five years have elapsed from the determination of the said contracts, whichever shall be the longest period, the customer (*a*) will purchase from the company all dyes which may be required by the customer for the purposes of the customer's business or such amounts and quantities thereof respectively as the company may from time to time be able and willing to supply to the customer of good quality and suitable for the purposes of the customer's business and at reasonable prices within a reasonable time after the same shall be ordered having regard to the obligation and requirements of the customer and (*b*) will not purchase from any company firm or person (other than the company) any dyes which may be so required as aforesaid excepting only such amounts and quantities thereof respectively as the company may from time to time be unable and (or) unwilling so to supply to the customer. Provided, always that the fulfilment by the customer of his legal obligations under the contracts set out in the schedule hereto shall not be deemed a breach of this clause.

"3—The prices to be charged by the company and paid by the customer to the company for the dyes during the period referred to in the preceding clause hereof shall be reasonable prices from time to time fixed by the directors of the company. Provided, that if the customer shall consider such prices unreasonable he shall in writing notify the fact to the company within seven days after being informed of the said prices indicating in such notice the prices he is willing to pay and in the event of the company being unwilling to accept the prices named by the customer he shall be at liberty to call upon the company to submit the question of whether the directors' prices are reasonable or not to the decision of a referee appointed by the president for the time being of the Association of Chambers of Commerce of the United Kingdom. The referee shall decide whether the prices charged by the directors are reasonable and in so deciding he shall have regard to all the circumstances including the fair current prices at which dyes are being sold by other suppliers and if he shall come to the conclusion that they are not reasonable he shall prescribe what prices shall be charged by the company to the customer.

"4—Strikes, breakdowns, war, fire, flood and all similar occurrences which might curtail or render impossible either the manufacture or the consumption of the dyes shall be regarded as *force majeure* and as mutually releasing either party from its obligations in respect to the time stipulated for delivery of any dyes bought or sold in pursuance of this agreement during the period of derangement.

"5—The expression the company and the expression the customer shall respectively include their respective successors in business where the context so admits.

THE SCHEDULE ABOVE REFERRED TO

| Date of contract | With whom contract was made | Description of goods and quantity remaining undelivered under contract | Period over which undelivered goods are to be delivered" |
|---|---|---|---|

The question of the national dye scheme came up for full discussion in Parliament, on February 23rd, and Mr. Runciman, the president of the Board of Trade, went into further details. He said: "The Government had entered into an arrangement with the Swiss manufacturers for new and intermediate products to go out immediately, and arrangements had been made for those products to pass through France. They had organized at home the production of some of these raw materials on a wider basis, and although some of these bases were necessary for the production of explosives, they had seen to it that the manufacture of explosives should not altogether exclude the possibility of their having some of the surplus produce to send to Switzerland to be turned into finished dyes. The gas companies had helped them in nearly all the great centers where they had been invited to put up a plant. The coke oven owners had turned over to the Government practically the whole of their benzoline, from which they had drawn a large percentage of toluol. The Government had obtained an option on the works of Messrs. Read, Holliday, and Sons (Limited), of Huddersfield, producers of dyes and intermediate products. The Government wanted these works to be specialized more highly on the later processes. The firm had been a well-managed and profitable concern and had shown that it was possible, even under the hottest German competition, to make a creditable profit out of the manufacture of dye products in the United Kingdom without any import tariff. The option enabled the Government to take over that firm at a price in relation to which the average annual profits during the last six years represented about six per cent. He did not think the Government had driven a bad bargain, though naturally they had had to pay more than their nominal capital. The money would be paid in cash. The Government made an outright purchase, but the staff of Messrs. Read, Holliday & Sons would assist the new company, and the organization of the old company would not be broken up. The proprietors would be eliminated, and the managers and staff retained. There were other concerns in pretty much the same position.

"Provisional agreements had been entered into with one or two concerns in England for the purchase of intermediate products. They had also made arrangements with the gas companies and these would go on in conjunction with the control exercised by the High Explosive Committee. None of these arrangements could go through unless they were linked up. The only way to bring about an increase in the production of the dyes we needed was by reorganizing these concerns under one control so that the best was produced from them. They had also to safeguard the small consumer and must see that he was not 'squeezed out.' The severest criticism of this scheme had come from the three greatest dye users in the United Kingdom. These great concerns could, to a large extent, take care of themselves. If the scheme fell to the ground the large consumers would not regret it anything like so much as the small consumers.

"The success of the concern would depend largely on the way in which the German patents were administered. The Act passed last autumn as an emergency measure provided that the operators of German patents in this country should have a full chance of conducting them under license, and it was the intention of the Government not to cripple this company when the war was over, but to give them every opportunity of making the most of German patents. They would leave over for discussion as between Germany and this country the payment of royalty in respect of these patents. There were English patents in Germany on which he hoped a royalty was being paid there. We should hand over these royalties if Germany would bargain fairly with us. But the operating of these patents which would be undertaken by the new company would proceed after the war was over without interruption and without hindrance. The regulations of the Board of Customs with regard to alcohol would enable the company to obtain permission to use alcohol for

industrial purposes free from duty by arranging that the denaturing of such alcohol should be carried out under conditions which would not hamper the industry."

The company, British Dyes, Ltd., was registered at Somerset House on March 4th, and the prospectus advertised on March 6th.

A meeting of the subscribers was held on March 4th to consider the question of the failure to raise sufficient capital. It was there resolved unanimously that the company should be proceeded with and the meeting pledged itself to use its best endeavors to support it, and further asked the directors to consider the advisability of dropping the agreement between the users of dyes and the company.

It was announced later that, in view of the fact that, of 1,000,000 $5 shares offered only 571,000 had been applied for, and 83,000 of these conditionally, the directors did not feel justified in proceeding to allotment.

NOTE (Received May 12, 1915)

The flotation of the company British Dyes, Ltd., has been carried through. The clause restricting shareholders of the new Company from buying dyes from outside sources was abandoned and the removal of this restriction probably was one of the chief reasons why the later appeal of the directors of the Company to subscribers met with success.

A meeting of subscribers was held on March 24th to consider the situation, and the chairman, Mr. James Falconer, M. P., put the following figures before the meeting.

Practically $2,400,000 had been offered to the company, eliminating subscriptions that were conditional and those they did not propose to allot upon. This result would give them $600,000 of paid-up capital, and the Government advance of $2,400,000 would make a total of $3,000,000. They had asked the Government if they would increase their advance, but they did not see their way to do so. The Grants Committee had agreed to advance $1,000,000 for the extension of Read Holliday's business in order that these extensions should proceed, and they had agreed to allow the $1,000,000 to remain if the directors took over Read Holliday's business on the same terms as a Government loan. That would make their total available cash capital $4,000,000.

The directors had carefully considered the position, and did not think that was enough to justify them in going on. The meeting would sympathize with the board in the feeling that they ought not to undertake what was going to be an arduous and difficult task, and be constantly beggared for want of capital. It was not in the interests of the subscribers or the trade. It was absolutely necessary to increase the capital. They ought to aim at getting at least $1,000,000 more, and if what had been said with regard to the withdrawal of the agreement was general that amount ought to be reached. That would give them $250,000 of called-up capital, and $1,000,000 Government loan, which would be $1,250,000 additional. With that he thought the board could quite comfortably proceed to do their best to carry out the program they had put before the subscribers in the prospectus.

It was announced later, at a meeting of the directors of the Company, that new subscriptions to the extent of $780,000 had been received and that further applications were expected. The Calico Printers' Association, and also practically all those who had at first made conditional applications, including the Bradford Dyers' Association, Ltd., had now subscribed. The directors therefore decided to go to allotment.

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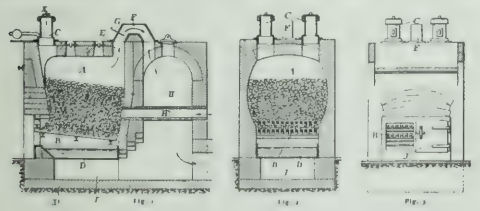
# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

## CONTINUOUS PRODUCTION OF WATER GAS

The Société Française d'Exploitation de Fours Spéciaux à Haute Température, in association with M. Antoine Verzier, have taken out a French patent (No. 473,149 of 1914) for apparatus for the continuous production of water gas. The patentees claim that their plant makes it possible to vaporize water contained in a chamber in the ash-box and also superheat the steam produced at a constant temperature by mere radiation, during its passage under pressure in the collector, from the combustion substances provided by the gasifying plant itself



—thus dispensing with a separate boiler. They also claim that they can obtain, as required (by conveying the excess of superheated steam, produced as already explained, through the incandescent layer of fuel), decomposition of the steam, the necessary quantity of air being supplied by a fire-clay pipe which runs across the collector, and the air being superheated before being brought into contact with the fuel. Apparatus thus constructed obviates the period of transition due to the introduction of cold air to complete the reaction.

A form of plant constructed according to this invention is shown in the accompanying illustrations, taken from the *J. Gas Lighting*, **130** (1915), 31; Fig. 1 is a longitudinal section, Fig. 2 a section on the line X, and Fig. 3 a front view.

The plant comprises a combustion chamber, A, into which the fuel, resting on the grate B, is introduced by charging-boxes C. Below the fuel is a chamber, D, always full of water. The gas liberated by the incandescent fuel issues from the chamber A through a channel, E, and then passes into a pipe, G, provided with a damper, by which it is conveyed into a collector, H, communicating with a compartment, I, under D, which is thus heated by simple radiation from the hot gases coming from the fuel in the collector and the compartment I. Doors J (Fig. 3) hermetically close the front of the ash-box and chamber, and the latter also closes the compartment I. The fire-clay pipe $H^1$ conveys hot air to the fuel.

The water in the chamber is continually and naturally converted into steam, which is automatically superheated in passing through the incandescent fuel above, where the oxygen and hydrogen are separated, as previously described. The chamber D, in the ash-box, may be of any suitable shape favoring the evaporation of water.

## AUTOMATIC MEASURING OF THE MOISTURE CONTENT OF CELLULOSE

An apparatus described in the *Papierfabrikant*, 13 (1915), 33 and 50, has been built by O. Nordström for automatically measuring the moisture content of cellulose during manufacture. It is based on the principle that the dry substance is electrically non-conducting. Since the conductivity, how-

ever, increases with the moisture content and with the amount of dissolved electrolyte, an electric measure of moisture is possible. But since the amount of dissolved electrolyte in the factory water supply, and hence the moisture in the paper, varies within wide limits, a compensating device must be introduced. In this apparatus it is based on the principle of the Wheatstone bridge. A stream of water from the paper machine flows through a glass tube containing a fixed grounded contact at one end and a movable contact passing through the other, so that the column of water through which the current passes may be varied. By dividing and balancing the current, the instrument may be standardized so that no current passes when the paper has a given desired moisture content. Full details are given in the article.

## HYDROGEN FOR BALLOONS

Balloons are generally inflated with hydrogen from scrap iron and hot acid, unless there is some other source of the gas close at hand. The French army is also making use of some novel processes which would be far too expensive for most commercial purposes, but which have the advantage of requiring none but readily portable materials and apparatus [*Engineering*, **99** (1915), 415]. When the metals of the alkalies and alkaline earths are heated in hydrogen, so-called hydrides are formed. They are not metallic in appearance at all—liquid hydrogen itself, it will be remembered, disappointed chemists by turning out to be a snowy paste—but form whitish crystals or crystalline powders, which have to be kept hermetically sealed. In the case of calcium hydride the powder is decomposed, with liberation of hydrogen, when heated up to 600° C. in a vacuum, or when treated with water. The simple apparatus designed by G. F. Jaubert for the decomposition of his calcium hydride, or "hydrolith," which is essentially $CaH_2$ with some calcium oxide and nitride, yields 1 cubic meter of hydrogen per kg. of hydrolith. Jaubert has also worked out two other processes which make use of ferro-silicon. In the "silicol" process this material, or mangano silicon, is directly decomposed by means of water and caustic soda; the gas evolution proceeds on the ordinary lines, as in the case of the generation of acetylene from calcium carbide, for instance, but it appears to be difficult to control the reaction. Jaubert therefore introduced another "hydrogenite" process. Ferro-silicon is intimately mixed with dry caustic soda and quicklime, and the bricks obtained are sealed into tin cases to keep out moisture. When wanted, the brick is placed within a water-jacketed apparatus, and a hot wire is forced into the opened brick. The mass burns without giving any flame, some steam is generated in the jacket, and this steam enters the brick and hastens the liberation of hydrogen. The ferro-silicon used is of very high grade, containing more than 90 per cent of silicon. The reactions give hydrogen, lime, and sodium silicate; the iron is unessential, and is used only because it is cheaper to manufacture rich ferro-silicon than to isolate silicon itself.

## ACCIDENTS IN GERMANY FROM BENZINE

The following list of accidents from benzine during 1914 is published in the *Z. angew. Chem.*, **28** (1915), III, 73:

| Scene or character of accidents | Total No. | Persons Hurt: Slightly | Seriously | Deaths |
|---|---|---|---|---|
| Chemical cleaners and dyers | 6 | .. | 4 | .. |
| Druggists, etc. | 11 | .. | 3 | 1 |
| Benzine in technical use and transport | 62 | 27 | 56 | 76 |
| Benzine in drains and sewers | 3 | .. | 2 | .. |
| Benzine in automobile traffic | 104 | 38 | 55 | 27 |
| Benzine for illumination | 10 | 1 | 4 | 1 |
| Benzine for household uses | 42 | 7 | 30 | 10 |
| Narcosis from benzine vapors | 8 | 3 | .. | 5 |
| Totals | 246 | 76 | 154 | 120 |

There has been an increase of accidents from the use of pocket lighters, and the number of explosions of benzine used for automobiles has nearly doubled. Emphasis should be laid on the fact that non-inflammable substitutes for benzine exist which are perfectly suited for most uses except power production and illumination.

## THE FIRE DANGER FROM SLAKED LIME

In the Royal Saxon Mechanical-Technical Experiment Station, experiments have been carried out which prove that it is easily possible for wood to catch fire from slaking even the poorer qualities of lime [*Tonind.-Ztg.*, **1914** p. 1423]. Naturally the temperature reached depends, besides on other factors, on the quality of the lime; even limes poor in calcium oxide may produce a temperature of 270–300° C., at which point wood is charred on exposure to the air. Lime of poor quality then must be considered to a certain extent dangerous, and high-grade lime must be handled with special care, since it can produce temperatures of 400° and over; it must never be shipped in contact with wood.

## A WOOD CHARCOAL FILTER FOR THE WASTE GASES FROM A SULFATE PLANT

A paper by Reinhard on a charcoal filter used to deodorize the gases escaping from the sulfate plant of the gas works in Leipsic appeared in the *J. Gasbel.*, February 6, 1915.

The gases escaping from sulfate plant consist chiefly of carbonic acid and sulfuretted hydrogen, which on account of their very disagreeable smell, cannot be discharged directly into the atmosphere. The Government Factory Department of Saxony requires in most cases special treatment of these gases—such treatment generally consisting in their being passed through atmospheric or hydraulic tubular condensers or coolers, thence through iron oxide purifiers, and finally into a flue for combustion. The discharge of the gases without combustion led to some complaints of nuisance, and the management was compelled to take some action. The combustion of the waste gases could not be readily effected, as the boiler and other furnaces were far distant from the sulfate plant.

Some preliminary experiments on a small scale showed that the empyreumatic, strongly smelling substances in the waste gases could be gotten rid of by passage through wood charcoal, and as a result of these experiments a plant was erected. To the pipe which conveys the spent gases from the purifiers to a place above the roof, two vertical pipes $13^1/_2$ in. in diameter have been connected. These pipes are each packed with about 165 lbs. of wood charcoal, costing, for the two, about $3.24. After six weeks' working the wood charcoal has been taken out and regenerated by heating in a gas retort for about three hours. This regeneration causes a loss of about 20 per cent of the charge. Data cannot be given as to the quantity of waste gases purified in this way, but the liquor worked up in this period in the plant amounted to 550,000 gallons. It should be added that a steam-jet blower has been introduced into the vertical pipe leading to the roof in order to exhaust the waste gases, which are heavier than air. Hence the whole waste-gas connections are under suction. The process has answered quite satisfactorily, and there have been no further complaints from neighbors.

## GAS FROM SAWDUST

In a recent issue of the *American Gas Institute News*, a paper read by Messrs. James Lawrence and James C. Lawrence, before the New York Section of the Society of Chemical Industry, and published in **30**, 728 of their *Journal* is quoted on the subject of the distillation of sawdust, in answer to an inquiry by a correspondent. It had previously been supposed that wood less than 4 to 6 inches diameter could not be advantageously distilled, because of its tendency to burn up rapidly by reason of an exothermic reaction which starts when the temperature of the charge reaches about 275° C., but the authors found that by heating the retort very slowly up to 100° C., then a

little more rapidly to 280° C., and then stopping the external heating until the temperature reached a maximum, when the heat was again applied and the distillation finished by raising the temperature as rapidly as possible to a little over 400° C., fine wood and sawdust could be successfully distilled. They give the results of some ten distillations, but do not give any for sawdust. These results show that from 100 lbs. of wood they were able to get about the following products: Acid liquor, 43.75 lbs.; tar, 3.45 lbs.; charcoal residue, 31.12 lbs.; gas, 21.68 lbs. A specimen analysis of gas is given, which shows that 100 cu. ft. had a weight of 8.62 lbs., so that the yield per lb. of wood was about 2.5 cu. ft. The calorific value of the gas was given as 11,493 B. t. u. per lb., and this figures out at 990 B. t. u. per cu. ft. The percentage analysis of the gas is given, however, as being:

| | |
|---|---|
| Heavy hydrocarbons | 8.16 |
| Marsh gas | 12.32 |
| Carbon dioxide | 31.45 |
| Carbon monoxide | 35.08 |
| Hydrogen | 10.94 |
| Nitrogen | 2.05 |

From this analysis the calorific value is calculated as 436 B. t. u. per cu. ft.

If larger wood were being used, more gas could be obtained by carrying on the distillation at a higher temperature; but from what the authors say, it would be impossible to do this with sawdust, since it would burn up under this treatment and the charcoal remaining after the distillation was completed would be so fine that it would be impossible to keep it from burning, unless the retorts were discharged into an air-tight chamber.

## ECONOMY IN REINFORCED CONCRETE

In a paper on "Economy in Reinforced-Concrete Construction" read by Mr. T. A. Watson before the British Concrete Institute on February 18th, and quoted in *Engineering*, **99** (1915), 246, it was stated that while great savings can be made on retaining walls, it is generally not economical to employ reinforced concrete for the external walls of buildings, as brick walls up to a thickness of 14 in. are cheaper, but that when walls have to be thicker than this the use of reinforced concrete is advisable. As under the proposed London County Council regulations nearly all external walls need not exceed 14 in. in a framed building, it is probable that reinforced concrete walls for this purpose will soon cease to be used from the point of view of economy. With regard to the economy of reinforced-concrete framed buildings outside the London area the economy is very considerable; inside the London area the London County Council, by their regulations, propose to reduce it as much as possible. There are, however, opportunities to effect savings over a steel-framed building even in London. In the construction of bridges, say up to 300 ft. span at least, reinforced concrete is nearly always the most suitable material. There are, of course, exceptions, but the mere question of the cost of maintenance of a steel bridge seems enough to condemn it. The question of maintenance is also enough to decide an architect or engineer to choose reinforced concrete for the construction of, say, small water towers, coal-bunkers, gasometer tanks, or any similar structure heretofore built in steel, and exposed to atmospheric conditions, even if reinforced concrete is not cheaper in the first instance.

## THE RUSSIAN PEAT INDUSTRY

The remunerative exploitation of the vast peat deposits which many countries possess has for years been the subject of many experiments and much labor, although the results, perhaps, in most cases have been somewhat disappointing. In no country, according to *Engineering*, **99** (1915), 477, is there a greater wealth of raw material of this kind than in Russia, with her 60,000,000 acres of bogs, about 6.7 per cent of the country's entire European area. Efforts are now being made to encourage the peat industry, which in some districts has attained to a fair importance, although the bulk of the deposits are still left unexploited. A special section for peat exploitation has been formed under the Department for Agriculture, with a staff of experts, who in the first place are to examine and report upon the peat deposits near the railway stations and the large industrial centers. The State owns a very material portion of the country's peat deposits, which, where this is found practicable, are let to private contractors for a fee of from 4 to 6 cents per cubic meter of peat. Only a small portion of the production is retailed out, the bulk being worked by large industrial concerns for their own requirements of fuel. Some few years ago seventy large manufacturing concerns in Central Russia produced 1,230,000 tons of air-dried peat. The output averages 2000 to 2500 tons per season per machine, and the cost of production, as a rule, lies between $2.00 and $2.25 per ton. In Russia, as elsewhere, the use of peat fuel for locomotives is at present much to the fore, and extensive experiments are being carried on with a view to arriving at a satisfactory practical solution. Pulverized peat seems to have attracted most attention, and the Russians are being guided, to some extent at least, by the results obtained in Sweden in this direction.

## IRON, COBALT AND CARBON

In a paper on cobalt steels, by Prof. J. O. Arnold and Prof. A. A. Read of Sheffield University, read at a recent meeting of the (British) Institute of Mechanical Engineers, a comparison of the effects of cobalt and nickel in steel will be of interest, because nickel and cobalt have been commonly considered to be identical in their properties [*Engineering*, **99** (1915), 363]. Cobalt is not nearly such a great graphite precipitator as nickel. Cobalt-steel ingots can be hammered down to 1-in. bars with only a very small separation of graphite, 0.07 per cent in the highest member of the series, containing 20.85 per cent of cobalt. In the case of nickel-steel ingots treated in exactly the same way as the cobalt-steel ingots, a small separation of graphite began with only 3 per cent of nickel, and when 7 per cent of nickel was present the precipitation of graphite amounted to about 42 per cent of the total carbon. Cobalt carbide appears, then, to be much more stable than nickel carbide, a conclusion which is also borne out by the analysis of the carbide residues obtained by electrolysis from cobalt and nickel steels.

Cobalt does not form a definite solid solution or cobaltide of iron like that formed by nickel, having a composition corresponding to the formula $Fe_7Ni$, which, with only 0.1 per cent of carbon present, registers a maximum stress of about 90 tons per sq. in., associated with a reduction of area of 45 per cent. An alloy containing about 13 per cent of nickel, and, say, 0.6 per cent carbon, is so hard that it is impossible to machine it, whereas in the present series of cobalt steels, in which the carbon ranged from 0.62 to 0.93 per cent, and the cobalt from about 2.7 to 20.9 per cent, all the alloys, without any annealing, machined with the greatest ease. The hardness, as measured by maximum stress, seems, with equal carbon, to rise with the cobalt

## MANUFACTURE OF LABORATORY GLASSWARE IN GREAT BRITAIN

A very important stage has now been reached in the investigations made by British scientists into the question of the manufacture of glassware to replace the supplies which were formerly obtained from Germany and Austria. Early in the war the Council of the Institute of Chemists appointed a Glass Research Committee to conduct experiments with a view to establishing suitable formulas which should be available to British manufacturers willing to assist in making laboratory glassware. The chief aims of the research work, which has been going on continuously, were to produce working formulas for glass used in

laboratories and to ascertain the influences of various ingredients on the physical and chemical properties of glasses. At the suggestion of the Home Office the work was extended to include glass for miner's lamps, and to meet the needs of wholesale druggists engaged in the production of army medical requirements.

The Research Committee has now reported 11 formulas for glasses for various purposes based on the results of about 400 experimental melts on a scale large enough for drawing rods and blowing small vessels. The formulas are published in the *Chemical Trade Journal*, 1456 (1915) and are as given below.

GLASS FORMULAS IN TERMS OF PARTS TO BE USED

| | | | |
|---|---|---|---|
| (1) Sand | 67.0 | Antimony oxide | 1.0 |
| Sodium carbonate ($Na_2CO_3$) | 34.2 | Potassium nitrate | 3.0 |
| Calcium carbonate | 11.6 | Sodium carbonate ($Na_2CO_3$) | 14.0 |
| Alumina | 6.5 | Boric anhydride | 24.0 |
| (2) Sand | 67.0 | (7) Sand | 65.0 |
| Sodium carbonate ($Na_2CO_3$) | 29.0 | Alumina | 1.0 |
| Calcium carbonate | 9.6 | Calcium carbonate | 0.6 |
| Alumina | 8.3 | Arsenious oxide | 2.0 |
| Calcium fluoride | 1.6 | Antimony oxide | 1.0 |
| Boric anhydride | 2.0 | Potassium nitrate | 3.0 |
| (3) Sand | 67.0 | Anhyd. borax ($Na_2B_4O_7$) | 26.68 |
| Alumina | 10.0 | Boric anhydride | 5.5 |
| Calcium carbonate | 12.5 | (8) Sand | 65.5 |
| Magnesia | 0.5 | Alumina | 2.5 |
| Potassium nitrate | 1.0 | Magnesia | 5.0 |
| Sodium carbonate ($Na_2CO_3$) | 17.0 | Zinc oxide | 8.0 |
| Boric anhydride | 8.0 | Sodium carbonate ($Na_2CO_3$) | 10.2 |
| (4) Sand | 68.2 | Anhydrous borax ($Na_2B_4O_7$) | 13.0 |
| Alumina | 6.2 | (9) Sand | 72.0 |
| Barium carbonate | 8.8 | Alumina | 10.0 |
| Calcium carbonate | 13.0 | Calcium carbonate | 11.0 |
| Potassium nitrate | 4.3 | Magnesia | 0.5 |
| Sodium carbonate ($Na_2CO_3$) | 5.5 | Potassium nitrate | 3.0 |
| Boric anhydride | 5.5 | Sodium carbonate ($Na_2CO_3$) | 11.2 |
| Calcium fluoride | 1.0 | Anhydrous borax ($Na_2B_4O_7$) | 7.2 |
| (5) Sand | 68.2 | (10) Sand | 68.0 |
| Alumina | 6.2 | Alumina | 4.0 |
| Barium carbonate | 8.8 | Calcium carbonate | 12.8 |
| Calcium carbonate | 14.2 | Potassium nitrate | 14.5 |
| Potassium nitrate | 4.3 | Sodium carbonate ($Na_2CO_3$) | 2.6 |
| Sodium carbonate ($Na_2CO_3$) | 5.5 | (11) Sand | 68.0 |
| Boric anhydride | 5.5 | Alumina | 4.0 |
| (6) Sand | 65.0 | Calcium carbonate | 12.8 |
| Alumina | 1.0 | Potassium carbonate | 10.0 |
| Calcium carbonate | 9.6 | Sodium carbonate ($Na_2CO_3$) | 26.0 |
| Arsenious oxide | 2.0 | | |

No. (1) is a soft glass which does not give up alkali readily to water, works well in the blowpipe, and does not devitrify readily.

No. (2) is a soft glass of higher quality than (1). It does not give up alkali under severe tests and is a kindly working glass before the blowpipe, and very difficult to devitrify.

No. (3) is a resistant glass suitable for pharmaceutical purposes, ampoules, etc. It is intermediate in hardness between soft glass and combustion tubing, is highly resistant to chemical action, stands changes of temperature well, and should be a very suitable glass for beakers, flasks, etc.

Glass (4) resembles Jena combustion tubing very closely. It has practically the same fusing point and fuses on to Jena glass perfectly. It is indistinguishable from it before the blowpipe and in behavior on prolonged heating below its fusing point. The presence of the small quantity of calcium fluoride facilitates the incorporation of the ingredients. The sodium carbonate can be reduced to 1.34 parts, provided 7.93 parts of anhydrous borax be used in place of boric anhydride.

Glass (5) is practically the same as (4). It is not so easy to make or to work, but it does not become so opaque as Jena combustion tubing on prolonged heating.

Glass (6) is suitable for miner's lamps. It is colorless and fusible, and withstands rapid changes of temperature.

Glass (7) is similar to (6) but the ingredients have been varied to avoid the use of so much boric anhydride which is at present difficult to obtain on a commercial scale.

Glass (8) is almost identical in its behavior with Jena resistance glass. It stands change of temperature well, but is not very suitable for working before the blowpipe; operations such as sealing side tubes into flasks are difficult.

Glass (9) is an alternative for combustion tubing; it is capable of withstanding high temperatures and rapid changes of temperature; works well before the blowpipe, and is free from the chief defect of Jena glass—namely, the readiness with which it becomes cloudy and finally quite opaque after prolonged use. By slight modification of this formula almost any degree of hardness can be obtained.

Formulas (10) and (11) are for soft-soda glasses suitable for tubing and for X-ray bulbs. These glasses do not lose their easy working qualities after repeated heating and blowing, and are plastic over a long range of temperature. They require a temperature of at least 1,400 to 1,500° C. for complete incorporation of the ingredients. Formula (10) is considered the better of the two formulas.—D. G. ANDERSON.

## BRITISH BOARD OF TRADE

During the month of April the Commercial Intelligence Branch of the British Board of Trade received inquiries regarding sources of supply for the following articles:

Agar-agar
Albumen, dried egg
Alcohol (absolute)
Aluminum ware
Aluminum foil
Aluminum powder for paints
Ammonium bifluoride
Aniline dyes
Antimony salt
Arsenic and arsenides
Asbestos
Bakelite
Barium peroxide
Benzoates
Benzene
Bisulfite of soda
Billiard chalk
Bottles
Bone and ivory substitutes
Boot trade accessories
Bronze powder
Bricks. Furnace bricks for very high temperatures
Calabar beans
Caustic soda
Celluloid articles
Centrifugal oil separators for separating oil from brass turnings
Chlorates
Composition wax for polish
Crayons
Cream of tartar
Electroplate
Electro-magnetic separators
Enamelware
Epsom salts
Fabric gloves
Ferric ammonium citrate
Fiberboard
Fluorides
Formic acid
Galalith
Galalith substitutes
Gelatine
Glucose
Ichthyol
Ink
Insulation material
Magnesite
Mantles, incandescent
Manganese jointing paste
Magnetos similar to "Bosch"
Methyl chloride
Mica
Mirrors, stereoscopic
Muriate of ammonia
Nitrate of lime
Nitro-naphthalene
Nickel and nickel ware
Oxalic acid
Peat dust
Permanganate of potash
Potassium ferrocyanide
Pyridine
Pyrolignite of iron
Pyrophosphate of soda
Saccharin
Salicylates
Silica
Sodium cyanide
Sodium acetate
Springs
Steel wool
Sodium hydrosulfite
Sodium sulfide
Sulfo acids of the petroleum hydrocarbons
Sulfate of baryta
Tannic acid
Tartar emetic
Tanning materials
Tin foil
Trinitrotoluol
Tungsten
Tungstates

—A.

## PATENT FUEL IN GREAT BRITAIN

Patent fuel, known on the Continent as briquettes, has hitherto been chiefly composed of small coal, with a binding agent, usually pitch, made into blocks of various sizes and shapes. The magnitude of the industry may be gauged from the fact that in Germany over 20,000,000 tons per annum are produced, while in France also there is a very large output. According to the *Times Engineering Supplement*, 485 (1915), Great Britain as yet ranks third with less than 2,000,000 tons per annum, made chiefly in South Wales. The production in the last few years has, however, more than doubled.

While possessing many advantages, patent fuel has had to contend with one great obstacle to its use as a naval fuel. The mixture of pitch causes it to give off considerable quantities of smoke, and for many years experiments have been made to find a binding substitute that would make the resulting fuel as smokeless as best Welsh coal, without reducing its high efficiency. For this purpose flour, glucose, molasses, and many other substances have been tried with only partial success. During the last 12 or 18 months, however, some important experiments have been carried on under the control of Mr. D. A. Thomas in conjunction with Mr. H. J. Phillips. The system is to produce blocks of nothing but pure coal by forming, under very great pressure, powdered coal into blocks of suitable size and shapes. It is claimed that the blocks thus made are weatherproof and are not more smoky than coal. It is understood that steps are being taken to establish works in South Wales to manufacture this new class of patent fuel on a commercial scale.—A.

# SCIENTIFIC SOCIETIES

## SEATTLE MEETING OF THE AMERICAN CHEMICAL SOCIETY

The recent vote on the route to the Seattle Meeting was overwhelmingly in favor of the Great Northern Railroad, which stops at Glacier National Park, and arrangements have been made for the party to leave Chicago at 5.05 P.M., Thursday, August 26th. One and one-half days will be spent at Glacier National Park, and Seattle will be reached at 6 P.M., August 30th. August 31st, September 1st and 2nd will be spent at Seattle; on the evening of September 2nd the party will take a special train to Mt. Ranier National Park, where they will remain on Friday, September 3rd, leaving there that evening and arriving at Portland the following morning, spending the day in Portland as the guests of the Oregon Section, leaving Portland Saturday night, passing through the Mt. Shasta and Mt. Lassen region on Sunday and arriving in San Francisco Sunday evening. At San Francisco the party will break up, returning *via* whatever route they choose.

The round-trip rates from various eastern points and sleeping-car rates from Chicago to San Francisco (one way) by route of the special train are as follows:

| Round Trip Starting from | Lines to Chicago Differential | Standard |
|---|---|---|
| New York | $111.80 | $116.30 |
| Boston | 115.20 | 121.70 |
| Washington | 110.45 | 110.45 |
| Baltimore | 110.45 | 110.45 |
| Philadelphia | 112.70 | 110.45 |
| Pittsburgh | 96.80 | 98.75 |
| Detroit | 91.00 | 91.00 |
| Cleveland | 92.00 | 93.70 |
| Cincinnati | 88.40 | 88.40 |
| Chicago | 80.00 | 80.00 |

| Sleeping Car Rates From Chicago to San Francisco By route of special train | |
|---|---|
| Lower berth | $22.50 |
| Upper berth | 18.00 |
| Compartment | 63.00 |
| Drawing room | 80.00 |

ADDITIONAL CHARGES—There will be an additional Pullman charge to Mt. Ranier National Park, which will, however, be little if any more than hotel accommodations, should the party remain in Seattle. There may be also a small additional Pullman charge for holding the train at Glacier and Portland. There will be a charge of $12.50 for 114 miles of automobile trip and 20 miles of launch trip in Glacier National Park, and $5.00 for the side trip from Tacoma to Mt. Ranier National park and return. From the National Park Inn at Mt. Ranier several side trips are available during the day at a small cost.

The following itinerary will be carried out:

| | | | | |
|---|---|---|---|---|
| LV | Chicago *via* Chicago, Northwestern Ry | 5.05 P.M. | Aug. | 26 |
| *Ar* | St. Paul | 5.00 A.M. | Aug. | 27 |
| LV | St. Paul *via* Great Northern Ry., passing through the scenic Lake Park country of northern Minnesota, and the immense grain fields of North Dakota and eastern Montana | 5.30 A.M. | Aug. | 27 |
| *Ar* | Glacier Park Station | 2.00 P.M. | Aug. | 28 |
| LV | Glacier Park Station *via* auto over the automobile highway for 32 miles through the Two Medicine and Cut Bank Valleys | 2.30 P.M. | Aug. | 28 |
| *Ar* | St. Mary Camp | 5.00 P.M. | Aug. | 28 |
| LV | St. Mary Camp, traveling *via* commodious passenger launch up beautiful Lake St. Mary | 5.00 P.M. | Aug. | 28 |
| *Ar* | Going-to-the-Sun Camp—Spend the night here | 6.00 P.M. | Aug. | 28 |
| LV | Going-to-the-Sun Camp *via* launch | 9.00 A.M. | Aug. | 29 |
| *Ar* | St. Mary Camp | 10.00 A.M. | Aug. | 29 |
| LV | St. Mary Camp by auto, traveling through the wonderful Sherbourne Lake country | 11.00 A.M. | Aug. | 29 |
| *Ar* | Many Glacier Camp | 1.00 P.M. | Aug. | 29 |
| LV | Many Glacier Camp by auto | 3.30 P.M. | Aug. | 29 |
| *Ar* | Glacier Park Station | 6.00 P.M. | Aug. | 29 |
| LV | Glacier Park Station *via* Great Northern Ry. | 6.00 P.M. | Aug. | 29 |
| *Ar* | Belton | 8.10 P.M. | Aug. | 29 |
| LV | Belton *via* Great Northern Ry., traveling over the scenic Cascade Mountains in daylight | 8.15 P.M. | Aug. | 29 |
| *Ar* | Seattle | 6.00 P.M. | Aug. | 30 |
| | American Chemical Society Meeting, Seattle: | Aug. 31, Sept. 1 and 2 | | |
| LV | Seattle | 11.55 P.M. | Sept. | 2 |
| *Ar* | Tacoma 1.20 A.M., Sept. 3. LV Tacoma | 1.35 A.M. | Sept. | 3 |
| *Ar* | Ashford | 4.35 A.M. | Sept. | 3 |
| | From Ashford the trip into Mt. Ranier Park is made, spending Sept. 3rd there. | | | |
| LV | Ashford 9.00 P.M., Sept. 3. *Ar* Tacoma | 11.55 P.M. | Sept. | 3 |
| LV | Tacoma *via* Great Northern Ry | 12.10 A.M. | Sept. | 4 |
| *Ar* | Portland | 6.00 A.M. | Sept. | 4 |
| | Entire day in Portland for sight-seeing. | | | |
| LV | Portland *via* Southern Pacific Ry | 8.15 P.M. | Sept. | 4 |
| | This itinerary is so arranged that the special train will pass through the best part of the Shasta Mountains in daylight, and affords an opportunity to see Mt. Lassen | | | |
| *Ar* | San Francisco | Sunday evening, | Sept. | 5 |

The hotel rates in Glacier National Park are from $3.00 to $5.00 per day on the American plan. Those who wish may spend the night at "Many Glacier Camp" instead of at "Going-to-the-Sun Camp" on August 29th, which will give them plenty of time to take a side trip to the wonderful Iceberg Lake on the morning of the 29th.

GLACIER NATIONAL PARK—As the Great Northern passes the very gates of Glacier National Park, a trip through the park is a very simple matter. The tremendous mountain land of Glacier National Park sits high up in the Rocky Mountains of northwestern Montana and stretches to the Canadian border. The park is of 1,525 square miles extent, with a veritable army of magnificent peaks rising from 8,000 to 10,000 feet, with their bases thickly timbered and their limestone crests painted in many colors—reds, browns, blues, and purples. On the tops of these mountains are 20 glaciers every bit as inspiring as those ice fields which Americans have been crossing to Switzerland to see; of these, the great Blackfeet Glacier has an area of five miles. There are more than 250 glacier-fed blue mountain lakes. So well have the most important sections of the Park been linked by Government auto stage roads that it is now possible to see within a short time what formerly required weeks.

MT. RANIER NATIONAL PARK—So much has been written about the wonders of Mt. Ranier National Park that there is little need to add detail here. The following quotation from the *Travelers' Magazine* will be sufficient: "Read as much about it as you will, see it pictured a thousand times, and believe all the tales you hear of it, and on going there you will find that it has been underrated. It is hard to believe when you see it. Mt. Ranier is the highest mountain in the United States and has a glacial system greater than that of the whole Swiss Alps. The National Park has an area of somewhat more than 200,000 acres. How bald and uninspiring are statistics! Let it be said, rather, that this is the most beautiful place in the world."

DESCRIPTIVE LITERATURE—Interesting, illustrated literature may be obtained on Glacier National Park from H. A. Noble, General Passenger Agent, Great Northern Railway, St. Paul, Minn.; and on Mt. Ranier National Park from the Chicago, Milwaukee and St. Paul Railway, Chicago, Ill., and Seattle, Washington.

The following beautifully illustrated publications may be obtained from the Superintendent of Documents, Washington, D. C., for the prices noted:

| | |
|---|---|
| Some Lakes of Glacier National Park | 10c. |
| Glaciers of Glacier National Park | 15c. |
| Origin of the Scenery Features of the Glacier National Park | 15c. |
| Glacier National Park, with map (Bulletin 600, U. S. Geological Survey) | 30c. |
| Mt. Ranier and Its Glaciers | 15c. |

Besides these, Mr. Stephen T. Mather, Assistant to the Secretary of the Interior, will gladly send free to any member writing in for same to Washington, D. C., circulars giving general information regarding Glacier National Park and Mt. Ranier National Park; also, Yosemite National Park, all three of which may be easily visited by members taking this trip. Mr. Mather is a member of our Society, whose courtesies at the time of the San Francisco trip will long be remembered. In writing for these circulars, membership in the American Chemical Society should be stated.

IMPORTANT

It is of the utmost importance for the success of this trip and for the convenience of the members that the Secretary be informed at the earliest possible moment of intention to be present, accommodations needed and the number of tickets required. In this connection it should be noted that in purchasing tickets,

free side trip tickets to the San Diego Exposition from Los Angeles, to Colorado Springs from Denver, to Salt Lake City from Ogden, may be had by any member of the party returning through these cities *if the request for this side trip is made at the time the ticket is purchased.*

*Lower* berths or special accommodations should be engaged early.

Members of other scientific societies and friends recommended by members of the Society will be gladly received on the special train.

Box 505, Washington, D. C. CHAS. L. PARSONS, *Secretary*
May 25, 1915

## BATTERY ASSAY OF COPPER[1]

Report of Subcommittee on Methods of Analysis of Non-ferrous Alloys of the Division of Industrial Chemists and Chemical Engineers:
WM. B. PRICE, *Chairman*, ALDEN MERRILL, GEO. L. HEATH, GILBERT RIGG, BRUNO WOICIECHOWSKI

Received February 16, 1915

The methods that follow, as given by the committee, are those originally proposed by Heath,[2] whose work has been checked and elaborated by Keller, Ferguson and members of the committee.

The methods are those generally accepted in the United States for standard analysis in all the larger laboratories of both producers and consumers of copper and copper products.

### GENERAL INSTRUCTIONS

SAMPLING INGOTS—Select six ingots at random from the lot. Considering three ingots as a rectangular unit, drill one hole in each ingot, one at the center and one at each end of a diagonal of the rectangle. Drill each hole entirely through the ingot, starting from the bottom. Start the drill on the surface sufficiently to remove the oxide before commencing to collect the drillings for the sample. Run the drill so as to prevent oxidation of the chips. Discard all drillings carrying oxide from the "set," or burned by the drill. Use no lubricant on the drill, and, if the sample shows oil or grease, remove this with ether. Sift all drillings on a screen with 250 meshes to the sq. cm. in order to remove material which is ground between the drill and sides of the hole. Extract with a strong magnet any iron which may have come from the drill. Keep the drillings in air-tight bottles.

WEIGHTS—Weights shall be calibrated and frequently rechecked. It is recommended[3] to use a special 5-gram brass weight in weighing the samples and to have the weight of the sample always within 5 mg. of 5 grams. When the cathode with its deposit is finally weighed the identical weights are to be used with which the cylinder was tared, plus the special 5-gram brass weight. This brings all the change or deficiency in the final weight on a small fractional weight and the beam and rider.

ELECTRODES—The cathode is a platinum sheet of 5 × 10 cm. giving a depositing surface, counting both sides, of 100 sq. cm. This sheet is formed into a cylinder of the open type, and the stem is riveted and soldered with gold to the middle of the sheet. There should be no seam which cannot be cleansed completely by two washings. The anode is made from 1-mm. platinum wire, formed into a spiral of seven turns having a diameter of 12.5 mm. and a height of 38 mm., the stem being straight and 125 mm. long.

### ELECTROLYTIC AND LOW-RESISTANCE LAKE COPPER

The method described below is applicable to such grades of copper as are covered by the specifications of the American Society for Testing Materials as given in its Year Book for 1913, pp. 241–247. The silver is deposited with the copper and is included as such; when it is desired to correct for the silver this is determined in a larger separate sample and the amount found is deducted from the deposit of copper plus silver. The deposition of the silver with the copper is said to work well up to the limit of 0.3 per cent silver or 100 oz. per ton. All assays are to be made in duplicate and must check within an outside limit of 0.015 per cent.

METHOD OF ANALYSIS—Place 5 grams of the drillings in a tall lipless beaker which is provided with a well-fitting cover glass and add a mixture of 7 cc. of nitric acid (1.42 sp. gr.), 10 cc. of sulfuric acid (1.84 sp. gr.) and 25 cc. of water. This mixture[1] is used as a stock "Assay Solution," 42 cc. being measured for each sample. The electrolysis beakers are from 100–125 mm. tall and 55 mm. in diameter across the bottom, with a total capacity of 225 to 300 cc. After the assays have stood for a few minutes and the action has nearly ceased, place them on a steam bath having a temperature of 80–90° C. and allow them to remain there until solution is completed and the red fumes have disappeared. Wash the cover and the sides of the beaker and dilute the solution to 150 cc. and electrolyze.

During electrolysis the beakers are covered with two pairs of split watch glasses placed at right angles to each other. The current[2] in each solution should be one ampere, which will require about 10 volts if the assays are arranged in parallel. It is convenient to start the assays at night; after about 15 hours wash the cover glasses, electrodes and beakers and reduce the current to 0.6 ampere per solution. As soon as the cathodes begin to evolve gas reduce the current to 0.4 ampere per solution. When this occurs take out about 1 cc. of liquid, place it in a depression in a porcelain test plate and add two or three drops of fresh hydrogen sulfide water. If the slightest discoloration occurs, continue the electrolysis, repeating the test until there is no discoloration whatever.[3] If possible the assay should finish without decided evolution of gas.

Without interrupting the current, siphon off the acid solution, at the same time filling the beakers with distilled water. Remove the cathodes quickly and rinse them in distilled water and two successive baths of alcohol. An experienced operator can quickly remove a cathode and immerse it in water without loss. Throw off the excess alcohol by a quick motion of the hand and ignite the remainder by bringing the cathode quickly to the flame of an alcohol lamp; then keep the cathode moving continually while the alcohol burns. This method of burning off the alcohol dries the cathode without causing oxidation, whereas drying in an oven at 100° C. generally causes increase in weight.

### LOW-GRADE OR CASTING COPPER

For all grades of copper which are not included in the specifications of the American Society for Testing Materials as Electrolytic and Low-Resistance Lake Copper the procedures given

[1] Approved by the Supervisory Committee on Standard Methods of Analysis, American Chemical Society.

[2] Heath, *Trans. Am. Inst. Min. Engrs.*, **27** (1897), 390–400.

[3] Greenwood, U. S. Metals Refining Co., Personal Communication.

[1] Use of the dilute solution above described prevents a violent reaction and a consequent loss of copper with the vapors. The solution should not be boiled, since this likewise may cause a loss of copper.

[2] By the use of rotating anodes, gauze or perforated electrodes or the Frary solenoid, it is possible to use a high current density and to reduce the time required for depositing the copper to about four hours. Good results can be obtained by experienced workers, but there is much more chance for error. The slow or over night method, which is more certain and which requires less of the operator's time, is, therefore, recommended.

[3] It has been shown by Heath, THIS JOURNAL, **4** (1912), 404, that a few thousandths of a per cent of copper may remain in the solution without being detected by the hydrogen sulfide test on the spot plate. This amount of copper is negligible in many instances, but when necessary to make exact determinations, as in the complete analysis of copper, make the solution, after electrolysis, slightly alkaline, neutralize with hydrochloric acid (1.19 sp. gr.) adding 3 cc. excess, evaporate to 50 cc. and precipitate with hydrogen sulfide. Filter off the copper sulfide, treat with nitric and sulfuric acids and deposit the small amount of copper from the solution by electrolysis and add it to that obtained in the original determination.

below are recommended. These brands may contain a considerable amount of arsenic and some antimony, tellurium, bismuth and nickel. All assays are made in duplicate and must check within an outside limit of 0.015 per cent.

It has been recommended[1] to use with solutions of these coppers about 2 cc. of an addition agent prepared by boiling "hard oil" with strong nitric acid, cooling and removing the grease. This, it is said, will permit the use of high current densities and yet allow the copper to be deposited pure and bright. Moreover, it is said that arsenic and antimony, when present, do not contaminate the copper. It seems probable,[2] however, that copper deposited from such solutions is not quite pure and that it is more accurate to purify the cathode deposit (Modification I below) or to give a preliminary treatment to the solution (Modification II).

The committee gives preference to Modification II, and Modification I should be used only in the presence of small amounts of impurities.

MODIFICATION I—Carry out the assay exactly as given for Electrolytic and Low-Resistance Lake Copper. Place the cathode in a clean beaker, cover with a watch glass perforated with a small hole just large enough to accommodate the stem of the electrode, add 42 cc. of stock "Assay Solution" and water enough to cover the sheet. Let it stand upon the steam bath until the coating is dissolved. Re-electrolyze in the regular manner.

MODIFICATION II[3]—Dissolve a 5-gram sample in 42 cc. of the "Assay Solution" and evaporate until all the nitric acid is expelled. Redissolve in 70 cc. water and add 3 cc. ferric nitrate solution (1 cc. = 0.01 g. iron). Transfer the solution to a lipped beaker and place the original beaker under a funnel fitted with a small filter paper. Precipitate the iron from the hot liquid by ammonia, filter and wash out salts. Place the solution on a hot plate to concentrate, reprecipitate the hydroxide from dilute sulfuric acid in a very small volume of solution and add the filtrate to the main solution. Reprecipitate the hydroxide once more from dilute sulfuric acid, filter, wash thoroughly and add the filtrate to the main solution. Make acid with dilute sulfuric acid and add 2 cc. of nitric acid (1.42 sp. gr.). Deposit the copper as in the method for Electrolytic and Low-Resistance Lake Copper.

MODIFICATION III[4] (For copper containing only traces of antimony or bismuth but sufficient selenium or tellurium to interfere)—Dissolve the 5 gram sample in 42 cc. of "Assay Solution" and evaporate until fumes appear, or until the residue is white. Redissolve in 60 cc. of water and saturate the boiling hot solution for 10 minutes with sulfur dioxide gas, removing the solution from the lamp when the gas is started. The gas may be generated by dropping cold saturated sodium sulfite solution into strong sulfuric acid. It is also conveniently obtainable in cylinders which are fitted with a valve. Let the precipitate settle for a few hours, filter and wash with a little hot water. Boil the filtrate gently to remove most of the sulfur dioxide gas. Ignite the filter in a porcelain crucible to volatilize the selenium[5] and tellurium, redissolve the oxidized residue in 1.5-2 cc. of nitric acid and add to the main solution. Deposit the copper as in the method for Electrolytic and Low-Resistance Lake Copper.

[1] Guess, *Trans. Am. Inst. Min. Eng.*, **36** (1905), 605.

[2] Keller, *Ibid.*, p. 2099 (1913), *Bull.* **80**; Heath, THIS JOURNAL, **3** (1911), 75.

[3] Heath (Senter modified), *J. Am. Chem. Soc.*, **26** (1904), 1123.

[4] Heath, *Ibid.*, **26** (1914), 1123; Keller, *Trans. Am. Inst. Min. Eng.*, p. 2098 (1913), *Bull.* **80**.

[5] The selenium is said to be carried down by sulfur dioxide as a selenide of silver, but the roasting sufficiently removes the elements selenium and tellurium. When silver is to be removed, the selenium, etc., are thrown down with the silver by the sulfur dioxide gas and the precipitation of silver is then completed by the addition of chlorides or hydrochloric acid.

MODIFICATION IV[1] (For copper high in arsenic only)—The committee gives preference to "B."

A—Dissolve the sample in 42 cc. of the "Assay Solution" in the regular way and add 5 grams of ammonium nitrate. Electrolyze as usual.

B—Dissolve the sample in 60 cc. of the "Assay Solution" instead of 42 cc. Electrolyze as usual.

SCOVILL MANUFACTURING CO., WATERBURY, CONN.

## ANALYSIS OF SPELTER[2]

Report from a Subcommittee on Methods of Analysis of Non-ferrous Alloys of the Division of Industrial Chemists and Chemical Engineers: WM. B PRICE, *Chairman*, ALDEN MERRILL, GEO L HEATH, GILBERT RIGG, BRUNO WOICIECHOWSKI

Received April 30, 1915

Spelter ordinarily used for brass and similar alloys is usually considered in three grades: A, "High Grade;" B, "Intermediate;" and C, "Brass Special;" according to the amounts of lead and other impurities present. A fourth grade, D, "Prime Western," principally used for galvanizing, contains more impurities than the three grades preceding. These grades are covered by the specifications of the American Society for Testing Materials in its Year Book for 1913, pages 248–251.

The methods of sampling and analysis described below are those generally accepted in the United States for standard analysis in all the larger laboratories of both producers and consumers of zinc and zinc products. The methods of analysis are those originally proposed by Elliott and Storer[3] and Price,[4] whose work has been checked and elaborated by the members of the committee.

### SAMPLING SLABS

Select ten slabs at random from a carload and saw each slab completely across from the middle of one long side to the middle of the other and use the sawdust as the sample; or, drill three 9 mm. holes along one diagonal of each slab, boring completely through and taking care to make fine drillings; the holes should be drilled as nearly as possible at the middle and one-half way between either end and the middle of such diagonals. Go over the drillings or sawings with a powerful magnet to take out any iron which may have come from the drill or saw, and mix the sample thoroughly. The drill or saw must be thoroughly cleaned before use, and no lubricant shall be used in either drilling or sawing.

### METHODS OF ANALYSIS

LEAD—The committee considers the Electrolytic and "Lead Acid" methods described below to be of equal merit, so far as accuracy is concerned, but where laboratories are equipped for electrolysis the electrolytic method is preferred as a time saver.

LEAD BY ELECTROLYTIC METHOD—Place 8.643 grams of the sample[5] in a 400-cc. beaker and add sufficient water to cover the sample. Then add gradually and cautiously 30 cc. of concentrated nitric acid (sp. gr. 1.42); when the action is complete boil the solution for a few minutes to expel nitrous fumes. Wash the watch glass and sides of the beaker and transfer the solution to a 200-cc. electrolytic beaker. Dilute to 125 cc. and electrolyze with a current of five (5) amperes. The time required for the electrolysis is from $^1/_2$ to $^3/_4$ of an hour, depending upon the amount of lead present in the sample. Test the solutions

[1] (A) Heath, *J. Am. Chem. Soc.*, **26** (1904), 1124; (B) Heath, THIS JOURNAL, **3** (1911), 75.

[2] Approved by the Supervisory Committee on Standard Methods of Analysis, American Chemical Society.

[3] *Mem. Am. Acad. Arts and Sciences*, **8**, Part 1, May 20 (1860).

[4] *The Chemical Engineer*, **9** (1909), 4.

[5] The empirical factor weight (8.643) is used instead of the theoretical one (8.66), as the dried dioxide is liable to contain some adherent and included water, expelled with difficulty. F. F. Smith's "Electro-analysis," 4th edition, p. 102.

for complete precipitation of lead by washing the watch glasses and sides of the beaker, so that the depth of the solution is increased about 12 mm. Then continue the current for fifteen minutes and if the newly exposed surface is still bright, the lead is completely deposited. Wash the anode three or four times with distilled water, once with alcohol and then dry in an oven, or on a hot plate, at 210° C. for 1/2 hour and weigh.

The weight of the $PbO_2$ in milligrams, divided by 100, will give the percentage of lead. The $PbO_2$ deposit can be readily removed by covering the anode with dilute nitric acid and inserting a rod of copper.

The electrodes are cylinders of platinum gauze with 400 meshes per sq. cm. The anodes are 30 mm. in diameter, by 30 mm. high, with a stem 105 mm. long of No. 16 Brown & Sharpe gauge wire (1.29 mm.), making the total height 137 mm. The cathodes are 12 mm. in diameter by 30 mm. high, with a stem 105 mm. long of No. 16 Brown & Sharpe gauge wire, making the total height 137 mm.

LEAD BY "LEAD ACID" METHOD[1]—Place in a 350-cc. beaker 25, 15, 10 or 5 grams of the drillings or sawings, according to whether the spelter is of Grade A, B, C or D, respectively, and add, according to the size of the sample taken, 300, 180, 120 or 60 cc. of "lead acid" (prepared as indicated in footnote below). After all but about one gram of the zinc is dissolved, filter on a close filter and wash out the beaker a couple of times with "lead acid" from a wash bottle. Wash the undissolved matter from the filter into the original beaker with water and dissolve with a small amount of hot 1 : 1 nitric acid. Add 40 cc. of "lead acid," and evaporate until strong fumes of sulfuric acid escape. When cool, add 35 cc. of water (which is the quantity of water evaporated from the "lead acid"), and heat to boiling. Add the first filtrate (containing the greater part of the zinc, and possibly a small amount of lead sulfate), stir well, and allow to stand for at least five hours, preferably over night. Filter on a Gooch crucible, wash with "lead acid," then with a mixture of equal parts of alcohol and water, and finally with alcohol alone. Set the Gooch crucible inside a porcelain crucible in order to avoid reduction of lead by flame gases and mechanical disintegration of the asbestos mat. Ignite for five minutes at the full heat of a Tirrell burner. Cool and weigh as $PbSO_4$.

IRON—Place 25 grams of zinc in a tall 700-cc. beaker and dissolve cautiously in 125 cc. of nitric acid (sp. gr. 1.42). Boil, dilute to about 300 cc., add 10 grams of ammonium chloride, and then ammonia until the precipitated zinc hydroxide has redissolved. Boil, let settle and filter on an 11-cm. S. & S. "Black Ribbon" or similar filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitated ferric hydroxide with hot 1 : 4 sulfuric acid, add 40 cc. of 1 : 1 sulfuric acid, pass through a Jones reductor,[2] wash first with 150 cc. of dilute sulfuric acid and then with 100 cc. of water and titrate with potassium permanganate. The potassium permanganate solution contains approximately 0.2 gram of the crystals per liter. One cc. of permanganate solution will equal about 0.000334 gram of iron. Run a blank with the same amounts of acid and water and correct accordingly.

[1] "Lead Acid" is a solution of one volume of sulfuric acid in seven volumes of water, saturated with lead sulfate. It is prepared as follows: 300 cc. of sulfuric acid (sp. gr. 1.84) are poured into 1800 cc. of water; one gram of lead acetate is dissolved in 300 cc. of water and is added to the hot solution with stirring. The solution is allowed to settle for several days and is siphoned off through a thick asbestos filter for use. When "lead acid" is used it is unnecessary to consider the solubility of the lead sulfate, since the solution is always brought back to the same volume as the volume of "lead acid" originally added; consequently, when the lead sulfate is filtered no more lead remains in the filtrate than was originally added in the "lead acid."

[2] If, before passing the solution through the reductor a large amount of lead sulfate is present it is well to filter it off so as to prevent it from clogging the reductor.

Standardize the potassium permanganate against sodium oxalate. Weigh duplicate samples of sodium oxalate, 0.0200 gram each, an amount which may require between 49 and 50 cc. of the permanganate solution. To convert sodium oxalate to iron, use the factor 0.833.

CADMIUM—Place 25 grams of drillings in a tall 500-cc. beaker; add 250 cc. of water and 55 cc. of concentrated hydrochloric acid and stir. When the action has almost ceased add more acid with stirring, using about 2 cc. at a time, and allowing to stand after each addition of acid, until finally all but about two grams of the zinc have been dissolved. About 60 cc. of acid in all are usually required; it is best to allow the first 55 cc. of acid to act over night. Filter, first transferring one of the undissolved pieces of zinc to the filter, and wash a couple of times with water. Discard the filtrate. Wash the undissolved matter on the filter paper into the 500-cc. beaker, cover, and dissolve in nitric acid. Transfer to a casserole, add 20 cc. of 1 : 1 sulfuric acid and evaporate until fumes appear, take up with about 100 cc. of water, boil, cool, and let settle for several hours (best over night). Filter off the lead sulfate on paper, wash with water, retain the filtrate and discard the lead sulfate. Dilute the filtrate to 400 cc., add about 10 grams of ammonium chloride, and pass hydrogen sulfide for one hour. It is occasionally necessary to start the precipitation of the cadmium sulfide by the addition of a drop or two of ammonia to the dilute solution. Allow to stand until the precipitate has settled, and then filter off the impure cadmium sulfide in a loose-bottomed Gooch crucible; remove the cadmium sulfide by carefully punching out the bottom into a tall 200-cc. beaker. Wipe off any cadmium sulfide remaining on the sides of the crucible, using a little asbestos pulp, add 60 cc. of 1 : 5 sulfuric acid and boil for one-half hour. In case of spelters carrying large amounts of cadmium it may be necessary to add more acid. The dilute acid dissolves cadmium and zinc sulfides, but not lead sulfide. Filter and dilute to 300 cc., add about 5 grams of ammonium chloride and precipitate with hydrogen sulfide again in order to get rid of traces of zinc. In case a large amount of cadmium is present, a third precipitation may be necessary. After the final precipitation, let settle, filter and transfer to a weighed platinum dish, cover, and dissolve in 1 : 3 hydrochloric acid. Also dissolve the sulfide remaining on the filter paper in hot 1 : 3 hydrochloric acid, and add it to the solution in the platinum dish. Add a little sulfuric acid and evaporate the solution until copious fumes escape. Dilute with water, add a few cc. of concentrated nitric acid to oxidize any filter paper shreds, and again evaporate the solution until fumes of sulfuric acid come off freely. Remove the excess of sulfuric acid by heating the dish cautiously, and finally heat to between 500° and 600° C. or to dull redness, and weigh the cadmium as sulfate.

ALTERNATE METHOD FOR CADMIUM—Proceed as above until the cadmium sulfide has been dissolved in hydrochloric acid. Oxidize with nitric acid and filter from sulfur. Transfer the solution to a 200-cc. electrolytic beaker, add a drop or two of phenolphthalein and then pure sodium or potassium hydroxide solution until a permanent red color is obtained. Add a strong solution of pure potassium cyanide with constant stirring until the precipitate of cadmium hydroxide is completely dissolved. Avoid using an excess of the potassium cyanide. Dilute the solution to 150 cc. and electrolyze with a current of five amperes, using gauze electrodes of the same size as in the lead determination. The time required is 1 to 2 hours. The solution should always be tested for cadmium as follows: Raise the liquid in the beaker and then note after twenty minutes the newly exposed surface of the electrode. If it is still bright, the cadmium is completely deposited. Next wash the electrodes with distilled water and then with alcohol. Dry at 100° C., cool and weigh. The increase is metallic cadmium.

SCOVILL MANUFACTURING CO. WATERBURY, CONN.

# NOTES AND CORRESPONDENCE

## NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES NEW YORK CITY, SEPTEMBER 20 TO 25, 1915

America's first Exposition of Chemical Industries will be held in New York City during the week of September 20th, in the New Grand Central Palace. The exposition is to be managed by Messrs. Charles F. Roth and Adriaan Nagelvoort, assisted by an advisory committee composed of the following prominent chemists and chemical engineers:

RAYMOND F. BACON, Director Mellon Institute of Industrial Research.
CHARLES H. HERTY, President American Chemical Society.
A. D. LITTLE, President A. D. Little, Inc.
R. P. PERRY, Gen. Manufacturing Manager Barrett Manufacturing Co.
WM. COOPER PROCTER of The Procter & Gamble Co
E. F. ROEBER, Editor *Metallurgical and Chemical Engineering.*
GEORGE D. ROSENGARTEN, President American Institute of Chemical Engineers.
T. B. WAGNER, Corn Products Refining Co.
UTLEY WEDGE, Tennessee Copper Co.

Expositions of Chemical Industries have been held in the past at Turin, Stuttgart, Berlin and other European cities with great success. The first Exposition of Chemical Industries held in London in 1911 and the second in 1913 were limited in scope and embraced only a few of the industries, but were tremendously successful.

The mind of the whole country is at this time particularly interested in all that pertains to chemical industries, and the movement toward an exposition of this character has met with unparalleled enthusiasm, both in the profession and industries.

This exposition will be conducted in keeping with the national importance and dignity of the chemical industries. Its scope is a broad one, being designed to embrace the products, processes, apparatus and machinery manufactured for, of, and by the American Chemical Industries, such as: coal products, wood products, petroleum and its products, metals, minerals, water and sewage purification, air, gases, glass and ceramics, oils, varnishes, plastics, rubber, leather and glue, etc.

Working exhibits will be in continuous operation while the exposition hall is open, giving visitors ample opportunity of seeing for the first time the processes or apparatus in actual work.

A convention hall will be devoted to meetings of the various chemical societies, to lectures, and lantern slide and motion picture exhibits to which the public will be invited.

All inquiries should be addressed to the "National Exposition of Chemical Industries, New Grand Central Palace, 46th St. and Lexington Ave., New York City."

## ON THE INDUSTRIAL SYMPOSIUM AT NEW ORLEANS

*Editor of the Journal of Industrial and Engineering Chemistry:*

The industrial symposium at New Orleans was apparently an attempt to present concisely the achievements of applied chemistry. This effort on the part of the Industrial Section to have short papers of somewhat general interest presenting the results attained by chemists in the various branches of industry is good, since it gives chemists an opportunity to become acquainted with a large number of processes and the methods employed for their development. Such data, if properly prepared and presented, should be of valuable assistance to any chemist, in that it may be suggestive and helpful in the development of his own particular investigations.

The fate and value of the symposium idea will, however, depend largely on the care taken in the preparation of the papers to be presented. Though it is not reasonable to expect that during the preparation of articles for the first symposium all the possibilities and difficulties could be foreseen, still it should be possible so to develop this idea that each successive symposium will be a closer approach to some ideal.

The present statement is an attempt to show some of the possibilities which might be developed for future symposiums. For this purpose a general criticism is given of the papers presented at the first symposium. Let it be understood, however, that there were several excellent papers to which this criticism does not apply. In fact these few interesting papers inspired the criticism of those others which did not show as much thought and care in preparation as the subjects deserved.

Insofar as the titles of papers given at the symposium are concerned, one is led to suspect that the subject matter in each is of a similar nature. In a way this is true—the papers do deal with "contributions of the chemist" to the various industries. But they do *not*, in most cases, as one might infer, tell what the chemist, *as a chemist*, has contributed. Instead we have given what the chemist, as an engineer, a business man, a statistician, or as an advertiser, has been able to do for a given industry. Now there surely can be no objection to a chemist being, besides a chemist, an engineer, a business man or an advertiser, or all put together. But if a so versatile chemist is to give a talk, it might be of interest to some of his audience to know beforehand just which one of his various interests or accomplishments he is to tell about.

Many chemists use their chemistry as a "stepping stone" to a business career; others have ideas which they wish to "put across;" this requires that they advertise themselves in order to get a hearing, and there are others with still different "axes to grind," but sad to relate, there seem to be but few who are in chemistry to develop it as a science without much regard to personal ambitions.

Most of us, however, are in chemistry for what *we* can get out of it and it does not appear that this is anything to be particularly ashamed of. If there is any curse in this, it certainly could be made a blessing if those who have been able to use chemistry as a means to an end would frankly tell others how they attained that end.

This can best be done at a symposium. In this first attempt it would appear that the titles given to papers were misleading and that the papers themselves were in many cases difficult to comprehend, due to the fact that they were made up of a confused mass of statistics, chemistry, business methods, engineering practice and perhaps a personal advertisement of what the author can do for a consideration. Taken alone, any one of these topics would be interesting; as a confused jumble, they may be impressive but are certainly not very illuminating.

A short, clear statement of a single subject will carry more weight and be remembered longer and certainly will be less of a bore to an audience than a large mass of poorly digested facts and fancies.

It would seem, therefore, that the aim of such a symposium should be to have presented papers which are short, clear statements of achievements or possibilities, each one dealing with a single subject whose title gives at least some indication of the context.

All this, of course, requires work and probably an editor or editing committee whose duties would not be altogether pleasant. It might become their duty to refuse some of our *very best* chemists the privilege which they have so long enjoyed, of talking at great length in the attempt to impress their audience, apparently, rather than to educate them.

It would appear, nevertheless, that there are great possibilities in the symposium idea, and *these* suggestions are offered for what they may be worth.

G. A. RANKIN

WASHINGTON, D. C.
May 10, 1915

## ON ZINC POISONING

*Editor of the Journal of Industrial and Engineering Chemistry:*

The comment of Dr. J. W. Luther, in the May issue, on the review of W. Gilman Thompson's "Occupational Diseases" is of interest as adding to the evidence that industrial diseases due to zinc are rare in zinc works. His statement that the connection between zinc fumes and brass founders' ague ("brass shakes," "spelter chills") is not proven and that the balance of evidence is in favor of the trouble being due to copper vapor, seems to be based on the negative evidence that in seven years professional connection with a modern zinc plant he has never seen a case of illness attributable to zinc.

There is considerable evidence that "spelter chills" may be caused by the inhalation of the vapor of pure zinc. Lehmann[1] produced the malady in several different persons, including himself, by the inhalation of the oxide fumes resulting from the burning of Merck's C. P. zinc. The symptoms were carefully studied, and agreed with those of the "shakes."

Siegel[2] found that the "shakes" occurred in foundries where no copper could be found in the fume. Hayhurst[3] states that zinc chills existed in 1910 among the zinc smelters of La Salle, Ill., where the ores used contain no copper. Hayhurst also gives the term "smelters' shakes" as one of the common names for the disease.

A gentleman now in the brass foundry business stated to the writer that he had formerly been connected with zinc smelting and that he had seen cases of "spelter shakes" in the smelters that were of the same nature as the "brass shakes."

The chief chemist of a large zinc company stated to the writer that he had never heard of a case of "shakes" in the smelters. Not long afterward, a younger chemist of the same firm told the writer that the "shakes" were known there to the furnace men at least, and that in work where zinc chloride was present and fumes were evolved the trouble was worse than when the oxide only was present, as would be expected from the greater volatility of zinc chloride.

It is doubtless true that in modern zinc smelters, the "chills" are either absent, uncommon, or not severe enough to cause those afflicted to seek medical aid. It is extremely rare that a case of "shakes" gets to a physician, even in the heart of the brass rolling mill district,[4] and since it is a question whether even oft-repeated cases of "shakes" injure a workman's general health in addition to giving temporary discomfort, even careful physical examinations might not show whether or not a workman had had the "shakes."

Hansen's account of poisoning by copper fumes gives no mention of chills among the symptoms. Anyone who has experienced the "shakes" as often as the writer has, will, he feels sure, agree that had the effects of the copper fumes been the same as those of fumes from brass high in zinc, no one would be likely to omit this symptom.

It is very possible that the traces of copper volatilized or mechanically carried along with the zinc oxide may aid in producing the "shakes" or aggravate the effect that would be produced by zinc fumes alone. But since copper is so slightly volatile at the pouring temperatures of brass, and zinc so greatly volatile, it is only reasonable to ascribe a part at least of the ill effects of the fumes from brass to the constituent present in largest amount, namely, zinc oxide.

Anyone who wants to satisfy himself of the truth of the matter can emulate Lehmann, by heating a pound or so of C. P. zinc to 920° C. in a small unventilated room and inhaling the fume for a few minutes. If Dr. Luther is correct, there should be no ill after-effects. If Lehmann is right, the experimenter will pass a miserable evening after the experiment. Since Dr. Luther attacks the zinc oxide theory of the cause of "shakes," the writer feels that the burden of proof is on Dr. Luther and will gladly give him a chance to repeat Lehmann's experiment before the writer tries it.

ITHACA, NEW YORK
May 10, 1915

H. W. GILLETT

[1] Lehmann, K. B., *Giess-oder Zinnfieber. Arch. f. Hyg.*, **72** (1910), 358–381.
[2] Siegel, *J. Das Giessfieber. Vrtjschr. f. gerichtl. Med.*, **32** (1906), 174.
[3] Hayhurst, E. R., "Occupational Brass Poisoning—Brass Founders' Ague," *Am. Jour. Med. Sci.*, **145** (1913), 730.
[4] See Gillett, H. W., "Brass Furnace Practice in the U. S.," Bureau of Mines, *Bull.* **73** (1914), 263.

## ON THE CAUSE OF "BRASS FOUNDERS' AGUE"

*Editor of the Journal of Industrial and Engineering Chemistry:*

Referring to my review of Thompson's "Occupational Diseases,"[1] Dr. J. W. Luther states[2] that "In this review the statement is made that 'brass founders' ague is more likely due to the inhalation of zinc oxide and not zinc fume.' This statement is based on visits made to brass foundries."

The above-mentioned quotation by Dr. Luther had no such basis, but was made on the authority of one who has the highest reputation as an expert on industrial hygiene, Professor K. B. Lehmann, of the University of Würzburg. Lehmann has reported[3] that "brass founders' ague" is a zinc poisoning due to the inhalation of zinc oxide he found that he could easily produce typical symptoms in man by inhalation of the fumes given off in burning chemically pure zinc. Prior to this careful experimental inquiry, Sigel had expressed the opinion[4] that the symptoms of poisoning resulted from the inhalation of superheated zinc fumes.

For Dr. Luther's further information, I may say that Hayhurst[5] has considered occupational brass poisoning ("brass founders' ague") at some length; Grempe[6] has investigated the industrial diseases among workers in brass, lead and copper, and regards brass and lead poisoning as equally dangerous; Moerl[7] had discussed sanitation in the brass foundry, and gives an account of the measures which may be adopted to minimize brass poisoning; Graham-Rogers[8] regards "brass founders' ague" as zinc poisoning; and Schwartz and Sicard[9] conclude that zinc, and not copper, is the cause of the disease, although in finishing processes the copper may be inhaled and give rise to symptoms of chronic poisoning.

I do not agree with Dr. Luther when he contends that "the balance of evidence is in favor of the trouble being due to the vapor of copper." Notwithstanding the finding of Goodman,[10] who detected copper in the urine and sweat of a brass worker, it is clear from the investigations of Lehmann that while "brass founders' ague" does not occur among zinc workers, it may be regarded as a form of acute industrial zinc poisoning. So far as I can learn, Lehmann has conducted the only thorough investigation of the pathology of the peculiar train of symptoms which may be set up by the pouring of brass; and he shows experimentally that "castors' fever" is directly or indirectly caused by zinc poisoning.

W. A. HAMOR

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
PITTSBURGH, May 10, 1915

[1] THIS JOURNAL, **6** (1914), 871.
[2] *Ibid.*, **7** (1915), 451.
[3] *Arch. Hyg.*, **72** (1910), 358; see also *Idem*, **28**, 300.
[4] *Vierteljahrsschr. ger. Med.*, **32** (1906), 185.
[5] *Trans. 15th Intern. Congr. Hyg. and Dem.* **3**, 764.
[6] *Chem. Techn. Rep.*, **38** (1914), 191; also *Elektrochem. Z.*, **21**, 57 and 85.
[7] *Am. Inst. Metals*, September 7–11, **1914**.
[8] *Rept. N. Y. State Commissioner of Labor*, **1911**.
[9] *Med. Rept. Cornell Univ. Med. College*, January, **1905**.
[10] *Munch. med. Wochschr.*, **58**, 624; cf. Schwartz and Sicard, *supra*.

# PERSONAL NOTES

The Franklin Medal, the highest recognition in the gift of The Franklin Institute of the State of Pennsylvania, has recently been awarded to Heike Kamerlingh Onnes for his low-temperature research, and to Thomas Alva Edison for his "numerous basic inventions and discoveries forming the foundation of world-wide industries, signally contributing to the well-being, comfort and pleasure of the human race." The Medal Fund was founded on January 1, 1914, by Samuel Insull. Awards of the medal are to be made annually to those workers in physical science or technology, without regard to country, whose efforts, in the opinion of the Institute, have done most to advance a knowledge of physical science or its applications. The medal awarded to Prof. Onnes was received on his behalf by His Excellency, Chevalier van Rappard Minister from the Royal Netherlands Government, at the stated meeting of the Institute on the evening of Wednesday, May 19th, and at this meeting Mr. Edison was the guest of the Institute and received his award in person. Following the presentations, an address entitled "Electricity and Modern Industrial Growth" was delivered by Mr. Insull.

M. Louis Moissan, son of the late Professor Moissan, and assistant at the École supérieure de Pharmacie at Paris, who died on the field of battle on August 10th, left to his school, in addition to the scientific books and apparatus of his father, the capital sum of 200,000 francs for the foundation of two prizes —one for chemistry (prix Moissan), and one for pharmacy (prix Lugan), in memory respectively of his father and his mother, *née* Lugan.

Dr. Frank K. Cameron spoke on "The Utilization of Natural Resources for Fertilizers," before the Rochester Section of the A. C. S., on May 3rd. Dr. Cameron also lectured on the "Cement Industry as a Source of Fertilizer Material," at the Spring Meeting of the Lehigh Valley Section of the A. C. S., held at the Country Club of Northampton County, Pennsylvania, on May 12th.

Franklin Guiterman, General Manager of the Colorado Department of the American Smelting and Refining Company, and one of the leading metallurgists of the country, died of pneumonia at the age of 52 years at his residence in New York City, on May 9th. He was educated in this country and studied mining engineering at the University of Freiburg, Germany, which has honored him for his discoveries of improvements in the processes of extracting gold, silver, copper and lead. Mr. Guiterman was also President of the Chesapeake Coal and Coke Company and of the New River Collieries Company.

The program of the June 11th meeting of the New York Section of the A. C. S. is as follows: "Studies on Amylase VIII–XII," by H. C. Sherman, M. D. Schlesinger, A. W. Thomas, A. P. Tanberg and P. W. Punnett, all of Columbia University; "Nephelometry (Photometric Analysis), History of Method and Demonstration of Instruments," by P. A. Kober and S. A. Graves, Harriman Research Laboratory; "On the Rate of Evaporation of Ether from Oils and Its Application in Oil-Ether Anesthesia," by Charles Baskerville, College of the City of New York.

A joint excursion of the Pittsburgh Sections of the American Electrochemical Societies and the A. C. S. was made to the plant of the American Zinc and Chemical Company at Langelogh, Pa., on Saturday afternoon, May 22nd.

The Maryland Section of the A. C. S. made an inspection trip by motor of the water system of the Baltimore County Water and Electric Supply Company, on May 15th.

A meeting of the Maine Section of the A. C. S. was held in Auburn and Lewiston on May 1st; the program included the following papers: "Recent Progress in Synthetic Dyestuffs," Mr. W. N. Watson, Instructor in Chemistry, Bates College; "A City's Milk Supply," Mr. H. F. Ryder, Bacteriologist to the Turner Center Dairying Association; "Coal Specifications, Sampling and Analysis," Mr. P. Barker, Fuel Engineering Dept. of A. D. Little, Inc., Boston; "Sodium Silicate in the Paper Mill," Mr. J. N. Stephenson, Instructor in Chemistry, University of Maine; "Preparation of Monochloracetic Acid," Mr. C. H. Higgins, Bates College. Three excursions were conducted, one to the Bleachery, another to a shoe-shop and the Turner Center Creamery, and the third to the Tourmaline mines at Mt. Apatite.

A Technical Section has been organized within the American Paper and Pulp Association for the interchange of ideas among its members, the encouragement of original research, and to stimulate interest in the science of pulp and paper making. Henry E. Fletcher, of the Fletcher Paper Company, Alpena, Mich., is chairman of the section, and Thomas J. Keenan, F. C. S., editor of *Paper*, New York, is secretary-treasurer.

The Iowa Section of the A. C. S. has elected the following officers: *President*, J. N. Pearce; *Vice-President*, J. A. Coss; *Councillor*, W. S. Hendrixson; *Secretary-Treasurer*, P. A. Bond. The Spring Meeting of the Section was held on May 1st, in connection with the meeting of the Iowa Academy of Science at Iowa City.

Secretary Olsen of the American Institute of Chemical Engineers extends an invitation to the members of the A. C. S. to participate in the Institute's trip to the Pacific coast and their subsequent meetings. Copies of this program may be obtained from John C. Olsen, Cooper Union, New York City.

The 28th General Meeting of the American Electrochemical Society will be held in San Francisco, September 16, 17 and 18, 1915. The American Society of Civil Engineers, the American Society of Mechanical Engineers, the American Institute of Electrical Engineers and the American Institute of Mining Engineers expect to hold their meetings at the same time and arrangements are under way for joint sessions with some of these societies.

Dr. Otto N. Witt, professor of chemical technology in the Technical High School at Charlottenburg, Germany, died on March 23rd, aged sixty-four years.

The Rensselaer Polytechnic Institute announce that Mrs. Russell Sage has given $100,000 to the school, and Mr. Alfred T. White of Brooklyn, a graduate, $50,000. The money is to be used in the erection of dormitories and a dining hall.

A new publication called the *Illinois Chemist* made its appearance at the University of Illinois in May. Four chemistry organizations coöperate with the chemistry department in issuing this new quarterly. It will publish among other things, information in regard to research work, results of experiments and notes on the work of alumni in the science.

Handsomely engraved invitations have been issued by the Trustees and Faculty of the Worcester Polytechnic Institute, for the celebration of the Fiftieth Anniversary of the founding of the Institute, to be held in Worcester, Massachusetts, June 6th to 10th inclusive. A program consisting of the annual Commencement exercises and speeches by men of international reputation, has been arranged. President Wilson, who was the Commencement orator twenty-five years ago, has expressed a desire to be present at this anniversary, and he will probably be in Worcester on the ninth of June. General George W. Goethals has already accepted an invitation to be present.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Foreign Commerce and Navigation of U. S.** 907 pp. Cloth, $1.00. This is a voluminous set of statistics covering the commerce of this country for the year ending June 30, 1914. Only a few of the data are of chemical interest.

**South American Market for Soap.** Special Consular Reports 66. 16 pp. Paper, 5 cents. This is one of the series of publications of this Bureau intended to increase the commerce of the South American countries. Information is given as to prices, consumption, grades, packing, etc., as well as some data on the character of the soaps which are in demand or in common use in the various South American countries.

**Foreign Markets for Coal.** Special Consular Reports 69. 24 pp. Paper, 5 cents. This is similar to the article described in the previous abstract. It covers however, the principal European and some other countries as well as the South American countries. Information is given as to the character of the coal in demand for different purposes in the several districts.

**The Pottery Industry.** Miscellaneous Series 21. 709 pp. Paper, 50 cents. This is a detailed report on the cost of production in the earthenware and china industries in the United States, England, Germany and Austria. It is the result of a detailed study of the origin and growth of the industry in each country and includes a description of the buildings, machinery and equipment employed, the materials used, the methods of manufacture, costs, the character of the employees and their wages, and a general discussion of the conditions which affect manufacturing costs and efficiency. The elaborate technical descriptions included make it a valuable guide to the commercial processes in use at the present time for each portion of the work. The character of the raw materials used and various criteria for judging its quality are discussed in an extended section.

**Japanese Market for American Lumber.** Special Agents Series 94. Franklin H. Smith. Paper, 5 cents. This describes the forest resources of Japan; the importations; the wood-using industries; methods of buying; and gives general information including freight rates, and names of buyers and users of wood and wood products.

**Tobacco Trade of the World.** Special Consular Report 68. 48 pp. Paper, 5 cents. A statistical review of the conditions of the tobacco trade with general export and import data.

**South American Market for Jewelry and Silverware.** Special Consular Report 70. 23 pp. Paper, 5 cents. Similar to the above report on soap.

**Cooking Fats in South America.** Special Consular Report 67. 15 pp. Paper, 5 cents. Similar to above report on soap.

### COMMERCE REPORTS—APRIL, 1915

Although the German embargo on **potash** still exists, the German Potash Syndicate has published the amounts that will be furnished when the embargo is raised. (P. 10.)

The United States Department of Agriculture is stimulating the cultivation of **soy beans** in the southern states. (P. 28.)

The English government has acquired almost the entire crop of natural **indigo** in India. (P. 34.)

Arrangements have been made in Germany for an unrestricted **sugar beet** crop, 75 per cent of which is to be used for sugar production, and the balance for stock food or **alcohol** manufacture. The planting of sugar beets for seed is to be only 50 per cent of the normal. (P. 69.)

While the American demand for **paper pulp** from Norway and Sweden continues, the output is restricted, owing to difficulty in importing sulfur, coal, etc., and to high freight rates. (P. 70.)

Results of exploration for **petroleum** in Alberta, Canada, are promising, though not yet definite. (P. 74.)

Sweden now imports **coal and coke** from Germany. (P. 91.)

Statistics of the mineral products of Canada include **gold, silver, copper, lead, coal, coke, talc, feldspar, mica and pyrites.** (P. 104.)

While natural **indigo** is again being cultivated in China there will be little or none available for export. (P. 107.)

The Philippine Insular Government has just put into effect new standards for **fiber,** etc. (P. 161.)

The cultivation of "New Zealand flax" in the Azores, as a source of **fiber for paper stock** is increasing. (P. 174.)

The cultivation of **peanuts** is an important industry in Argentine. (P. 178.)

Efforts are being made to reorganize the **sugar industry** of western China, through the aid of American experts. (P. 212.)

The use of henequen fiber (commonly known as sisal) from Yucatan as a **substitute for jute** in the manufacture of bagging, etc., is being urged. (P. 218.)

A joint meeting of American and British committees on **electrical standards** has been held in London, the results of which will be confirmed by the American Institute of Electrical Engineers. (P. 239.)

Arrangements have been made for the release of two cargoes of German **dyestuffs** *via* Rotterdam, for consignment to the Secretary of Commerce and distribution to the American Textile Alliance. (P. 257.)

A factory has been started in Scotland for the extraction of **radium** from uranium ores and residues. (P. 268.)

"Jatoba gum," from Brazil, is now being used in **varnishes.** (P. 269.)

The Russian government has announced an international competition for premiums to be awarded to persons inventing new methods or processes which will consume considerable quantities of **alcohol.** (P. 293.)

The price of **drugs** in England and the United States has increased materially, examples being **aspirin, salicylic acid, phenacetin, acetanilide, morphine, codeine, atropine, hyoscyamine, cocaine, lanolin, veronal, and salvarsan.** (P. 298.)

A conference of the various government departments has been called by the Bureau of Standards for the purpose of drawing up **standard specifications for soap.** (P. 299.)

A company has been organized to develop the **asphalt and mineral oil** deposits of Leyte Province, Philippine Is. (P. 307.)

In notes on the manufacture of American **dyestuffs,** attention is called to the increasing number of plants for the recovery of benzene, etc., and to additional plants or expansion of plants, for making dyestuffs. As yet no alizarin or synthetic indigo have been made in this country. An increased production of vegetable dyes and mineral dyestuffs is noted. (Pp. 338–40.)

Statistics of the **sugar industry** of Russia are given. (P. 343.)

The price of **tin plate** in England has advanced considerably, due to shortage of steel, tin and acid. (P. 349.)

The extraction of **mercury** in Austria is confined to the India mine. (P. 355.)

The new **weights and measures** law of China recognizes the metric as well as Chinese units. (P. 382.)

An **antimony smelter** is being erected at San Luis Potosi, Mexico. (P. 432.)

**Anthracite coal** now mined in China contains 78.81 per cent carbon, 14.88 per cent volatile matter, 0.17 per cent sulfur, 5.29 per cent ash, and 0.85 per cent moisture. (P. 442.)

The Bureau of Foreign and Domestic Commerce has requested all American consumers and manufacturers of **dyestuffs and chemicals** to use that Bureau as a mutual clearing house of information. (P. 465.)

The price of **rubber** in Russia has doubled. (P. 475.)

The manufacture of **superphosphate** has been started in Slobodsk Province, Russia. (P. 481.)

Statistics of the United States imports of **potash salts** are given. (P. 484.)

The present shortage of the Russian **coal supply** is due principally to lack of workmen and poor transportation. (P. 500.)

**Copper pyrite and other copper ores** have been discovered near Elisavetpol, Russia. (P. 502.)

SOME SPECIAL SUPPLEMENTS TO COMMERCE REPORTS—APRIL

British West Indies—Trinidad and Tobago—No. 22*a*.
Spain—Canary Islands—No. 15*a*.
Japan—No. 55*a*.
Scotland—No. 19*f*
Birmingham—No. 19*g*.
France—No. 5*a*.
United Kingdom—Manchester—No. 19*e*.
Argentina—Rosario—No. 38*b*.
Algeria—No. 63*a*.
New Zealand—No. 61*a*.
Portugal—No. 11*a*.

RECENT DEMANDS FOR AMERICAN GOODS OWING TO THE WAR (PP.)

Hongkong—42, 136
Steel and Iron
Window glass
Japan—113
Paints
Venezuela—193
Cottonseed oil
Brazil—274
Cement and Metal lath
France—282
Lithopone
South Africa—283
Fertilizers
Azores—507, Cement
Spain—421
Dyes
Drugs
Fats
Lubricating oils
Nitrates
Phosphates

STATISTICS AND INFORMATION REGARDING EXPORTS TO THE U. S.

Trinidad—Sup. 22*a*
Asphalt
Balatex gum
Copaiba balsam
Bitters
Bones
Cocoa and Copra
Cocoanuts
Cocoanut oil
Divi-divi
Gold
Hides
Kola nuts
Molasses
Tonka beans
Petroleum
Canary Islands—Supplement 15*a*
Cochineal
Hides
Pumice
Japan—Sup 55*a*
Agar-agar
Soya bean oil
Camphor
Charcoal
Coke and coal
Ginger
Copper
Glass
Gold
Graphite
Gut strings
Hides
Iron
Manganese
Matches
Drugs
Menthol
Antimony
Bronze and Brassware
Paper
Peanuts
Porcelain
Sulfur
Superphosphate
Vegetable wax
Manchester, England—Sup. 19*e*
Asbestos
Chemicals
Dyestuffs
Glassware
Hides
Pig iron
Linoleum
Paper
Paper stock
France—Sup. 5*a*
Albumen
Aluminum
Bones
Carbons
Chemicals and Drugs
Artists' colors
Peanut oil
Glassware
Glue and gelatine
Glycerine
Hides
Millstones
Mineral waters
Paper
Photographic supplies
Platinum
Iridium
Palladium
Radium
Rags
Saffron
Precious stones
Vanilla
Wines
Hongkong—291
Cassia and Cassia oil
Birmingham, England—Sup. 19*g*
Celluloid
Precipitated chalk
Ammonium carbonate
Ammonium chloride
Phosphorus
Potassium bicarbonate
Sulfur
Sodium bicarbonate
Copper articles
Diamond dust
Earthenware
Explosives
Gelatine and Glue
German silver
Glass
Hides
Rubber goods
Steel
Watch jewels
Leather
Chamois
Nickel alloys
Olive oil
Paints
Photographic films
Artificial silk
Silver plate
Soap
Tinware
Rosario—Argentina—Sup. 38*b*
Bones
Copper
Quebracho extract
Fertilizers
Hides
Algeria—Sup. 63*a*
Dyewood
Cork
Crude tartar
Geranium oil
Hides
Rags
Vegetable fiber
Glasgow—Sup. 19*f*
Aluminum
Antimony
Potash
Ammonium sulfate
Creosote oil
Tanning extract
Magnesite
Coal and coke
Copper articles
Fire-clay goods
Flax
Ramie
Glass
Hides
Gutta percha
Pig iron
Steel
Paper stock
Paper
Whiskey
New Zealand—Supplement 61*a*
Hemp
Hides
Kauri gum
Portugal—Supplement 11*a*
Beeswax
Ergot
Gum copal
Argols
Uranium compounds
Cork
Olive oil
Hides
Rubber
Rags
Sulfur ore
Glycerine
Tungsten ore
Wood pulp
Wines

BUREAU OF LABOR STATISTICS

**Lead Poisoning in the Manufacture of Storage Batteries.** Alice Hamilton. Bulletin 165. 38 pp. Paper, 10 cents. This is a well illustrated bulletin which includes a description of the processes used commercially in this country and abroad for making storage batteries. Each part of the manufacture is described in considerable detail, primarily, of course, from the standpoint of the poisoning hazard, but nevertheless in such form that considerable interesting information on this industry is made available.

WATERTOWN ARSENAL

**Report of Tests of Metals and Other Materials Made with United States Testing Machine at Watertown Arsenal, Fiscal Year 1914.** War Department Document, 477. 217 pp. and 112 plates. Cloth, 75 cents. This report covers the large number of tests made on iron, steel, and other structural materials, at Watertown Arsenal during the year ending June 30, 1914.

GENERAL SUPPLY COMMITTEE

**Specifications and Proposals for Supplies for Executive Departments and Other Government Establishments.** Additional sections of this publication on which bids for Government supplies are submitted have appeared as follows: Class 4, Drugs and medicines, and chemicals; Class 10, Groceries and provisions, meat and meat products, fish, and household supplies; Class 14, Fuel and ice, including as Appendix A, a description of the methods of sampling coal deliveries. See This Journal, **7**, 455.

OFFICE OF INDIAN AFFAIRS

**Proposals for Supplies.** This is a bid form indicating supplies purchased by this Office for the Indian Service including the following materials some of which are of chemical interest. Groceries, earthenware, glassware, lamps, harness, leather, shoe findings, saddlery, etc., agricultural implements, glass, paints and oils, tin and stamped ware, stoves, hollow ware, tin, hose goods, hardware, iron, nails, plumbers' and steam and gas fitters' tools, fittings, and supplies, etc.

BUREAU OF STANDARDS

**The Composition, Properties, and Testing of Printing Inks.** Circular 53. 35 pp. This circular gives a brief, historical review of printing inks and describes composition of inks now used, discussing the oils, pigments, and driers employed. The essential criteria for judging inks and suggestions as to tests and analyses and the interpretation of analyses are indicated.

**A Study of Some Recent Methods for the Determination of Total Sulfur in Rubber.** J. B. Tuttle and A. Isaacs. Technical Paper 45. 16 pp. This report will be printed in full in This Journal in the near future.

**Standards for Gas Service.** Circular 32, 3rd edition. 197 pp. A thoroughly revised and enlarged edition of the circular which discusses proper requirements as to the quality, purity and pressure of city gas supplies and regulations as to the testing of meters and certain matters of relations between company and consumer. A proposed form for municipal ordinances on this subject and a set of rules suggested for adoption by State Commissions is included and there is a full summary of such requirements as are now in force on this subject in the U. S.

NATIONAL ACADEMY OF SCIENCES

**Turquoise.** Joseph E. Pogue. Memoirs of National Academy of Sciences, Volume 12, Part 2, 3rd memoir. 206 pp. Paper, 40 cents. This memoir gives a study of the history, mineralogy, geology, ethnology, archaeology, mythology, folklore, and technology, with bibliography, etc., of this gem.

GEOLOGICAL SURVEY

**Lavas of Hawaii and Their Relations.** Whitman Cross. Professional Paper 88. 97 pp. Paper, 20 cents. This paper describes in detail the petrography of the Hawaiian Archipelago,

treating each of the larger islands individually. "The paper also discusses the mineral, chemical, and normative composition of the Hawaiian lavas, as well their distribution and association, and the theoretical bearings of the data presented. A map of the islands, photomicrographs of the rocks, a diagram illustrating variation in normative composition of the lavas, and a table of normative ratios and symbols accompany the report."

**Composition of Muds from Columbus Marsh, Nevada.** W. B. HICKS. Professional Paper 95–A. 11 pp. This paper tells of the work done in 1913 and supplements that described previously in Bulletin 540–N. It relates particularly to samples of surface muds and those obtained from drilling a shallow well. "After considering all the facts at hand, the author expresses his belief that large amounts of potash have been absorbed from surrounding or percolating solutions and are held in loosely combined form by the muds of Columbus Marsh and perhaps by the muds of the desert basins in general, while the other salts, being less completely absorbed, have been gradually concentrated through evaporation. This theory explains the presence of the natural brines and salt incrustations with low potash content found in the desert regions of the United States at the present time."

**Reconnaissance of the Geology and Oil Prospects of Northwestern Oregon.** CHESTER W. WASHBURNE. Bulletin 590. 111 pp. Although primarily of a geologic nature this report includes a number of analyses of the natural gas in this district.

**Geology and Water Resources of Tularosa Basin, New Mexico.** O. E. MEINZER AND R. F. HARE. Water Supply Paper 343 317 pp. and 70 illustrations. "Describes the physiography, drainage, and geology of Tularosa Basin, New Mexico, with special reference to its underground resources and their availability for use in irrigation. The paper outlines the routes of travel through the basin, briefly describing the watering places to be found on these routes, and contains analyses of some of the well, spring, and stream waters in this and adjoining areas."

**Ground Water in Southeastern Nevada.** EVERETT CARPENTER. Water Supply Paper 365. 86 pp. This report discusses the quality and sources of the water in several counties of Nevada and gives other related information of interest.

**List of Publications.** A revised list of all publications of the Geological Survey up to March, 1915, has been prepared. This gives the names, scope, prices, etc., for more than one thousand publications, most of which are still available. A finding list of subjects and authors is included.

### DEPARTMENT OF AGRICULTURE

**Availability of the Nitrogen in Pacific Coast Kelps.** GUY R. STEWART. "Journal of Agricultural Research," **4**, 21–38; also available as a separate. Contribution from the University of California Agricultural Experiment Station. This article discusses the availability of the nitrogen in the several species of kelp which are commercially obtainable and the variation of the quantity of the useful nitrogen with different conditions of the kelp and different methods of treatment. It is concluded that "when using kelp in field practice, it is probable there would be no interference with either ammonification or nitrification from either the kelp or the salts present in it."

**Organic Constituents of Pacific Coast Kelps.** D. R. HOAGLAND. "Journal of Agricultural Research," **4**, 39–58; also available as a separate. A contribution from the University of California Agricultural Experiment Station. A large number of analyses are given to indicate the percentage of the organic constituents of various groups. The economic phases of the question with reference to feeding value and utilization of the organic by-products of the kelp industry are discussed, but no marked commercial possibilities in this direction are noted.

**A Bacteriological Study of Methods for the Disinfection of Hides Infected with Anthrax Spores.** F. W. TILLEY. "Journal of Agricultural Research," **4**, 65–92; also available as a separate. Contribution from the Bureau of Animal Industry. This is primarily a comparison of the Seymour-Jones and the Schattenfroh methods of disinfection. Some tests on other disinfectants are also indicated. It is concluded that neither of the two methods mentioned exerts any injurious effects on the hides or the leather. From the standpoint of effectiveness of the disinfection the Shattenfroh method is given preference although it "cannot be regarded as perfect."

**Home-Made Lime-Sulfur Concentrates.** E. W. SCOTT. Department Bulletin 197. From the Bureau of Entomology. 6 pp. Paper, 5 cents. This describes experiments in making lime-sulfur concentrates and suggests the most satisfactory formulas for this work.

**Potash from Kelp.** Department Report 100. 122 pp. 40 plates and portfolio of 54 maps. Paper, $2.00. This report includes the following five articles: Pacific Kelp Beds as Sources of Potassium Salts (with bibliography), by FRANK K. CAMERON; Kelp Beds from Lower California to Puget Sound, by W. C. CRANDALL; Kelp Beds of Puget Sound, by GEORGE B. RIGG; Kelp Beds of Southeast Alaska, by T. C. FRYE; Kelp Beds of Western Alaska, by GEORGE B. RIGG.

### BUREAU OF MINES

**The Smelting of Copper Ores in the Electric Furnace.** D. A. LYON AND R. M. KEENEY. Bulletin 81. 80 pp. Paper, 10 cents. The bulletin presents: "(1) a critical discussion of the possibility of smelting copper ores in the electric furnace; (2) the results of the experimental work of other investigators on the electric smelting of copper; (3) the results of experiments by the authors on the electric smelting of native copper concentrates and sulfide copper ores; (4) a comparison of the electric with the blast and the reverberatory furnace for copper smelting."

The discussion of the several parts of the subject is accompanied by diagrammatic illustrations of the furnaces employed and experimental data which show results of operation on a small scale. It is concluded that the application of an electric furnace as a substitute for reverberatory or blast furnace is almost always possible since it is usually merely a question of substituting electric heat for the heat derived for the combustion of carbon. It is pointed out in that "in some cases the reaction would take place to better advantage in the neutral atmosphere of the electric furnace than in the reducing or partly reducing atmosphere of the combustion furnace." It is apparent therefore that the relative cost of coke and of electric power is usually the determining factor in choice between an electric furnace and a furnace of coke-fire type.

**The Vapor Pressure of Arsenic Trioxide.** H. V. WELSH AND L. H. DUSCHAK. Technical Paper 81. 20 pp. Paper, 5 cents. The need for further knowledge as to the vapor pressure of arsenic trioxide in the proper designing and control of equipment for condensation of arsenic trioxide from smelter fumes has led to this investigation. A method is described for the determination of the vapor pressure of solids at temperatures at which the vapor pressure is very low (from 0.001 mm. up to a few millimeters). Data are given for the vapor pressure, the heating of sublimation, and the melting points of the two forms of $As_2O_3$. "Preliminary experiments with rather richly arsenical dust from the main flue of a copper smelter show that the arsenic trioxide vapor pressure exerted by it was only about half that exerted by the pure material.

**Coal-Tar Products and the Possibility of Increasing Their Manufacture in the United States.** HORACE C. PORTER. With a chapter on Coal-Tar Products Used in Explosives. C. G. STORM. Technical Paper 89. 19 pp. Paper, 5 cents.

# BOOK REVIEWS

**Hydraulic Cements: Die Chemie der hydraulischen Bindemittel.** By Dr. Hans Kuhl and Dr. Walter Knothe. 51 illus. S. Hirzel, Leipzig, 1915. 347 pp. Price: unbound, 12 Marks; bound, 14 Marks.

This book presents, as stated in the preface, a résumé of our present-day knowledge of the chemistry of hydraulic cements and of the results obtained by the numerous investigators who have been engaged on this subject from the time of Le Chatelier to the most recent work of the Geophysical Laboratory of the Carnegie Institution: the last paper of Rankin and Wright in the *American Journal of Science* for January, 1915, which paper in itself is really a summary of the entire work of this laboratory during the past decade, was not, of course, available to the authors.

This is a valuable summary of the work which has been carried on by numerous chemists and is the first book which covers in a comprehensive way the results of attempts to demonstrate the constitution of Portland cement clinker in the light of the phase rule.

The purely technical side of the cement industry is touched upon only in so far as it is necessary to do so from the chemical point of view, since this has been amply covered in other books. In addition to Portland cement, hydraulic lime, natural cements, puzzolans and slag cements are given adequate consideration.

In general the work presents the completeness in detail which is characteristic of German writers on technical subjects. It can be recommended to all who are interested in such an encyclopaedic work.

Clifford Richardson

**Food Industries: An Elementary Text-book on the Production and Manufacture of Staple Foods.** By Hermann T. Vulté, Ph.D., F.C.S. and Sadie B. Vanderbilt, B.S. 8vo. viii + 309 pages. Published by the Chemical Publishing Co., Easton, Pa., 1914. Price, $1.75.

This new and interesting text-book on the production of foods should prove of value to high school teachers and teachers of household arts on account of its elementary nature. It is not absolutely essential that the student have a knowledge of physics and chemistry because the book takes up the descriptive phase of food production only. The authors also "do not claim to deal with any industry from the purely technical standpoint, but aim to point out the most essential parts of each."

The book is divided into twenty-one chapters dealing with water, wheat, milling, mill products, cereals, breakfast foods, coffee substitutes, breadmaking, leavening agents, starch industries, sugar industry, alcoholic beverages, fats, meat and meat packing, milk, food preservatives, canning, tea, coffee, coco, spices and condiments.

A. W. Thomas

**Stamp Milling and Cyaniding.** By Francis Andrew Thompson, E.M., Head of Department of Mining Engineering, State College of Washington. Published by McGraw-Hill Book Co., New York. 6 x 9, 285 pp., illustrated. Price, $3 net.

This is a text-book on stamp milling and cyaniding of gold and silver ores. The physical and chemical properties of gold and silver, their occurrence and metallurgical properties are briefly outlined in the first three pages, followed by a short summary of the principles of amalgamation. Chapter III is devoted to the stamp mill and its accessories. The stamp and its mechanism, the mortar, foundations and framework, feeders, etc., of several types are described in a general way (34 illustrations). A chapter on stamp mill amalgamation presents the subject in a clear and concise manner. There follows a short outline of variations in practice and of other mills and grinders, with some very good but incomplete notes on tube milling and comparisons of various mills. Part II deals with cyaniding, starting with an outline of the history and chemistry of cyaniding; it treats in the same concise manner the subjects of the preparation of ores for treatment, dissolving gold and silver by agitation and leaching, filtering, precipitation, and the treatment of precipitates. Part III presents the flow sheets of 18 mills in a very interesting way and gives quite a few interesting details.

It is apparent that the author made no attempt to present details of costs in connection with stamp milling or cyaniding as throughout the work costs are referred to only in a general way. The book is clearly for the use of the student and will serve as an excellent introduction to the subjects mentioned; but unless frequent use is made of a little over 1000 references, contained in a well arranged bibliography, to articles in technical journals, society papers, and books, the book will hardly serve the purpose of a complete text-book for stamp milling and cyaniding.

Heath Steele

**Die Nitrocellulosen.** By Dr. C. Haeussermann, Em. Professor at the Technische Hochschule, Stuttgart. Braunschweig: Fried. Vieweg und Sohn, 1914. 34 pp. Price, unbound, 1.60 Marks.

This monograph is a short treatise on the chemical side of the nitrocelluloses. After a four-page introduction, discussing the application and uses of nitrocellulose products in a general way, the author turns his attention to the chemistry involved in the manufacture and, in turn, to the physical properties, effects of light and heat, solubility, behavior towards reagents, and chemical structure of nitrocelluloses. Sections on nitrohydro- and nitrohydroxycelluloses, the nitroderivatives of starches and dextrines, and the nitrous esters of cellulose, complete the pamphlet. The treatment of the material is brief, concise and direct. The references to the literature are almost complete, making the paper a valuable compilation for rapid reading and as a guide to the literature of nitrocellulose.

H. C. P. Weber

**The Examination of Hydrocarbon Oils, and of Saponifiable Fats and Waxes.** By Professor Dr. D. Holde, Subdirector of the Royal Bureau for Testing Materials of Berlin-Lichterfelde, Docent at the Technische Hochschule, Berlin. Authorized translation from the 4th German edition by Professor Edward Mueller, Ph.D., of the Massachusetts Institute of Technology. John Wiley & Sons, Inc., New York. 8vo. 483 pp. Price, $5.00.

This is a most excellent translation of Holde's well-known book, of which the reviewer wrote in 1905 (*J. Am. Chem. Soc.*, **28**, 550), "the work contains much valuable information not to be found elsewhere, and may be warmly recommended to all interested in the subjects treated." The title "Hydrocarbon Oils" is unfortunate (although it is a correct rendering) for they occupy barely half the book. A better one would seem to have been "Oils, Fats, Waxes, Tars, Asphalts, Etc.," for all these subjects are treated in the clear and concise manner which gives the book its value—but naturally from the German standpoint and requirements.

The only slip in translation which has been noticed, is that of "sikkativ" which would better have been rendered "drier" than "siccative."

A. H. Gill

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Boilers: The Design of Steam Boilers and Pressure Vessels.** By G. B. HAVEN AND G. W. SWETT. 8vo. Price, $3.25. Chapman and Hall, London.

**Chemistry—General: Vorschule der Chemie.** By W SCHWARZE 8vo. 176 pp. Price, $0.60 Leopold Voss, Leipzig.

**Chemistry—General: Laboratory Exercises in General Chemistry.** By R. H WILLIAMS AND W. G. WHITMAN 8vo. 161 pp. Price $0.36. American Book Co., New York.

**Chemistry—History: Geschichte der Chemie.** By HUGO BAUER. 2nd Ed. 8vo. 140 pp. G. J. Göschen, Berlin.

**Cyaniding: Stamp Milling and Cyaniding.** By F A THOMSON 8vo. 258 pp. Price, $3.00. McGraw-Hill Book Co., New York.

**Electrical Instruments in Theory and Practice.** By W. H. F. MURDOCH AND U. A. OSCHWALD. 8vo. 374 pp. Price, $2.50. Whittaker and Co., London.

**Engineering: Cyclopedia of Engineering.** 7 vol. 8vo. Price, $19.80. American Technical Society, Chicago.

**Engineering Economics.** By J. C. L. FISH. 8vo. 217 pp. Price, $2.00. McGraw-Hill Book Co., New York.

**Engines: Gas, Gasoline and Oil Engines.** By G. D. HISCOX. 21st Ed. 8vo. 640 pp. . Price, $2.65. Constable and Co., London.

**Explosives: Die Nitrosprengstoffe.** By RICHARD ESCALES. 8vo. Price, $3.75. Veit and Co., Leipzig.

**Explosives: Their Manufacture, Properties, Tests and History.** By ARTHUR MARSHALL. 8vo. Price, $7.00. P. Blakiston's Son and Co., Philadelphia.

**Heat Engineering.** By ARTHUR M GREENE. 8vo 462 pp Price $4.00. McGraw-Hill Book Co., New York.

**Illumination: Modern Illuminants and Illuminating Engineering.** By LEON GASTER AND J. S. DOW. 8vo. 462 pp. Price, $5.00. Macmillan Co., N. Y.

**Iron and Steel: A. B. C. of Iron and Steel.** By A. O. BACKERT. 4to. 338 pp. Price, $5.00. Penton Publishing Co., Cleveland.

**Lathes: Their Construction and Operation.** By G W BURLEY 8vo. Price, $1.00. Scott, Greenwood and Co., London.

**Machinery: Machinenelemente.** By FRIEDRICH BARTH. 138 pp. G. J. Göschen, Berlin.

**Mechanics: Applied Mechanics for Engineers.** By HERBERT HANCOCK. 12mo. Price, $2.40. Macmillan Co., New York.

**Oil Geology: Practical Oil Geology.** By DORSEY HAGER. 16mo. 149 pp. Price, $2.00. McGraw-Hill Book Co., New York.

**Oils: The Examination of Hydrocarbon Oils.** By D. HOLDE. 8vo. 483 pp. Price, $5.00. John Wiley and Sons, New York.

**Oils and Fats: The Chemical Technology of Oils, Fats and Waxes.** Vol. 3. By JULIUS LEWKOWITSCH. 5th Ed. 8vo 492 pp. Price, $5.00. Macmillan Co., New York.

**Paints: The Chemistry of Paints and Painting.** By A. H. CHURCH. 4th Ed. 12mo. 388 pp. Price, $2.50. Macmillan Co., New York.

**Petroleum: Researches sur la Toxicité du Pétrole et Quelque-unes de ses Actions Physiologiques.** By H. LEGUIDIC AND C. TURLAIS. 8vo. 120 pp. Price, $0.60. J. B. Bailliére et Fils, Paris.

**Phase Rule and Its Applications.** By ALEXANDER FINDLAY. 4th Ed. 8vo. 381 pp. Price, $1.50. Longmans, Green and Co., London.

**Pottery Making.** By JUDSON T. WEBB. 12mo. 72 pp. Price, $1.00. Lewis Institute, Chicago.

**Pumps: Centrifugal Pumps.** By ROBERT L. DAUGHERTY. 8vo. 192 pp. Price, $2.00. McGraw-Hill Book Co., New York.

**Pumps: Direct-acting Steam Pumps.** By FRANK F. NICKEL. 8vo. 258 pp. Price, $3.00. McGraw-Hill Book Co., New York.

**Rare Earths: The Rare Earth Industry.** By SYDNEY J JOHNSTON 8vo Price, $4.80. Crosby Lockwood, London

**Thermodynamics: A Text-book of Engineering Thermodynamics: an Abridgment of "Engineering Thermodynamics."** By C. E LUCKE AND J. J. FLATHER 8vo. 688 pp. Price, $5.00 McGraw Hill Book Co., New York.

**Valves and Valve Gears.** By FRANKLIN FURMAN. 8vo. 253 pp. Price, $2.50. John Wiley and Sons, New York.

**Water Conservation: Conservation of Water by Storage.** By G. F. SWAIN. 8vo. 84 pp. Price, $3.00. Yale University, New Haven.

**Welding: A Text-book on Welding and Cutting Metals by the Oxy-acetylene Process.** By THE VULCAN PROCESS CO 3rd Ed 8vo. 134 pp. Price, $1.50. The Vulcan Process Co., Minneapolis.

**X-Rays: X-Rays and Crystal Structure.** By W. H BRAGG AND W. L. BRAGG. 8vo. 228 pp. Price, $2.25. Macmillan Co., New York.

## RECENT JOURNAL ARTICLES

**Aluminum Nitride: Ueber Sublimation und Dissoziation von Aluminiumnitrid.** By F FICHTER AND G. OESTERHELD. *Zeitschrift für Elektrochemie*, Vol. 21, 1915, No. 3/4, pp. 50-54.

**Ammoniac: Untersuchungen uber Ammoniak.** By F HABER *Zeitschrift für Elektrochemie*, Vol. 21, 1915, No. 5-6, pp. 89-106.

**Asphalt: Natur- und Kunstasphalt.** By J. MARCUSSON. *Kunststoffe*, Vol. 5, 1915, No. 7, pp. 75-78.

**Ball-bearings: Ueber Kugellager.** By J. FISCHER. *Elektrotechnik und Maschinenbau*, Vol. 33, 1915, No. 12, pp. 141-142.

**Barite of the Appalachian States.** By THOMAS L. WATSON AND J. S. GRASTY. *The Chemical Engineer*, Vol. 21, 1915, No. 4, pp. 135-143.

**Cadmium: Physikalisch-chemische Studien am Kadmium.** *Zeitschrift für physikalische Chemie*, Vol. 89, 1915, No. 4, pp. 493-510.

**Coal: Occurrence of Chlorine in Coal.** By A. DEWAELE. *The Analyst*, Vol. 40, 1915, No. 469, pp. 146-147.

**Coke: The Soluble Chlorides and Total Chlorine in Some English Cokes.** By STANLEY W BRIDGE *The Analyst*, Vol. 40, 1915, No. 469, pp. 143-146.

**Concrete: Moment of Inertia of Reinforced Concrete Sections.** By JOHN A. DAVENPORT. *Concrete*, Vol. 10, 1915, No. 4, pp. 179-186.

**Copper Ores: A Case of Copper Hydrometallurgy.** By GEORGE C. WESTBY. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 5, pp. 295-296.

**Copper Ores: Solution Control in Ferric-chloride Leaching of Sulfide Copper Ores.** By F. N. FLYNN AND R. H. HATCHETT. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 5, p. 291.

**Cyanamid: The Cyanamid Process.** By FRANK S. WASHBURN. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 5, pp. 309-314

**Electric Furnace: The Electric Furnace in the Foundry.** By W. G KRANZ *Bulletin of the American Institute of Mining Engineers*, 1915, No. 101, pp. 927-930.

**Electricity in Slate Mining.** By R. C. BERLIN. *The Electric Journal*, Vol. 12, 1915, pp. 177-181.

**Flotation in Gold Metallurgy.** By W. B. BLYTH. *Metallurgical and Chemical Engineering*, Vol. 13, 1915, No. 5, p. 308.

**Flotation of Copper Ores.** ANONYMOUS. *Mining and Scientific Press*, Vol. 110, 1915, No. 18, pp. 680-682.

**Glass: Die Glasfabrikation.** By PAUL SCHNURPFEIL. *Die Glashütte*, Vol. 45, 1915, No. 11/12, pp. 72-74.

**Grinding Machines.** By JOSEPH HORNER. *Engineering*, Vol. 99, 1915, No. 2572, pp. 423-426.

**Grinding Machines: Die Schleifmaschinen, ihr Bau und ihre Aufgaben in der moderne Fabrikation.** By F. SCHWERD. *Zeitschrift des Vereins Deutscher Ingenieure*, Vol. 59, 1915, No. 14, pp. 280-286.

**Industrial Chemists: Sur la Role des Chimistes Industriels.** By W. K. MAIN. *Revue générale de chimie pure et Appliquée*, Vol. 18, 1915, No. 3, pp. 73-78.

**Lead Plating: Preparation and Operation of All Lead Plating Baths.** By FRANK C. MATHERS. *The Metal Industry*, Vol. 13, 1915, No. 5, pp. 184-185.

**Motors: Method of Applying Small Motors.** By H. F. BOK. *The Electric Journal*, Vol. 12, 1915, No. 5, pp. 182-185.

**Ore Concentration: Development of Ore Concentration.** By HENRY A. MARVIN. *Engineering Magazine*, Vol. 49, 1915, No. 2, pp. 218-230.

**Radioactivity of the Water at Hot Springs and at Saratoga Springs, N. Y., and at Other Points in America.** ANONYMOUS. *Radium*, Vol. 5, 1915, No. 1, pp. 10-14.

**Radium and Plant Life.** ANONYMOUS. *The Mining Magazine*, Vol. 12, 1915, No. 4, pp. 196-197.

**Rosin-Sizing: The Preparation of Rosin-sizing.** By LEO SCHLICK. *Paper*, Vol. 16, 1915, No. 8, pp. 13-15.

**Steam: The Flow of Steam in Pipes.** By WM. KENT. *Industrial Engineering*, Vol. 15, 1915, No. 2, pp. 51-52.

**Steel: Modern Steels and Their Heat Treatment.** *Journal of the American Society of Mechanical Engineers*, Vol. 37, 1915, No. 5, pp. 267-271.

**Steel Industry and Export Trade.** By H. H. CAMPBELL. *Engineering Magazine*, Vol. 49, 1915, No. 2, pp. 167-173.

**Tin: An Attempt at Tin Concentration.** By JESSE SIMMONS. *The Engineering and Mining Journal*, Vol. 99, 1915, No. 19, pp. 816-817.

**Titanium-Aluminum Bronze.** By W M. CORSE AND CHARLES VICKERS. *The Metal Industry*, Vol. 13, 1915, No. 5, pp. 190-192.

**Turbines: Steam Turbine Diagrams.** By F. R. LOW. *Power*, Vol. 41, 1915 No 18 pp 596-600

**Vacuum Furnaces: Ein elektrischer Vakuumofen von allgemeinen Verwendbarkeit.** By G. OESTERHELD. *Zeitschrift für Elektrochemie*, Vol. 21, 1915, No. 3/4, pp. 54-60.

**Wood: Treated Wood Block Pavements.** ANONYMOUS. *Municipal Engineering*, Vol. 48, 1915, No. 2, pp. 94-100.

**X-Rays.** By WHEELER P DAVEY. *General Electric Review*, Vol. 18 1915, No. 5, pp. 353-358.

**Zirconia: Further Notes on the Refractory Properties of Zirconia.** By H CONRAD MEYER *Metallurgical and Chemical Engineering*, Vol 13, 1915, No. 4, pp. 263-6.

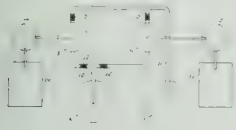
# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. Parker

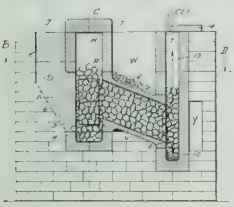
Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Carbon Tetrachlorid. C. J. Strosacker, Dec. 22, 1914. U. S. Pat. 1,121,880.** Sulfur chlorid is mixed with carbon tetrachlorid distillate high in carbon disulfid and distilled producing a second distillate relatively low in carbon disulfid. To the still residue is added sulfur chlorid and carbon disulfid and the mixture redistilled, producing a distillate relatively high in carbon disulfid. The cycle of steps is repeated with the last distillate and the products thereof, the first and second distillations being alternately conducted in each of the two stills 6 and 7 illustrated.



**Sodium Carbonate. M. Spazier, Dec. 29, 1914. U. S. Pat. 1,122,323.** Sodium carbonate crystals are produced by mixing screened soda ash and water in an open tank, the mixture being agitated to prevent the formation of lumps and until a complete solution is obtained. The solution is exposed to the air for a period of about 70 hours and the crystallized product withdrawn.

**Electric Zinc Furnace with Integral Condenser. C. V. and M. Thierry, Dec. 29, 1914. U. S. Pat. 1,122,664.** This furnace is primarily intended for the reduction of zinc oxid, the resulting fumes being condensed to liquid metal. Heat is derived by conduction or radiation or by both from the resistor R formed of a bed of broken carbon interposed between terminals 3 connected with a power circuit.



**Waterproof Paper. J. Kindleberger, Feb. 2, 1915. U. S. Pat. 1,126,783.** The paper is parchmentized by the sulfuric acid method, impregnated with glycerin and carbolic acid and coated with paraffin.

**Bast Fiber, Such as Flax or Hemp, for Spinning. B. S. Summers, Feb. 2, 1915. U. S. Pat. 1,127,311.** The fibers are treated with an alkali and then subjected to the action of decomposed casein.

**Waterproof Match. F. V. D. Cruser, Feb. 9, 1915. U. S. Pat. 1,127,410.** The head composition of the match is covered and protected by an integral film formed by the action of formaldehyde on the glue or binding constituent of the composition.

**Finishing Plastered Surfaces. S. W. Ramsey, Feb. 9, 1915. U. S. Pat. 1,127,514.** The composition consists of 74 parts of hydrated lime, 25 parts of gypsum, and one part of tartaric acid.

**Flavoring Oil. N. Sulzberger, Feb. 9, 1915. U. S. Pat. 1,127,545.** The flavor of cottonseed oil is improved by the addition of about 3 per cent of peanut oil.

**Ammoniated Acid Phosphate. T. L. Willson and M. M. Haff, Feb. 9, 1915. U. S. Pat. 1,127,840.** Acid phosphate is first dried until the amount of moisture is reduced to from six to seven per cent. It is then treated with ammonia gas

## BRITISH PATENTS

By D. Geddes Anderson

Chemical Engineer and Patent Chemist, Glasgow, Scotland

The following abstracts are taken direct from the patent specifications as soon as these are published by the British patent office. The date given at the end of the abstract is the date of acceptance.

**Treatment of Zinc Solutions for the Production of Zinc Sulfite and Oxide. P. Ferrère. May 28, 1914. Brit. Pat. 13,333.** The zinc solution is saturated with an excess of sulfurous acid, and an oxide of the alkaline earth metals is added in such proportion as to be always less than that which is necessary for fixing half of the dissolved sulfurous acid in the form of earthy alkaline sulfite. The three reactions which take place simultaneously may be represented by (1) $BaO + SO_2 = BaSO_3$; (2) $ZnSO_4 + BaSO_3 = BaSO_4 + ZnSO_3$; (3) $ZnSO_3 + nSO_2 = ZnSO_3.nSO_4$. The zinc sulfite is precipitated by driving off the sulfurous acid in any convenient manner. The zinc oxide is obtained by calcining the zinc sulfite.

**Explosive Mixtures Containing Chlorates. E. C. R. Marks, Dec. 22, 1913. Brit. Pat. 29,507.** Explosive mixtures of the type, potassium chlorate 81 to 84 per cent; starch 8 to 15 per cent; oil 4 to 8 per cent; a metallic combustible element such as aluminium, iron carbide, or ferro-silicon 2 to 6 per cent; and less than 2 per cent of a detonating body, such as permanganate or chromate of potassium.—March 11, 1915.

**Sterilizing Milk and Cream. A. Rutter, Jan, 3. 1914. Brit. Pat. 216.** Sodium peroxide 0.05 per cent to 0.15 per cent by weight, is added to the milk, and thereafter an amount of citric acid in quantity just sufficient to neutralize the alkalinity. The milk is then warmed to between 30° C. and 52° C.—March 18, 1915.

**Vulcanized Rubber Goods. W. E. Muntz, Feb. 25, 1914. Brit. Pat. 4,955.** Sulfurous acid and sulfuric acid are formed by the oxidation of vulcanized rubber, and this invention deals with a process by which any deleterious action of these acids on the fabrics or the rubber is prevented. The materials comprised in vulcanized rubber goods are impregnated with either (1) addition compounds of ammonia with certain metallic salts, (2) organic acids to be subsequently acted upon by an alkali, (3) ammonia mixed with, or subsequently acted upon, by carbon dioxide.—Feb. 25, 1915.

**Artificial Manures. T. Twynam, Feb. 28, 1914. Brit. Pat. 5,184.** Basic phosphate slag is treated with a restricted amount of nitric acid, insufficient to act upon the iron compounds in the slag, or to form much gelatinous silica. The deliquescent mass so obtained is treated with either dry ammonium sulfate or dry potassium sulfate.—March 10, 1915.

**Manufacture of Lime and Gas. R. Pearson and The Chalk Fuel Corporation Ltd., March 6, 1914. Brit. Pat. 5,734.** Briquettes are made of chalk 75 per cent, solidified tar $12^1/_2$ per cent, small coal 10 per cent, crude oil $2^1/_2$ per cent. These briquettes are fed into a gas generator on to a bed of fuel blown into a state of incandescence, and a gas mixture suitable for heating or lighting is formed.—March 4, 1915

**Manufacture of Hydrogen. J. G. Buchanan and E. B. Maxted, March 13, 1914. Brit. Pat. 6,477.** An iron-copper couple is used as a catalyst in the manufacture of hydrogen from water gas or similar gas mixtures. Steam and water gas are brought into contact with the iron-copper couple at 500° C. and the whole of the carbon monoxide is converted into carbon dioxide.—Feb. 25, 1915.

# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF MAY, 1915

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid C. P. (bbls.) | Lb. | 1.00 | @ | 1.10 |
| Acetic Acid (28 per cent) | C | 2.00 | @ | 2.25 |
| Acetone (drums) | Lb | 20 | @ | 23 |
| Alcohol, denatured (180 proof) | Gal. | 34 | @ | 36 |
| Alcohol, grain (188 proof) | Gal. | 2.52 | @ | 2.55 |
| Alcohol, wood (95 per cent) | Gal | 45 | @ | 47 |
| Amyl Acetate | Gal. | 2.70 | @ | — |
| Aniline Oil | Lb | 70 | @ | 80 |
| Benzoic Acid (ex-toluol) | Lb | — | @ | 1.75 |
| Benzol (90 per cent) | Gal. | nominal | | |
| Camphor (refined in bulk) | Lb. | 42 | @ | 43 |
| Carbolic Acid (drums) | Lb. | 1.25 | @ | 1.[illegible] |
| Carbon Bisulfide | Lb. | 6 1/2 | @ | 7 1/2 |
| Carbon Tetrachloride (drums) | Lb. | 16 | @ | |
| Chloroform | Lb. | 30 | @ | 35 |
| Citric Acid (domestic), crystals | Lb. | 55 | @ | 55 1/2 |
| Dextrine (corn) (carloads, bags) | C. | 3.10 | @ | — |
| Dextrine (imported potato) | Lb | 10 | @ | 12 |
| Ether (U. S. P., 1900) | Lb. | 15 | @ | [illegible] |
| Formaldehyde (40 per cent) | Lb. | 8 1/2 | @ | 9 1/2 |
| Glycerine (dynamite) | Lb. | 20 | @ | — |
| Oxalic Acid | Lb. | 19 | @ | 20 |
| Pyrogallic Acid (bulk) | Lb. | 1.35 | @ | 1.50 |
| Salicylic Acid | Lb. | 1.60 | @ | 1.70 |
| Starch (cassava) | Lb. | 3 3/4 | @ | 4 |
| Starch (corn) (carloads, bags) | C. | 2.43 | @ | — |
| Starch (potato) | Lb. | 5 1/4 | @ | — |
| Starch (rice) | Lb. | 7 | @ | 8 |
| Starch (sago) | Lb. | 3 3/4 | @ | 4 |
| Starch (wheat) | Lb. | 7 | @ | 7 1/2 |
| Tannic Acid (commercial) | Lb. | 60 | @ | 66 |
| Tartaric Acid, crystals | Lb | 40 | @ | — |

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lead (brown, broken) | Lb. | 7 1/4 | @ | 7 1/2 |
| Acetate of Lime (gray) | C. | 2.10 | @ | 2.20 |
| Alum (lump) | C. | 2.50 | @ | 3.00 |
| Aluminum Sulfate (high-grade) | C. | 1.50 | @ | 1.75 |
| Ammonium Carbonate, (domestic) | Lb. | 8 1/4 | @ | 9 |
| Ammonium Chloride, (gray) | Lb. | 5 1/2 | @ | 6 1/2 |
| Aqua Ammonia (drums) 16° | Lb. | 2 1/4 | @ | 2 1/2 |
| Arsenic (white) | Lb. | 4 | @ | 4 1/2 |
| Barium Chloride | Ton | 65.00 | @ | 75.00 |
| Barium Nitrate | Lb. | 15 | @ | 18 |
| Barytes (prime white, foreign) | Ton | 19.00 | @ | 22.00 |
| Bleaching Powder (35 per cent) | C. | 1.40 | @ | 1.50 |
| Blue Vitriol | Lb. | 7 | @ | 7 1/4 |
| Borax, crystals (bags) | Lb. | 4 1/2 | @ | 5 |
| Boric Acid, crystals (powd.) | Lb. | 7 1/2 | @ | 9 |
| Brimstone (crude, domestic) | Long Ton | 22.00 | @ | 22.50 |
| Bromine (bulk) | Lb. | 85 | @ | 87 |
| Calcium Chloride (lump) | Ton | 11.70 | @ | 12.00 |
| Chalk (light precipitated) | Lb. | 4 1/2 | @ | 5 1/2 |
| China Clay (imported) | Ton | 14.00 | @ | 18.00 |
| Feldspar | Ton | 8.00 | @ | 12.00 |
| Fuller's Earth (powdered, foreign) | C. | 80 | @ | 85 |
| Green Vitriol (bulk) | C. | 90 | @ | |
| Hydrochloric Acid (18°) | C. | 1.15 | @ | 1.65 |
| Iodine (resublimed) | Lb. | 3.75 | @ | 3.80 |
| Lead Nitrate | Lb. | | @ | 8 |
| Litharge (American) | Lb. | 5 1/4 | @ | 5 1/2 |
| Lithium Carbonate | Lb. | 1.00 | @ | 1.10 |
| Magnesium Carbonate | Lb. | 4 1/4 | @ | — |
| Magnesite "Calcined" | Ton | 35.00 | @ | 40.00 |
| Nitric Acid (36°) | Lb. | 3 7/8 | @ | 4 1/4 |
| Phosphoric Acid (sp. gr. 1.75) | Lb. | 28 | @ | 30 |
| Phosphorus | Lb. | 35 | @ | 95 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate | Lb. | 15 | @ | 16 |
| Potassium Bromide | Lb. | 1.10 | @ | 1.11 |
| Potassium Carbonate (calcined), 80 @ 85% | C. | 15 | @ | 15 1/2 |
| Potassium Chlorate, crystals spot | Lb. | 35 | @ | 40 |
| Potassium Cyanide (bulk), 98-99% | Lb. | 18 | @ | 25 |
| Potassium Hydroxide | Lb. | 24 | @ | 25 |
| Potassium Iodide (bulk) | Lb. | 3.15 | @ | — |
| Potassium Nitrate (crude) | Lb. | 12 | @ | — |
| Potassium Permanganate (bulk) | Lb. | 60 | @ | 75 |
| Quicksilver, Flask (75 lbs.) | | 74.00 | @ | 75.00 |
| Red Lead (American) | Lb. | 6 | @ | |
| Salt Cake (glass makers') | C. | 55 | @ | 65 |
| Silver Nitrate | Oz. | 33 | @ | 34 |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash (48 per cent) | C. | 67 1/2 | @ | 72 1/2 |
| Sodium Acetate | Lb. | 4 | @ | 4 1/2 |
| Sodium Bicarbonate (domestic) | C. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate (English) | Lb. | 3 1/2 | @ | 3 3/4 |
| Sodium Bichromate | Lb | 5 1/4 | @ | 5 3/4 |
| Sodium Carbonate (dry) | C. | 1.10 | @ | — |
| Sodium Chlorate | Lb. | 14 | @ | 16 |
| Sodium Hydroxide (60 per cent) | C. | 1.95 | @ | 2.05 |
| Sodium Hyposulfite | C. | 1.60 | @ | 2.00 |
| Sodium Nitrate (95 per cent, spot) | C. | 2.30 | @ | 2.32 1/2 |
| Sodium Silicate (liquid) | C. | 85 | @ | 1.10 |
| Strontium Nitrate | Lb. | 17 | @ | 17 1/2 |
| Sulfur, Flowers (sublimed) | C. | 2.20 | @ | 2.60 |
| Sulfur, Roll | C. | 1.85 | @ | 2.15 |
| Sulfuric Acid (60° B) | C. | 85 | @ | 1.00 |
| Talc (American) | Ton | 10.00 | @ | 15.00 |
| Terra Alba (American), No. 1 | C. | 75 | @ | 80 |
| Tin Bichloride (50°) | Lb. | 14 3/4 | @ | 15 |
| Tin Oxide | Lb. | 50 | @ | 52 |
| White Lead (American, dry) | Lb. | 5 1/4 | @ | 5 1/2 |
| Zinc Carbonate | Lb. | 8 1/2 | @ | 9 |
| Zinc Chloride (granulated) | Lb. | 6 1/4 | @ | 6 1/2 |
| Zinc Oxide (American process) | Lb. | 5 1/2 | @ | 6 1/2 |
| Zinc Sulfate | C. | 2.50 | @ | 2.75 |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax (pure white) | Lb. | 42 | @ | 45 |
| Black Mineral Oil, 29 gravity | Gal | 12 1/2 | @ | 13 |
| Castor Oil (No. 3) | Lb. | 9 3/4 | @ | 10 1/4 |
| Ceresin (yellow) | Lb. | 10 | @ | 25 |
| Corn Oil | C. | 6.26 | @ | 6.41 |
| Cottonseed Oil (crude), f. o. b. mill | Gal. | 40 | @ | 40 1/4 |
| Cottonseed Oil (p. s. y.) | Lb. | 6.20 | @ | 6.40 |
| Cylinder Oil (light, filtered) | Gal. | 20 | @ | 25 |
| Japan Wax | Lb. | 12 | @ | 12 1/2 |
| Lard Oil (prime winter) | Gal. | 88 | @ | 90 |
| Linseed Oil (raw) | Gal. | 65 | @ | — |
| Menhaden Oil (crude) | Gal. | 37 | @ | 39 |
| Naphtha, 68 @ 72° | Gal. | — | @ | 12 |
| Neatsfoot Oil (20°) | Gal. | 93 | @ | 94 |
| Paraffine (crude, 120 & 122 m. p.) | Lb. | 2 1/2 | @ | 3 |
| Paraffine Oil (high viscosity) | Gal | 22 | @ | 23 |
| Rosin ("F" grade) (280 lbs.) | Bbl. | 3.55 | @ | — |
| Rosin Oil (first run) | Gal. | — | @ | 25 |
| Shellac, T. N | Lb. | 14 | @ | 14 1/2 |
| Spermaceti (cake) | Lb. | 25 | @ | 27 |
| Sperm Oil (bleached winter), 38° | Gal | 70 | @ | 71 |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid (double-pressed) | Lb. | 11 | @ | 12 |
| Tallow (acidless) | Gal. | 62 | @ | 63 |
| Tar Oil (distilled) | Gal. | 30 | @ | 31 |
| Turpentine (spirits of) | Gal. | 42 1/2 | @ | 43 1/2 |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum (No. 1 ingots) | Lb. | 21 1/2 | @ | 22 |
| Antimony (Hallet's) | Lb. | 38 1/2 | @ | 40 |
| Bismuth (New York) | Lb. | 2.90 | @ | 3.00 |
| Bronze powder | Lb. | nominal | | |
| Copper (electrolytic) | Lb. | 18 5/8 | @ | — |
| Copper (lake) | Lb. | 18 1/2 | @ | 19 |
| Lead, N. Y. | C. | 4.20 | @ | — |
| Nickel | Lb. | 42 | @ | 45 |
| Platinum (refined) | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | 49 3/4 | @ | — |
| Tin | C. | 37.50 | @ | — |
| Zinc | Lb. | 16 3/4 | @ | — |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | C. | 3.20 | @ | — |
| Blood (dried) | Unit | 2.70 | @ | — |
| Bone, 4 1/2 and 50 (ground, raw) | Ton | 30.00 | @ | — |
| Calcium Cyanamid | Unit of Ammonia | 2.20 | @ | — |
| Calcium Nitrate (Norwegian) | C. | — | @ | — |
| Castor meal | Unit | — | @ | — |
| Fish Scrap (domestic, dried) | Unit | — | @ | — |
| Phosphate, acid (16 per cent bulk) | Ton | 7.50 | @ | 8.00 |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble (68 per cent) | Ton | 2.65 | @ | 3.00 |
| Tennessee (70-80 per cent) | Ton | 5.00 | @ | 5.50 |
| Potassium, "muriate," basis 80 per cent | Ton | 135.00 | @ | 155.00 |
| Pyrites (furnace size, imported) | Unit | 13 | @ | 13 1/4 |
| Tankage (high-grade) | Unit | 2.70 | @ | 10 |

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# EDITORIALS

## THE SEATTLE MEETING

The Fifty-first Meeting of the American Chemical Society, to convene in Seattle on August 31st, with the final social session in San Francisco, offers unusual inducements for a large attendance. The itinerary arranged over the Great Northern Railway, with a special train west of Chicago, was outlined in our last issue. The opportunity to observe such natural scenery, including extensive glaciers, numberless lakes, no end of mountains, and a real live volcano—all "made in America"— is alone ample reason for the trip.

The Exposition in San Francisco, which members can visit at their own convenience after the meeting, has been especially planned to present in detail a broader range of industries than has ever been attempted at any previous exhibit. Scientists and technologists of all classes will find it both instructive and suggestive.

The papers presented at the meeting will of course be interesting and valuable: they always are. Since the majority will eventually appear in the Journals of the Society, however, the main object of their presentation is to bring out discussion. The extent and value of this depends upon the attendance.

The multitude of problems brought forward by the European war has quickened anew the chemical industries of America; these problems must be solved; and they will not be unless the American chemists co-operate. Only by closer intercourse among themselves can they know even their own strength. The informal conferences made possible by the meetings of the Society offer one of the most valuable means of getting into touch with the varied talents of our many Sections.

Hundreds of our members have never attended a general meeting of the Society. And yet no member has ever attended a meeting without being glad of it afterwards, because he realizes that he has been benefited by the invaluable experiences of travel, instruction in his specialty, personal contact with his co-workers and the general broadening of view that is the basis of all progress.

Now that chemists are actually receiving some public recognition, it behooves them to take an added interest in the activities of the Society. In this way they can attain the recognition that is theirs by right, among the professions of the nation.

The Seattle and San Francisco Sections are making preparations for the largest meeting of the Society to date. Are you going to be there?

## THE EXPOSITION OF CHEMICAL INDUSTRIES

No better proof that chemistry and chemists "have arrived" is needed than the fact that a National Exposition of Chemical Industries will be held in New York, September 20th to 25th. The managers report that requests for space are arriving daily and that the list of exhibitors is already representative of the many great divisions of American industry. The United States Bureau of Foreign and Domestic Commerce is contemplating an elaborate and comprehensive exhibit, which alone will attract thousands of manufacturers anxious to learn the needs of the many markets at present abandoned by the warring nations of Europe.

The time is at hand when the public must be taught that chemists are most often *not* druggists and that there are other chemicals than drugs, dyes and explosives. Furthermore, there are indeed many who still need to be convinced of the truth of President Herty's statement that "Chemistry is no 'black art'."

The all-absorbing nature of the pursuit of chemistry as a profession is responsible for the present conviction of the public that the science is incomprehensible and inaccessible to the lay mind. Until they actually see chemical processes turning out useful and desirable articles and can get some clear idea of the part the chemist plays in this operation, it is useless to expect public support and sympathy for our profession. Those who like the secretive methods of the past are protesting, naturally, against this invasion of their realms, but they will have to submit, for it is now necessary to give the people concrete examples. Since they cannot go into the factories for this information, it must be brought to them. The exposition method is certainly the quickest and most effective manner of accomplishing this result. The value of the chemist is not appreciated because so few people realize that he really works; they think his results are attained by chance or inspiration.

Provision is being made for the illustration of processes by means of working models of machinery, product displays, motion pictures and lantern slides. Rooms have also been provided for meetings of chemical and engineering societies.

Another phase of special importance in this exhibit is that chemical industries are so interlocked that all producers are consumers and *vice versa*. Also, many industries, between whose products there is no relation, make use of similar machinery, so that even the narrowest specialist cannot afford to neglect the study of the methods of other workers.

Concerning the reluctance of many to demonstrate their processes, we venture that no manufacturer will disclose as much as he learns and that many will be surprised to find that some of their most cherished "secrets" are already common property.

In view of the present public interest in things chemical and the inherent value of the exhibits being prepared, we predict that this first National Exposition of Chemical Industries will be successful from every standpoint, and we see no reason why it should not move on to other large cities with profit to its exhibitors and the various communities sufficiently progressive to welcome it.

# ORIGINAL PAPERS

## A STUDY OF THE QUALITY OF PLATINUM WARE WITH SPECIAL REFERENCE TO LOSSES ON HEATING[1]

By George K. Burgess and P. D. Sale

There was presented at the 49th Meeting of the American Chemical Society an account[2] of the examination of the purity of a number of platinum crucibles by a thermoelectric method in which the crucible forms one element of a thermocouple. This method has been found useful by ourselves and others for the ready classification of platinum utensils of various kinds and especially for the determination, in the case of purchases of platinum ware, whether or not such articles conform to specifications as to platinum purity. This thermoelectric test, which in no way mars the crucible or other article examined, is now a part of the routine of the Bureau of Standards and many samples of platinum have been so tested the past year; these were secured for the most part through Dr. W. F. Hillebrand, Chairman of the Committee of the American Chemical Society on "Quality of Platinum Utensils."

In Table I is shown the quality of platinum utensils of various sorts expressed in terms of equivalent iridium content as measured thermoelectrically at this Bureau. Of the 164 pieces examined it is seen

Table I—Classification of Platinum Ware Submitted to Bureau of Standards for Thermoelectric Purity Test

| Class of Ware Investigated | Crucibles | Crucible covers | Dishes | Misc. | Total No. |
|---|---|---|---|---|---|
| No pieces of each class | 84 | 47 | 11 | 22 | 164 |
| Equivalent Ir-content—per cent | Per cent in each class | | | | |
| 0.0 to 0.5 | 36 | 26 | 9 | 0 | 26 |
| 0.5 to 1.0 | 17 | 23 | 36 | 18 | 20 |
| 1.0 to 2.0 | 34 | 38 | 19 | 9 | 31 |
| 2.0 to 4.0 | 13 | 13 | 36 | 27 | 17 |
| 4.0 to 25.0 | 0 | 0 | 0 | 45 | 6 |

that nearly 75 per cent have impurities equivalent to over 0.5 per cent of iridium, and of the crucibles, 65 per cent have over 0.5 equivalent iridium content. Dishes and miscellaneous ware, in which stiffness is usually required and which are often not subject to heating and weighing, are heavily charged with impurities, usually iridium, the miscellaneous ware showing, for example, nearly half of the samples with over 4 per cent iridium.

In addition to data on the purity of platinum ware now in use, more exact information was desired by the committee concerning the losses on heating. The experiments here outlined, it is believed, furnish information concerning losses sustained by platinum crucibles of several grades of purity when subjected to continued heating. By suitable acid treatment after heating, it has been possible to give an estimate of the relative amount of iron present, and the crucibles have also been examined microscopically, and through the kindness of Dr. Burrows, magnetically.

As will be shown, a combination of these several methods, or some of them, usually gives sufficient data for the ready classification of various grades of platinum ware.

Method of Determining Losses on Heating—For an exact determination of the loss in weight of a crucible on heating, ignition over the blast lamp is not satisfactory. A preliminary series of experiments, using electric resistance furnaces with platinum and other metals as heating coils, carried out by members of the chemical staff of this Bureau, showed that one could not expect to obtain consistently reliable results in a furnace containing metal. A considerable number of measurements of losses on heating at sev-

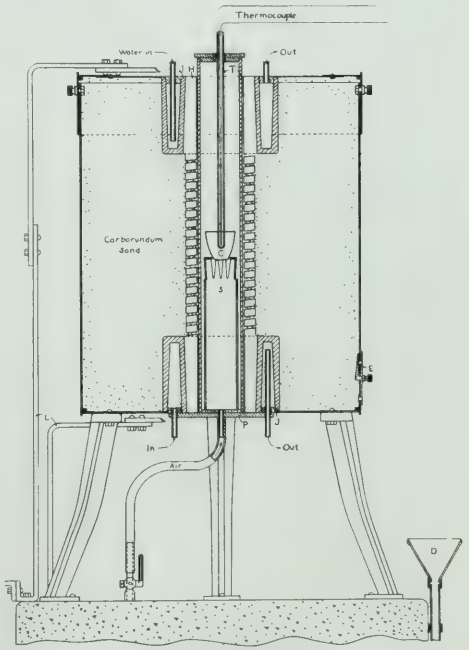


Fig. 1—Heating Furnace

C—Platinum Crucible
D—Water Drain
E—Sand Emptying Door
H—Graphite Heater
J—Water Jackets
L—Current Leads
P—Bottom Cover Plate
S—Crucible Support
T—Marquardt Protecting Tube

eral temperatures were so taken, but no very definite conclusions can be drawn from these preliminary observations, which were obtained before the thermoelectric method of classification was put into practice.

The method finally adopted for determining heat losses in crucibles is based on the use of a metal-free electrically heated furnace, similar to one which had been in use for other purposes at the Geophysical Laboratory, accompanied by exact weighings of the crucible before and after each heating of 2 hours duration at 1200° C., together with a weighing to determine the iron loss after washing in acid.

[1] Paper read at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915. It will be published in full as a Scientific Paper of the Bureau of Standards.

[2] "A Thermoelectric Method for the Determination of the Purity of Platinum Ware," by George K. Burgess and P. D. Sale, This Journal, 6 (1914), 452.

The essentials of the furnace are shown in Fig. I. The heating spiral *H* is of graphite set into brass water-cooled terminals. The crucible *C* is supported on a Marquardt porcelain stand, *S*, as shown and enclosed within a tube, *T*, of the same material. Temperatures were measured by a platinum platinum-rhodium thermocouple enclosed in Marquardt. The furnace takes about 3.5 kw. A. C. at 1200° C.

For a region of about three crucible heights at the center of the furnace, there was maintained a practically uniform temperature, 1200° C., and this inner portion of the furnace never became blackened. A slight current of air was maintained about the crucible, as shown, but great care was taken, by means of a sand and paraffine seal, at *P*, to prevent vapors passing from the heating spiral into the inner chamber The crucible was not placed in the furnace until this had reached 1000° C.; a temperature of 1200° C. was then attained in about 10 min. and held constant for exactly 2 hrs. and cut off, the crucible being removed 10 min. later or at about 900° C.

Crucible weighings were made on an enclosed precision balance, at first to 0.001 mg. and later to 0.01 mg. as this latter was found sufficient. All weights are reduced to a common basis of loss per 100 cm². of total crucible surface.

ACID TREATMENT—Iron and other soluble materials were removed, and determined by weighing, after each heating. For several of the crucibles examined, the characteristic reddish coating due to iron oxide appeared after each heating. The acid treatment consisted in boiling the crucible for 5 min. in 25 per cent hydrochloric acid contained in a large covered porcelain crucible. The iron was determined by precipitation with ammonia upon ashless filter paper, ignited in platinum for 1 min. at about 1200° C., and weighed as ferric oxide.

EXPERIMENTAL RESULTS—Fourteen crucibles were carried through a series of identical operations consisting of a determination of their equivalent iridium or rhodium content by the thermoelectric method[1] (see lines I, I′ of Table II); the determination of losses of weight after each of three heatings of two hours each at 1200° C. (see lines II, III, IV, each followed by determination of loss by acid treatment, lines II′, III′, IV′, and of iron content, lines IX, X, XI). As seen from Table III, these fourteen crucibles range in equivalent iridium content from 0.05 (*a*) to 2.65 (*l*) per cent; crucibles *m* and *n* were supposed to be 90 platinum-10 rhodium; but as measured thermoelectrically, they contain 7.30 and 7.95 per cent

[1] Loc. cit.

TABLE II—HEATING AND ACID TREATMENT ON PLATINUM CRUCIBLES (MILLIGRAMS PER CM² — SEE TABLE III FOR KEY TO CRUCIBLES)

E. M. F. measurements: Millivolts at 1100° C., crucible *vs.* pure Pt (I, I′)
Heat treatment loss: Milligrams per 100 cm². for 2 hrs. heating at 1200° C. (II, III, IV)
Acid treatment loss: Milligrams per 100 cm². for 5 min. boiling in 25 per cent HCl (II′, III′, IV′)
Recovered $Fe_2O_3$: Milligrams per 100 cm². per treatment with $NH_4OH$ and ignition on ashless paper (IX, X, XI, XII)

| Crucible reference letter | *a* | *b* | *c* | *d* | *e* | *f* | *g* | *h* | *i* | *j* | *k* | *l* | *m* | *n* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. E. M. F. at beginning | 0.10 | 0.50 | 0.65 | 0.70 | 0.70 | 1.90 | 2.80 | 3.00 | 6.40 | 6.70 | 7.00 | 7.30 | 9.30 | 9.70 |
| I′ E. M. F. at end | 0.07 | 0.50 | 0.62 | 0.70 | 0.70 | 1.85 | 2.80 | 2.95 | 5.95 | 6.10 | 6.00 | 6.50 | 9.30 | 9.70 |
| E. M. F. mean I and I′ | 0.09 | 0.50 | 0.64 | 0.70 | 0.70 | 1.88 | 2.80 | 2.98 | 6.18 | 6.40 | 6.50 | 6.90 | 9.30 | 9.70 |
| II 1st heat, 2 hr. at 1200° C. | 2.18 | 1.98 | 2.16 | 1.27 | 2.46 | 2.00 | 1.08 | 1.38 | 7.47 | 1.94 | 6.24 | 2.16 | 1.74 | 0.61 |
| II′ 1st acid, 25 per cent HCl | 0.05 | 0.24 | 0.06 | 0.19 | 0.83 | 0.16 | 1.76 | 3.82 | 0.81 | 9.50 | 1.14 | 5.33 | 0.46 | 0.02 |
| II + II′ | 2.23 | 2.22 | 2.22 | 1.46 | 3.29 | 2.16 | 2.84 | 5.20 | 8.28 | 11.44 | 7.38 | 7.49 | 2.20 | 0.63 |
| III 2nd heat, 2 hr. at 1200° C. | 0.84 | 0.96 | 1.93 | 1.36 | 0.26 | 2.20 | 2.18 | 0.43 | 4.42 | 4.93 | 5.45 | 2.32 | 1.08 | 1.44 |
| III′ 2nd acid, 25 per cent HCl | 0.30 | 0.35 | 0.18 | 0.17 | 0.56 | 0.09 | 0.99 | 1.24 | 0.16 | 1.84 | 0.39 | 2.47 | 0.13 | 0.13 |
| III + III′. M. F. | 1.14 | 1.31 | 2.11 | 1.53 | 0.82 | 2.29 | 3.17 | 1.67 | 4.58 | 6.77 | 5.84 | 4.79 | 1.121 | 1.57 |
| IV 3rd heat, 2 hr. at 1200° C. | 1.85 | 2.04 | 1.61 | 1.65 | 2.02 | 2.16 | 2.36 | 0.75 | 4.38 | 3.23 | 2.94 | 5.08 | 1.00 | 1.21 |
| IV′ 3rd acid, 25 per cent HCl | 0.06 | 0.15 | 0.11 | 0.09 | 0.26 | 0.07 | 0.40 | 0.34 | 0.08 | 0.66 | 1.01 | 2.79 | 0.10 | 0.04 |
| IV + IV′ | 1.91 | 2.19 | 1.72 | 1.74 | 2.28 | 2.23 | 2.76 | 1.09 | 4.46 | 3.89 | 3.95 | 7.87 | 1.10 | 1.25 |
| V Σ II, III, IV, heat loss | 4.87 | 4.98 | 5.70 | 4.28 | 4.74 | 6.36 | 5.62 | 2.56 | 16.17 | 10.10 | 14.63 | 9.56 | 3.82 | 3.26 |
| VI Σ II′, III′, IV′, acid loss | 0.41 | 0.74 | 0.35 | 0.45 | 1.65 | 0.32 | 3.15 | 5.40 | 1.05 | 12.00 | 2.54 | 10.59 | 0.69 | 0.19 |
| VII Σ V, VI, total loss | 5.28 | 5.72 | 6.05 | 4.73 | 6.39 | 6.68 | 8.77 | 7.96 | 17.22 | 22.10 | 17.17 | 20.15 | 4.51 | 3.45 |
| VIII Total charge E. M. F. | 0.03 | 0.00 | 0.03 | 0.00 | 0.00 | 0.05 | 0.00 | 0.05 | 0.00 | 0.60 | 1.00 | 0.80 | 0.00 | 0.00 |
| IX Iron as $Fe_2O_3$ after II′ | 0.147 | 0.125 | .. | 0.099 | 0.544 | 0.005 | 1.080 | 0.794 | 0.052 | 2.520 | ... | .. | .. | 0.090 |
| X Iron as $Fe_2O_3$ after III′ | 0.216 | 0.202 | .. | —0.022 | 0.357 | 0.113 | 0.272 | 0.714 | 0.026 | 0.603 | ... | .. | .. | 0.168 |
| XI Iron as $Fe_2O_3$ after IV′ | 0.103 | 0.102 | . | 0.123 | 0.628 | 0.270 | 0.072 | 0.454 | 0.057 | 0.295 | ... | .. | .. | 0.004 |
| XII Total iron as $Fe_2O_3$ | 0.466 | 0.429 | . | 0.200 | 1.529 | 0.388 | 1.424 | 1.962 | 0.135 | 3.418 | ... | .. | .. | 0.262 |
| XIII Total iron compared to T. L. in % | 8.82 | 7.50 | .. | 5.16 | 23.95 | 5.81 | 16.25 | 24.65 | 0.78 | 15.46 | ... | . | . | 7.59 |
| XIV Total iron compared to acid L. in % | 100.00 | 58.00 | .. | 53.30 | 92.60 | 100.00 | 45.40 | 36.35 | 12.87 | 28.45 | ... | .. | . | 100.00 |
| XV Total acid compared to T. L. in % | 7.76 | 12.93 | .. | 9.50 | 25.80 | 4.78 | 35.95 | 67.80 | 6.10 | 54.30 | ... | ... | .. | 5.51 |

TABLE III—CLASSIFICATION OF WARE BY E. M. F., VOLATILIZATION, CHEMICAL, MAGNETIC AND PHOTOGRAPHIC DATA

| Crucible reference letter | Mean E. M. F. millivolts | Equivalent content Per cent Ir | Rh | Equivalent Fe (magnetic) Per cent | Wt. of Fe remaining magnetic test | Maker's chemical statement Per cent | Relative Fe by susceptibility Table II | Fig. II | Classification with reference to Photomicrographs |
|---|---|---|---|---|---|---|---|---|---|
| *a* | 0.09 | 0.05 | 0.05 | 0.0001 | 0.018 | .. | 1.0 | Pt | Pt |
| *b* | 0.50 | 0.10 | 0.19 | 0.0022 | 0.576 | .. | 1.8 | Rh or Pt | Pt-Rh |
| *c* | 0.64 | 0.20 | 0.29 | .. | .. | .. | 0.9 | Pt-Ir | Pt-Ir |
| *d* | 0.70 | 0.21 | 0.30 | 0.0012 | 0.194 | <0.2 Ir | 1.1 | Pt-Ir or Rh | Pt-Ir-Fe |
| *e* | 0.70 | 0.21 | 0.30 | 0.0007 | 0.112 | .. | 4.0 | Pt-Ir | Pt-Ir-Fe |
| *f* | 1.88 | 0.55 | 0.85 | .. | .. | 0.70 Ir | 0.8 | Pt-Ir | Pt-Ir |
| *g* | 2.80 | 0.90 | 1.29 | .. | .. | .. | 7.5 | Pt-Ir-Fe | Pt-Ir-Fe |
| *h* | 2.98 | 1.00 | 1.40 | 0.0010 | 0.106 | .. | 8.5 | Pt-Rh | 7-Fe |
| *i* | 6.18 | 2.30 | 3.53 | .. | .. | 2.37 Ir | 2.6 | Pt-Ir | Pt-Ir |
| *j* | 6.40 | 2.40 | 3.70 | 0.0110 | 1.889 | 0.5 to 1.5 Ir | 29.0 | Pt-Ir-Fe | Pt-Ir-Fe |
| *k* | 6.50 | 2.42 | 3.75 | .. | .. | .. | 6.3 | Pt-Ir-Fe | Pt-Ir |
| *l* | 6.90 | 2.65 | 4.15 | 0.0080 | 0.198 | .. | 26.0 | Pt-Ir-Fe | Pt-Ir-Fe |
| *m* | 9.30 | 3.75 | 7.30 | .. | .. | i. e. { 10.0 Rh | 1.7 | Pt-Rh | Pt-Rh |
| *n* | 9.70 | 3.95 | 7.95 | .. | .. | { 10.0 Rh | 0.5 | Pt-Rh | Pt-Rh |

| KEY TO CRUCIBLES | Bought | Previously heated |
|---|---|---|
| *a* Heraeus normal thermoelement platinum | 1911 | 17 hr. |
| *b* Johnson, Matthey & Co., best crucible ware | 1911 | 67 hr. |
| *c* Johnson, Matthey & Co., best crucible ware | 1913 | 20 hr. |
| *d* American Platinum Works, "Tiegel Platin" (Heraeus) | 1911 | 24 hr. |
| *e* J. Bishop & Co., specially refined ware | 1911 | 31 hr. |
| *f* Baker & Company, special analyzed make | 1912 | 12 hr. |
| *g* Quenessen De Belmont, Legendre & Cie | 1911 | 10 hr. |
| *h* Baker & Company | 1909 | 3 yr. lab. use |
| *i* Baker & Company, special analyzed make | 1912 | 0 hr. |
| *j* American Platinum Works, commercial ware | 1911 | 11 hr. |
| *k* Baker & Company, commercial ware | 1908 | 10 hr. |
| *l* Baker & Company, commercial ware | 1908 | 20 hr. |
| *m* Baker & Company, special Rhodium ware | 1913 | 50 ignitions, bisulfates and cleaning |
| *n* Baker & Company, special Rhodium ware | 1913 | 0 hr. |

rhodium, respectively, the former having been used considerably and the latter an unused crucible; some of the others are of unknown composition and the non-platinum content of each is expressed both in terms of iridium and rhodium (see lines 2 and 3 of Table III). In Table IV the heating and acid losses are given for four crucibles which underwent additional heating.

The microscopic observations were helpful in finally classifying the crucibles in terms of their main impurity—iridium or rhodium (see last line of Table III), as it was found that the crystalline structures

TABLE IV—LOSSES IN WEIGHT DUE TO HEATING AND ACID TREATMENT ON FOUR CRUCIBLES IN MILLIGRAMS, PER 100 CM², AFTER SUCCESSIVE 2-HOUR HEATINGS AT 1200° C

| Treatment | Crucible *n* | | | Crucible *l* | | | Crucible *k* | | | Crucible *c* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Heat | Acid | Total | Heat | Acid | Total | Heat | Acid | Total | Heat | Acid | Total |
| 1st | 0.98 | 0.00 | 0.98 | 4.30 | 0.77 | 5.07 | 6.24 | 1.14 | 7.38 | 2.16 | 0.06 | 2.22 |
| 2nd | 2.30 | 0.18 | 2.48 | 2.32 | 2.47 | 4.79 | 5.45 | 0.39 | 5.84 | 1.93 | 0.18 | 2.11 |
| 3rd | 0.61 | 0.02 | 0.63 | 5.08 | 2.19 | 7.27 | 2.94 | 1.01 | 3.95 | 1.61 | 0.11 | 1.72 |
| 4th | 1.44 | 0.13 | 1.57 | 7.40 | 2.60 | 10.00 | 3.78 | 0.60 | 4.38 | 2.34 | 0.09 | 2.43 |
| 5th | 1.21 | 0.04 | 1.25 | 4.04 | 2.37 | 6.41 | ... | ... | ... | ... | ... | ... |
| 6th | 0.81 | 0.06 | 0.87 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| Total | 7.35 | 0.43 | 7.78 | 23.14 | 10.40 | 33.54 | 18.41 | 3.14 | 21.55 | 8.04 | 0.44 | 8.48 |
| Av. | 1.23 | 0.07 | 1.30 | 4.63 | 2.08 | 6.71 | 4.60 | 0.79 | 5.39 | 2.01 | 0.11 | 2.12 |

characteristic of these alloying metals imparted their appearance to the unetched crucible even when present in small percentages. On fresh platinum ware containing considerable rhodium a characteristic bluish color will usually appear after heating to a dull red.

The presence of iron appears to manifest itself in the microphotographs by pitting after heating. The relative amounts of iron in several crucibles were also determined, after the last heating and washing, by measurement of the magnetic susceptibility by a solenoid and balance method in a field of 60 gausses, the crucibles being arranged only approximately in the same order by chemical analysis following heating and by the magnetic measurements (see Table III). It is also of interest to note that iron-free platinum appears to have a susceptibility of zero, and that the susceptibility of "platinum" ranges from 1 to 125. A value of about 20, in the same units, has usually been found for the susceptibility of pure platinum, due undoubtedly to the presence of iron. The total amount of iron in a crucible cannot be determined readily from the magnetic measurements, as is seen by comparison of the magnetic and chemical data of Table III; and the iron, which is supposedly in solution in the platinum, on heating diffuses to the surface as fast as removed by oxidation, thus tending to establish an equilibrium between the iron oxide, oxygen and the iron-platinum solution at the temperature of the experiment. The iron was found non-uniformly distributed in some of the crucibles. The iron washed out in three acid treatments is seen to be greater than the total iron content calculated as iron from the magnetic data, showing that the Fe-Pt alloy containing only a few hundredths per cent iron is paramagnetic and also, from the data, that the susceptibility is not proportional to the iron content.

Considering further the inferences to be drawn from the results recorded in Tables II, III and IV, it is seen that, taking the E. M. F. as a criterion of purity, there is a purification of all crucibles containing over 0.5 per cent iridium after heating. The platinum-rhodium crucibles (*m* and *n*) do not change composition on heating; that is, the iridium passes out of the crucible and the rhodium does not appreciably.

The losses on heating and after acid treatment are seen to be fairly uniform for each crucible. For some of the less pure crucibles the loss in washing is greater than the heating loss (notably for crucibles *h*, *j*, and *l*). The total heating losses per 100 cm². range from 4.28 to 16.17 mg. for 6 hrs. at 1200°, and the total acid losses (due mainly to iron) from 0.32 to 12.00 mg., for the crucibles containing iridium. For the platinum-rhodium crucibles, *m* and *n*, containing 7 to 8 per cent rhodium, the total losses on heating and washing together are one-fourth less than for the heating loss alone for purest platinum (crucible *a*). In general, there is no relation between the acid loss and loss on heating of crucibles containing both iridium and iron, showing the independence of the determination of loss of soluble and insoluble materials by these

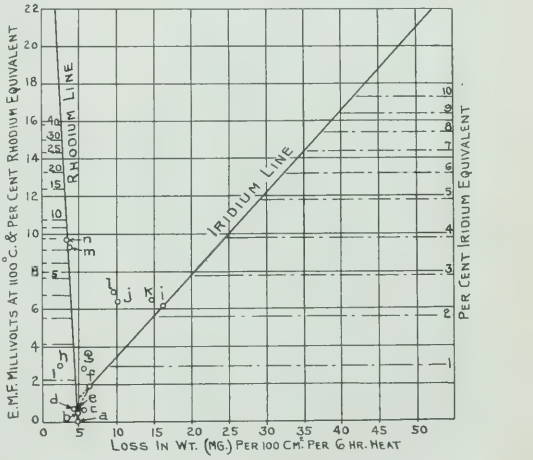


FIG. 2—VOLATILIZATION VS. THERMOELECTRIC FORCE

methods, although relatively large amounts of iron appear to lower somewhat the losses on heating that would otherwise be observed (see crucibles *h*, *j*, *l*). The acid losses are seen to vary from all iron to only 13 per cent iron.

THE PREDICTION OF HEATING LOSSES—The question arises, can the probable loss on heating of a given crucible of unknown composition be predicted from these data? Although a definite answer cannot be given, nevertheless the observations point to a reasonable probability of affirmative reply.

Consider Fig. 2, in which the heating losses are plotted against E. M. F. at 1100° C. against *pure* platinum for each of the 14 crucibles. The purest crucibles *a*, *b*, *c*, *d* and *e* all lie close together at 5 mg. loss and less than 1 millivolt. The platinum-rhodium crucibles *m* and *n* lie on a line inclined to the left of 5 mg., and which would reach to the heat loss for pure rhodium as a limit. The platinum-

iridium crucibles *f* and *i*, containing negligible iron, lie on a line inclined to the right of 5 mg. The platinum-iridium crucibles containing considerable iron, *h*, *l*, *j* and *k*, lie to the left of the iridium line; *h* may also contain rhodium.

It would follow, therefore, that one would expect a crucible nearly free from iron (which fact is readily tested by heating over the blast lamp) with a measured E. M. F. of say 8 millivolts against pure platinum, to lose 4 mg. per 100 cm². of surface in 6 hours at 1200° C. if made of a rhodium alloy of platinum, and would expect it to lose about 20 mg. if of an iridium alloy. The distinction between these iridium and rhodium alloys may usually be made microscopically, the former having definite smooth crystals with heavy boundaries and the latter a less pronounced and more irregular type of crystals. When iron is present these heat losses will be reduced somewhat and may be halved, since the effective disintegration area is reduced by the layer of iron oxide. Fig. 2 may therefore be used, at least approximately, as a basis for estimating losses on heating of platinum crucibles for the usual products found on the market and Fig. 2 is probably reliable for practically iron-free crucibles containing up to 40 per cent rhodium or to perhaps 10 per cent iridium.

In view of the fact that a satisfactory determination of the loss on heating for any type of crucible can be made only by elaborate experimentation, it is evidently of interest to be able to substitute the simple thermo-electric test and microscopic examination.

SUGGESTIONS AS TO SPECIFICATIONS—What is desired in a crucible for exact analytical work is a material which will strictly maintain its weight on heating and on treating with strong acid after heating; which will not exude any oxidizable or soluble matter on heating; which will not crack or develop other mechanical defects; and which is stiff enough to handle conveniently with tongs. Some of these requirements appear to be simultaneously difficult of realization in the present state of our science and of the art of working platinum and its alloys.

Iridium, which adds stiffness to platinum, renders the crucible subject to proportionally greater losses of weight on heating. The presence of iron appears to lower materially the heat losses but is very objectionable on account of the formation of a soluble oxide coating. The purest platinum is usually not stiff enough, although two or three of the apparently purest crucibles here examined were unaccountably stiff, perhaps because of the presence of a small amount of osmium or silica. Rhodium both stiffens the crucible and lowers the heat and acid losses and is much to be preferred to iridium as an alloying element, and crucibles containing small amounts of rhodium, say from 3 to 5 per cent, are to be preferred to crucibles of pure platinum. As the rhodium content is increased the crucible may develop cracks in service.

A requirement which might reasonably be met, at not too great expense for highest grade crucibles, would be: platinum containing 3 to 5 per cent rhodium, practically free from iron and iridium, and containing no other detectable impurities. For most purposes, these requirements could be checked by assuring one's self that the E. M. F. at 1100° C. against *pure* platinum was less than 8 and greater than 5 millivolts; that the characteristic crystal structure was that of rhodium and not iridium; and that *no* iron hydroxide precipitate was obtained after ignition for two hours over strong blast and applying the acid treatment as above described. If pure platinum were preferred, the E. M. F. at 1100° C. should be less than 1 millivolt. If other stiffening ingredients than rhodium be allowed, the 1 millivolt E. M. F. requirement should be maintained.

## SUMMARY AND CONCLUSIONS

I—There were examined by the thermoelectric method 164 pieces of platinum ware of which 26 per cent contained less than 0.5 per cent iridium and 67 per cent less than 2 per cent of iridium. Of 84 crucibles 36 per cent contained less than 0.5 per cent iridium and 87 per cent less than 2 per cent iridium.

II—A method has been developed for determination of the exact loss on heating of platinum crucibles, by means of a suitable electric furnace containing no heated metal parts.

III—Fourteen crucibles of various makes and grades were examined for loss in weight on heating and after acid treatment following each heating. Their magnetic susceptibilities were also determined. The susceptibility of pure platinum is zero and the range of susceptibility for seven crucibles is 1 to 125.

IV—The heating losses per 100 cm². of practically iron-free crucible surface at 1200° C. ranged from 0.71 mg. to 2.69 mg. per hour, the lesser losses being for crucibles containing rhodium and the greater losses being associated with iridium.

V—Iron appears to lessen somewhat the loss of weight on heating but its presence is objectionable on account of the soluble oxide formed on the crucible surface. The chemical analyses and magnetic measurements place the crucibles in only approximately the same order as to iron content; the magnetic susceptibility is not, however, proportional to the iron content.

VI—It appears to be possible, from a thermoelectric and microscopic examination of a crucible, to predict its probable loss of weight on heating within limits close enough for analytical purposes.

VII—Suggestions are offered concerning the specifications of highest grade platinum crucibles, including the substitution of rhodium to 5 per cent for iridium, and the practical elimination of iron.

VIII—Whether crucibles have been long in use or not, after the first two or three heatings and acid washings, appears to have little or no effect in their behavior as to losses on heating and washing.

We wish to express our obligation to Dr. W. F. Hillebrand who has furnished many valuable suggestions which have aided the progress of this investigation.

BUREAU OF STANDARDS, WASHINGTON, D. C.

## THE PREPARATION, PROPERTIES AND COMPOSITION OF SILUNDUM

By Samuel A. Tucker and Alexander Lowy

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Silundum is a product of the electric furnace, and was discovered by Bölling,[1] at Frankfort-on-the-Main, Germany. As early as 1900 he began the study of the use of the various silicon carbides as resistors, being led to this work by the fact that these carbides can be subjected to high temperatures without undergoing decomposition. His method was to mix the silicon carbide powder with various binders in order to hold the individual particles together. The mass is a non-conductor at low temperatures, but at about 700–800° C. it becomes conductive, thus being useless at a higher temperature.

By 1904 a process was worked out and patented by which it is possible to convert any piece of carbon, *e. g.*, a crucible, brick, rod, etc., into silicon carbide. By this method resistors without any binding material are obtained, which will stand temperatures as high as 1650–1700° C. Previous to 1904, silicon carbide had been known in two conditions only—amorphous and crystalline—and it was supposed to be formed by the interaction of sublimed carbon and sublimed silicon. Bölling, however, discovered that silicon penetrates carbon when both are in a highly heated condition, but at too low a temperature for the carbon to have any appreciable vapor tension. He claimed that silicon at about 1600° C. exists in the form of vapor. Carbon at this temperature has an extremely small vapor pressure. According to Bölling's definition, silundum is the product that is obtained when carbon is heated in an atmosphere of silicon vapor.

An electric furnace such as is used for the manufacture of carborundum was used for the preparation of silundum. Pieces of carbon pressed to the desired shape were introduced into a mixture of sand and carbon, and this was heated by using as a resistor a granular core of coke. The sand was reduced and the silicon, volatilizing, penetrated the carbon objects and thus "silundumized" them.

Moyat[2] criticized Bölling's work, and claimed that silundum was not a new chemical individual, but merely a new variety of silicon carbide.

Acheson's patent[3] No. 895,531 is interesting, inasmuch as it deals with a similar product. In order to protect crucibles, tuyères, bricks, muffles, and other articles of carbon from destruction at high temperatures in the presence of oxygen, or when exposed to molten metals, Acheson proposes to cover them with a coating of a highly refractory siloxicon, or silicon oxycarbide. This prolongs their life and prevents disintegration. A portion of the carbon on the surface of the article itself is utilized in producing the siloxicon coating. After having been shaped to the form desired, the carbon or graphite article is embedded in a mixture of silica and carbon in the proportion of two parts of sand to five of carbon, and is exposed to the proper temperature at which silicon, oxygen, and carbon combine to form siloxicon.

The product obtained by this method resembles in appearance the lighter-colored silundum, which is to be discussed later in greater detail.

Tucker and his co-workers[1] in 1909 made an experimental study of the formation of silundum. In their experiments the charge was made up according to the proportion $SiO_2 : 2SiC$. This charge was heated in a carborundum furnace, the core of which, instead of being of granular carbon, consisted of a number of small carbon plates, pressed together between two horizontal graphite electrodes. Around the core was placed a charge of sand and carborundum, in which were embedded, at varying distances from the core, the carbon articles to be silundumized. These workers also investigated the reactions between sand and carbon. Their experiments showed that silundum can be produced by either of the above reactions, *i. e.*, by the reaction of sand and carbon or of sand and carborundum. They also showed the relative difficulty of oxidizing silundum. Two plates, silundumized on the surface, were heated to a high temperature by means of an electric current. The graphite cores were completely oxidized, leaving only box-like shells of silundum.

Amberg-Bodio[2] also prepared silundum, and states that, "According to the temperature and the time, there is obtained a gray- to metallic-appearing silicon carbide, with a content of silicon greater or less than that which corresponds to the formula SiC. The process may be interrupted at any time and a coating of silundum of any desired thickness produced."

Within the past few years, F. J. Tone[3] has obtained four patents for the preparation and manufacture of dense, compacted silicon carbide. From his description, the term "dense compacted silicon carbide" is synonymous with the term "silundum."

Egly,[4] early in 1913, patented a substance called "Silit" which is prepared by heating to a fairly high temperature silicon carbide, silicon, and a binder, until a homogeneous mass results. "Silit" is a good resistor and has many industrial applications.

F. J. Tone[5] describes a silicidized carbon which he calls "Silfrax." In order to show the interior structure of the material, he gives microphotographs of it.

A survey of the literature and a careful preliminary examination of several samples of silundum, indicated to the writers that in all probability the material known as silundum exists in two modifications. The crudeness of the analytical methods used in determining the composition of these refractory materials made it impossible to draw any definite conclusion from the work already published. Moreover, little or no data are available on such important conditions for the preparation of silundum as temperature,

[1] F. Bölling, *Chem. Ztg.*, **32**, 1104; *Electrochem. and Met. Ind.*, **7**, 24.
[2] Moyat, *Chem. Ztg.*, **32**, 1166.
[3] Acheson, U. S. Patent No. 895,531, *Electrochem. and Met. Ind.*, **6**, 379.
[1] Tucker, Kudlich and Heumann, *Trans. Am. Electrochem. Soc.*, **16**, 207.
[2] Amberg-Bodio, *Z. Elektrochem.*, **15**, 725–727; *Chem. Abs.*, **4**, 149.
[3] Tone, U. S. Patents Nos. 913,324, 992,698, 1,013,700, 1,013,701.
[4] Egly, *Elektrotechn. Zeit.*, **34**, 263–267; *Chem. Abs.*, **6**, 536; **7**, 1142, 2357.
[5] Tone, *Trans. Am. Electrochem. Soc.*, **26**, 181.

proportions of reacting materials, and time of heating. It seemed, therefore, that by a careful investigation into the best conditions of temperature for preparing silundum, with an improved method of analysis and a careful examination of properties, considerable light might be thrown upon the question of the composition of silundum. With this purpose in mind the present investigation was undertaken.

Silundum, according to the conditions under which it is formed, exists in two modifications. One of these, a steel-gray variety, is formed at a temperature of about 1900° C. and analyzes very closely to the formula SiC; the other, a slate-green variety formed at about 1600° C., is an oxycarbide of silicon of the formula $Si_4C_4O$. It has been determined that silundum does not decompose below 2200° C. At higher temperatures silicon distils off, leaving a graphite skeleton of the same form as the original silundum, which action would indicate that the graphite does not vaporize at the temperature of decomposition, and would show, further, that silundum is formed by the reaction of silicon vapor and solid carbon, the temperature of formation being lower than the temperature of decomposition.

The action which takes place in the process of silundumization may be summarized as follows: The silicon which is liberated from silica by the reducing action of coke- or sugar-carbon penetrates the solid carbon or graphite objects, and there reacts with the carbon, forming a steel-gray variety of silundum. This takes place above 1800° C. Below this temperature the slate-green variety is formed, most likely by the penetration of the carbon by the silicon vapor and carbon monoxide.

The stumbling block in the analysis of such refractory substances as silundum has been the difficulty of completely decomposing the material and burning all the carbon to carbon dioxide. The silicon may be determined easily by means of the well-known sodium carbonate and potassium nitrate fusion. In order, therefore, to overcome the difficulties hitherto encountered in the carbon determination, various fluxes and oxidizing agents were tried, with the object of replacing the inadequate sodium peroxide and magnesia method[1] previously used. After considerable experimentation litharge was found to be an excellent flux for decomposing the material and partially oxidizing it, complete oxidation being effected by means of a stream of oxygen. Using this method on carborundum crystals, results were obtained that were accurate within 0.3 per cent of theoretical. Considering the nature of the material treated, this was satisfactory. Analyses of silundum samples were made by this new method, and the results checked on duplicates. Therefore, we consider this to be a good method for the accurate determination of carbon in refractory carborundum-like substances.

## DESCRIPTION OF EXPERIMENTS

PREPARATION OF SILUNDUM—In order to obtain sufficient amounts of the substance for the further study of its properties and composition, silundum was prepared in a coke resistance furnace (Experiments 1 to 7). Since this type of furnace does not lend itself to accurate temperature measurements, the temperatures of formation and decomposition were measured in a separate series of experiments (8 to 13) in the Arsem vacuum electric furnace.[1]

The coke resistance furnace[2] was chosen because with it a range of temperatures up to about 2600° C. can be obtained by varying the amount of electrical energy. The furnace, diagrammatically represented in Fig. 1, consists essentially of a coke resistor enclosed by cemented fire-clay brick walls with magnesia lining. The graphite electrodes extend through the walls into the coke.

The graphite crucible containing the charge and the articles to be silundumized were embedded in the coke core. The energy was supplied by a 50 kw. A. C. generator. The measurements and the

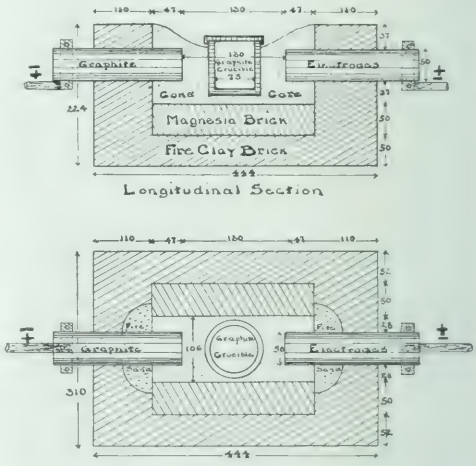


FIG. 1—RESISTANCE FURNACE (DIMENSIONS IN MMS.)

exact details of construction of the furnace are indicated in the diagram.

Carbon and graphite rods varying in diameter from 1/8 to 3/8 in., and 2 in. in length were used. In a few experiments carbon tubes were used. The charge consisted of clean sand and coke. For the samples that were to be analyzed, special charges, consisting of precipitated silica and sugar-carbon were used, in order to obtain a pure product. The objects to be silundumized in these cases were also made of graphite of the highest purity.

## EXPERIMENTS IN COKE RESISTANCE FURNACE

Experiments 1 to 7 were conducted in order to find out how the variation of the different factors of time, energy consumption and composition of charge would affect the nature of the product formed.

[1] Fitzgerald, *Electrochem. Ind.*, **2**, 443.

[1] Arsem, *Trans. Am. Electrochem. Soc.*, **9**, 153.

[2] Tucker, *Ibid.*, **11**, 307.

The readings taken during these experiments appear in Table I.

TABLE I—READINGS TAKEN DURING EXPERIMENTS IN COKE RESISTANCE FURNACE

| Experiment No. 1 | | | Experiment No. 2 | | | Experiment No. 3 | | | Experiment Number 5 | | | Experiment No. 7 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | Amperes | Volts | Time | Amperes | Volts | Time | Amperes | Volts | Time | Amperes | Volts | Time | Amperes | Volts |
| 10.00 | 0 | 40 | 1.30 | 0 | 35 | 9.30 | 0 | 34 | 9.55 | 0 | 35 | 10.00 | 0 | 40 |
| 10.10 | 75 | 38 | 1.45 | 200 | 30 | 9.45 | 200 | 32 | 10.05 | 75 | 34 | 10.10 | 100 | 36 |
| 10.20 | 100 | 36 | 1.55 | 300 | 30 | 9.55 | 310 | 30 | 10.10 | 100 | 30 | 10.20 | 200 | 30 |
| 10.30 | 150 | 34 | 2.00 | 400 | 30 | 10.00 | 405 | 25 | 10.15 | 200 | 29 | 10.30 | 500 | 28 |
| 10.40 | 150 | 34 | 2.10 | 400 | 26 | 10.15 | 400 | 25 | 10.20 | 250 | 30 | 10.40 | 500 | 26 |
| 10.50 | 150 | 34 | 2.20 | 400 | 26 | 10.30 | 410 | 25 | 10.25 | 350 | 29 | 10.50 | 550 | 25 |
| 11.00 | 200 | 28 | 2.30 | 400 | 26 | 10.45 | 410 | 25 | 10.30 | 450 | 28 | 11.00 | 650 | 25 |
| 11.10 | 270 | 26 | 2.40 | 410 | 26 | 11.00 | 400 | 25 | 10.35 | 550 | 28 | 11.10 | 650 | 25 |
| 11.20 | 300 | 26 | 2.50 | 410 | 26 | 11.30 | 400 | 25 | 10.40 | 550 | 28 | 11.30 | 650 | 25 |
| 11.30 | 300 | 26 | 3.00 | 410 | 26 | 12.00 | 400 | 25 | 10.45 | 550 | 28 | 12.00 | 650 | 25 |
| 12.00 | 300 | 26 | | | | 12.30 | 400 | 25 | | | | 12.30 | 650 | 25 |
| | | | | | | 1.00 | 400 | 25 | | | | | | |

EXPERIMENT 1 A charge consisting of a mixture of 60 g. coke and 150 g. sand (the theoretical amount to produce silicon) was placed in a graphite crucible. Four carbon rods $^1/_4$ in. in diameter and 2 in. long were then embedded in the charge and the crucible tightly covered with a graphite cover. Crucible and contents were placed in the furnace within the coke resistor, and the electric current turned on. After two hours the furnace was allowed to cool, and examination of the contents of the crucible showed that the rods were not silundumized. The sand was fused around the graphite rods. This experiment indicated that a higher temperature was necessary for the accomplishment of the desired reaction.

EXPERIMENT 2 was conducted in order to study the effect of higher temperature on the reaction. The electrical energy consumption was increased, as indicated above, with the object of obtaining this desired higher temperature. The composition of the charge was the same as in Experiment 1. The graphite rods upon fracture were found to be silundumized half way through. The line of demarcation between the silundumized portion and the portion not acted upon was very sharp (see the microphotograph, Fig. 2). The color of this product was slate-green.

EXPERIMENT 3 was intended to produce silundum extending through the entire cross-section of the rods. The charge was made up exactly as in Experiment 1, and the temperature conditions were also duplicated as closely as possible. This experiment, however, was carried on two hours longer than Experiment 2. The rods were completely silundumized, and no graphite core was visible. The color of the rods was slate-green. They were conductors of electricity even at ordinary temperatures.

EXPERIMENT 4 was carried out in order to determine whether there is any difference in the nature of the product obtained when the rods are embedded in the charge and when they are exposed. The charge in this experiment consisted of 120 g. silica and 48 g. coke. The rod was placed in the charge with the upper half extending above the surface of the charge. The other conditions of the experiment were the same as in Experiment 2. The product was of a slate-green color. Fracture showed that the part embedded in the charge was silundumized about half way through, while the part exposed had only a superficial coating of silundum. This experiment shows that more complete silundumization takes place when the rods are embedded in the charge than when they are exposed.

EXPERIMENT 5 was intended to show the effect of still higher temperatures than were used in the previous experiments. A charge like that in Experiment 1 was used. The rods upon fracture were found to be silundumized about half way through. The color of the product was steel-gray, resembling carborundum. Clearly defined characteristic carborundum crystals were found on the surfaces of the silundumized rods.

EXPERIMENT 6 was similar to Experiment 5 except that the heating was carried on for four hours. Subsequent examination of the rods showed that complete silundumization had taken place. The rods were steel-gray in color, and had small carborundum crystals on the surface. They were conductors of electricity even at ordinary temperatures.

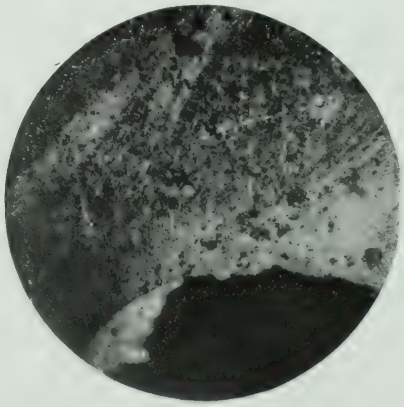

FIG. 2

EXPERIMENT 7 was designed to study the effect of high temperatures. A rod of silundum of the steel-gray variety was placed in the graphite crucible and heated for two hours under electrical conditions as given in Table I. The silundum rod was found to have lost all its characteristic properties, and on further examination proved to be graphite.

Experiments were also carried out in order to determine what would be the effect of varying the composition of the charge used. It was found, however, that no appreciable difference in the nature of the product resulted from such variation. Some of the sand in the charge sinks to the bottom, and the coke, because of its lower specific gravity, remains at the top. There is never, therefore, any very intimate mixture of the ingredients. It is not surprising, in consequence, that small differences in the ratio of the components of the charge should produce no differences in the results.

EXPERIMENTS IN ARSEM ELECTRIC VACUUM FURNACE

EXPERIMENTS 8 TO 13—As temperature determinations cannot be made with any degree of accuracy in the electric furnace used above, Experiments 8 to 13 were carried out in an Arsem electric vacuum furnace,[1] in order to determine the temperature of formation and decomposition of silundum. Details of the construction of this furnace, which is complex, are out of place in this article, and the reader is referred to the reference below. The temperature was measured with a Wanner optical pyrometer. As pyrometer readings are untrustworthy in the presence of fumes, blank runs were first made without any material in the furnace, noting at the same time the energy consumed and the temperature attained. These temperatures were then taken as the temperatures which would exist in the experiments made under the same conditions of time and energy consumed.

A graphite crucible, $^3/_4$ in. diameter and $2^1/_2$ in. high, was used. The carbon rod to be silundumized was placed in the center of this crucible and was surrounded with the charge, composed as usual of silica and coke. The energy consumption was recorded by a wattmeter. The results of these experiments are given in Table II.

TABLE II—RESULTS OF EXPERIMENTS IN ARSEM ELECTRIC VACUUM FURNACE

| Exp. No | Temp. ° C. | Ratio of $SiO_2$ to C in charge | Color of product | Remarks |
|---|---|---|---|---|
| 8 | 1300 | 30 : 12 | . | No silundum formed |
| 9 | 1606 | 30 : 12 | Slate-green | Surface silundumization |
| 10..... | 1712 | 30 : 12 | Slate-green | Surface silundumization |
| 11 | 1845 | 30 : 12 | Steel-gray | Surface silundumization— |
| 12 | 1900 | 30 : 12 | Steel-gray | most of charge volatilized |
| 13..... | Over 2200 | 30 : 12 | Product decomposed | |

Owing to the fact that a high vacuum was maintained as the temperature rose, some of the silicon distilled from the charge and the depth of silundumization was very small, but the surface layer was sufficiently characteristic to determine the nature of the product.

CONCLUSIONS FROM EXPERIMENTS

I—The temperature of formation of silundum is above 1300° C. (see Expts. 1 and 8).

II—Up to about 1800° C. the greenish slate-colored variety of silundum is formed (see Expts. 2, 3, 4, 9 and 10).

III—Above 1800° C. the steel-gray colored variety of silundum is formed (see Expts. 5, 6, 11 and 12).

IV—Continued heating above 2200° C. results in decomposition of the silundum with formation of graphite (see Expts. 7 and 13).

V—The extent of penetration of silundumization depends upon the duration of heating (see Expts. 2, 3, 4, 5 and 6).

VI—More complete silundumization takes place when the object is embedded in the charge (see Expt. 4).

PROPERTIES OF SILUNDUM

According to Bölling,[2] silundum is a form of silicon carbide, and possesses properties similar to those of carborundum. It is capable of being maintained for a long time at temperatures up to 1600° C. without change, and may be heated for a short time to 1700° C. without deterioration. It is a conductor of electricity, its resistance being about six times that of carbon. At 1000° C. its resistance is one-half to two-thirds of that at room temperature. The electrical resistance is variable, and depends upon the variety and hardness of the carbon used in the preparation, that made from porous carbon having a higher resistance than that made from compact. Silundum cannot be melted; in this respect it resembles carbon. It may be nickel-plated, or covered with a layer of platinum. It is a refractory material, but it is attacked by molten metals at high temperatures. It may be heated to a white heat and plunged into cold water without cracking.

Briefly, the results of the present investigation of the physical and chemical properties of silundum may be summarized as follows:

1—Silundum is a good conductor of electricity, with a negative temperature coefficient for its resistance.

2—Silundum is a very hard substance—with a hardness on Mohr's scale of about 9.

3—The specific gravity of silundum is 2.9 to 3.

4—Silundum is not attacked by hydrogen, oxygen, or nitrogen even at 1100° C.

5—Silundum is attacked by some fused salts.

6—Silundum is not attacked by acids.

ELECTRICAL CONDUCTIVITY—The following is the method for determining the electrical conductivity of silundum: A cylindrical rod of uniform diameter was used. In order to diminish the contact resistance as much as possible the ends were copper-plated, thus: the rods were dipped into paraffine, the ends scraped clean, coated with a very thin layer of graphite, and then copper-plated electrolytically. Copper wires were soldered on, and the rods were cleaned. The resistance was determined at various temperatures with a very accurate Wheatstone bridge.[1]

The rod of the slate-green variety was 1.871 cm. long and 0.635 cm. in diameter. The rod of the steel-gray variety was 2.078 cm. long and 0.348 cm. in diameter. Owing to the fusion of the solder, measurements could not be made above 225° C. The rods were heated in a small Hoskins electric furnace, and the temperature was read by means of an ordinary thermometer with its bulb in the heating chamber. Table III shows the measured resistances and the specific resistances in ohms at the various temperatures. The specific resistances are plotted against the temperatures in Fig. 3.

TABLE III—RESISTANCES OF THE TWO VARIETIES OF SILUNDUM

| | Slate-green Variety Rod 1.871 Cm. Long and 0.635 Cm. in Diameter | | Steel-gray Variety Rod 2.078 Cm. Long and 0.348 Cm. in Diameter | |
|---|---|---|---|---|
| Temp. ° C | Measured resistance Ohms | Specific resistance Ohms per cc | Measured resistance Ohms | Specific resistance Ohms per cc |
| 20 | 0.91450 | 0.1546 | 5.2250 | 0.2391 |
| 25 | 0.91270 | 0.1543 | 5.1886 | 0.2374 |
| 50 | 0.90000 | 0.1522 | 4.9786 | 0.2278 |
| 75 | 0.89092 | 0.1506 | 4.8186 | 0.2205 |
| 100 | 0.88192 | 0.1491 | 4.6291 | 0.2118 |
| 125 | 0.87212 | 0.1474 | 4.4191 | 0.2022 |
| 150 | 0.86202 | 0.1457 | 4.2791 | 0.1958 |
| 175 | 0.85392 | 0.1443 | 4.1541 | 0.1901 |
| 200 | 0.84522 | 0.1429 | 4.0441 | 0.1850 |
| 225 | 0.83530 | 0.1412 | 3.9541 | 0.1809 |

[1] Arsem, *Trans. Am. Electrochem. Soc.*, **9**, 153.

[2] Bölling, *Loc. cit.*

[1] This was done in the Electrical Testing Laboratory of Columbia University.

Attempts were made to spray the ends of the rods according to the Schoop[1] method, but when they were heated, the brass contacts became loosened from the ends of the rods.

It is evident from the above results that the resistance is practically a linear function of the temperature. The temperature coefficient of resistance is negative. The specific resistance is much less than that for carborundum, being, at 25°, 0.1543 ohm per cubic centimeter for the slate-green variety, and 0.2374 ohm per cubic centimeter for the steel-gray variety, while that of carborundum is 50 ohms per cubic centimeter at 25°.[2]

It was attempted to measure the ohmic resistance of the above rods at higher temperatures by clamping them between platinum plates. The resistance varied from 75 ohms to a fraction of an ohm, depending upon the pressure exerted upon the platinum plates, so that measurements of the same order of accuracy as those

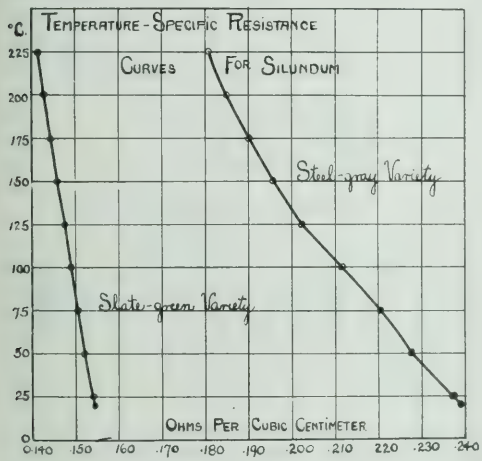


Fig. 3

determined above with plated ends could not be made above 225° C.

HARDNESS and specific gravity measurements are given in Table IV for the two varieties of silundum and for Tone's and Bölling's products.

SPECIFIC GRAVITY was determined by means of a specific gravity bottle, care being taken to expel all air bubbles by careful heating and subsequent cooling.

Table IV—Hardness and Specific Gravity of Silundum

| | Specific gravity | Hardness Mohr's scale |
|---|---|---|
| Tone's "Silifrax" | 3.96 | 9 plus |
| Bölling's silundum | 2.97 | 9 |
| Greenish variety silundum | 3.92 | 8 to 9 |
| Steel-gray variety silundum | 3.94 | 9 minus |

PROPERTIES OF BOTH VARIETIES OF SILUNDUM

ACTION OF GASES.—Oxygen, nitrogen, and hydrogen have no action on silundum heated to temperatures up to 1100° C. An attempt was made to oxidize silundum in a bomb calorimeter under a pressure of 25 atmospheres of oxygen, in a gelatine capsule containing a mixture of benzoic acid and silundum. The gelatine and the benzoic acid were completely oxidized, but the silundum was unattacked.

ACTION OF FUSED SALTS, ETC.—Silundum is not decomposed by the following fused salts: sodium silicate, borax, a mixture of potassium chlorate and potassium nitrate, potassium acid sulfate, cryolite, potassium dichromate.

Silundum is decomposed by fused sodium carbonate, sodium hydroxide, and potassium hydroxide in presence of air, yielding the corresponding silicates and carbon dioxide.

ACTION OF ACIDS.—Silundum is not acted upon by hydrochloric, nitric, or sulfuric acids, nor by a mixture of hydrochloric and nitric acids, a mixture of chromic and sulfuric acids, nor by fused boric acid. Commercial silundum, however, is slightly attacked by hydrofluoric acid and by a mixture of nitric and hydrofluoric acids, because of the presence of free silicon and silicon dioxide; but pure samples of silundum are not attacked by these acids.

ACTION OF OTHER SUBSTANCES.—Molten sulfur has no action on silundum. Sodium peroxide oxidizes it to sodium silicate plus sodium carbonate. Lead oxide also oxidizes it, producing metallic lead and carbon dioxide (pp. 566 and 570). Fused sodium in presence of air decomposes silundum, yielding sodium silicate and sodium carbonate. The action in this case is most likely due to the presence of sodium peroxide formed from the sodium.

COMPOSITION OF SILUNDUM

In order to obtain silundum as pure as possible for analysis, graphite rods were silundumized according to the previously described methods, in a charge consisting of sugar-carbon and precipitated silica. The resulting silundum was broken up into small pieces in a steel mortar, and subsequently ground to a very fine powder in an agate mortar. The powder was then purified. Depending upon the conditions of preparation, the product obtained was either silicon carbide or silicon oxycarbide, with probable impurities either from the charge or from the reaction, or from the mortar in which the material was ground. The impurities may be silicon, silica, carbon, and iron. Silicon was removed with boiling potassium hydroxide solution, any remaining silica by means of hydrofluoric acid, and the uncombined carbon by long oxidation with a strong blast lamp. Finally, in order to assure complete oxidation the material was boiled with chromic and sulfuric acids, and then with hydrochloric acid in order to remove any particles of iron which may have been abraded from the mortar. The material was then thoroughly washed, and when dried was ready for analysis.

For the silicon determination 0.3 to 0.4 g. of the above purified substance was weighed into a platinum crucible. To this were added 4 g. of chemically pure sodium carbonate and a small crystal of potassium nitrate. The contents were then well mixed and the covered crucible heated, great caution being used to

[1] *Met. Ind.*, **1914**, p. 457. This Journal, **4**, 853, **5**, 776, **7**, 72.

[2] Pamphlet, "Chemical and Physical Properties of Carborundum," published by The Carborundum Co., Niagara Falls, N. Y. 1913.

avoid spattering. The heating was continued until a quiet fusion resulted, then strongly increased until all the carbon particles were oxidized, leaving a clear melt. This upon cooling gave a clear, white mass, which was dissolved in hydrochloric acid and evaporated to dryness, dehydrated three times, and the determination of silica made as in rock analysis. The silica was weighed by difference after repeated evaporation with hydrofluoric acid. Duplicate analyses checked within 0.15 per cent. From the amount of silica obtained the percentage of silicon was calculated. The results are given in Table V.

TABLE V ANALYSES OF SILUNDUM FOR SILICON

| PER CENT SILICON FOUND | | THEORETICAL PER CENT SILICON | |
|---|---|---|---|
| Steel-gray silundum | Slate-gray silundum | in silicon carbide | in $SiC_2O$ |
| 69 46 | 63 16 | 70.22 | 63.88 |
| 69 59 | 63 28 | | |

The method[1] formerly employed for the determination of combined carbon in carborundum-like substances was to fuse about 0.3 g. of the substance with 3 g. of calcined magnesium oxide and 6 g. of sodium peroxide in a nickel crucible. A blank test had to be run at each set of experiments to determine the amount of carbon dioxide present in the magnesia and sodium peroxide. Furthermore, it was necessary to heat the crucible with a hydrogen flame until a vigorous reaction occurred, and the crucible while still hot was transferred to a desiccator charged with soda-lime and allowed to cool. The carbon dioxide was then determined by any suitable method.

This scheme is subject to grave error, owing to the appreciable amounts of carbon dioxide present in the magnesia and sodium peroxide. The carbon dioxide content of the sodium peroxide continually increases, and therefore, even with the blank corrections, the results are subject to error. The reaction is generally so violent that spattering is almost unavoidable. Moreover, the process is long, and involves too many operations to yield absolutely quantitative results under the conditions given.

The method worked out in this paper avoids these difficulties.

After preliminary experiments with various oxides, such as pure cupric oxide, ferric oxide, and manganese dioxide, as oxidizing agents, it was found that only molten litharge gave good results on carbon determinations in carborundum-like substances. Molten litharge disintegrates the particles of silundum, and at the same time oxidizes the carbon to carbon dioxide. The reactions may be written as follows:

$$SiC + 4PbO \longrightarrow SiO_2 + 4Pb + CO_2,$$

$$PbO + SiO_2 \longrightarrow PbSiO_3, \text{ and } 2Pb + O_2 \longrightarrow 2PbO.$$

PROCEDURE—0.20 to 0.25 g. of the sample was weighed out in a watch glass. This was thoroughly mixed with 5 g. of litharge whose carbon dioxide content had been determined in a blank test carried out under the same conditions as the analysis. The mixture of litharge and sample was placed in a C. M. Johnson combustion boat made of vitrified clay, 120 mm. long and 15 mm. wide.[2] Experiments were also made with combustion boats of porcelain, alundum, nickel, iron, and copper, but all except the vitrified clay were attacked and fused by the molten litharge.

The boat with its charge was placed in the silica tube of an electric combustion furnace, and the air in the furnace displaced by oxygen that had been thoroughly dried in a drying train. The current was turned on and the temperature raised slowly enough to avoid too rapid decomposition, which, if it occurred, would blow the charge out of the combustion boat. A gentle stream of oxygen was passed through the apparatus throughout the determination, and the course of the reaction was followed by observing the rate at which the bubbles of gas passed through the absorption apparatus. As soon as the evolution of carbon dioxide tended to become rapid, the electric current and the flow of oxygen were turned off until the reaction subsided, and no more bubbles of gas passed through the absorption apparatus. Then the current was turned on again, and a slow stream of oxygen passed through. The temperature inside the furnace was kept at about 600° C. for about 45 minutes, and then gradually raised to about 1000°. This was done to

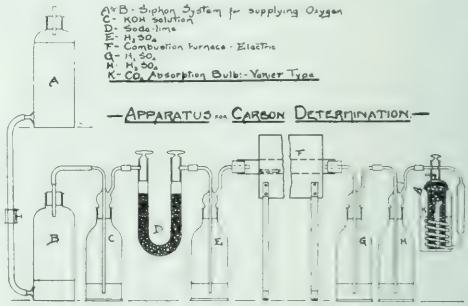


FIG. 4

eliminate any possibility of carbon dioxide remaining in the molten mass. The carbon monoxide that may be given off at this temperature is converted into carbon dioxide by passing over a heated coil of cupric oxide. The carbon dioxide evolved was absorbed in a Vanier KOH absorption apparatus.

The arrangement of the apparatus as set up is indicated in Fig. 4. Analyses made by this method are given in Table VI.

TABLE VI—CARBON IN CARBORUNDUM AND SILUNDUM
Correction for $CO_2$ in PbO = 0.0175 Gram

| SAMPLE | Weight Sample Grams | Grams $CO_2$ evolved | Weight $CO_2$ corrected | Per cent C in sample | Theoretical Per cent Carbon |
|---|---|---|---|---|---|
| Large carborundum crystals | 0.2004 | 0.2330 | 0.2155 | 29.33 | in SiC |
| | 0.2142 | 0.2488 | 0.2313 | 29.45 | 29.78 |
| Steel-gray silundum | 0.2509 | 0.2925 | 0.2750 | 29.89 | in |
| | 0.2214 | 0.2609 | 0.2434 | 29.95 | SiC |
| | 0.2187 | 0.2586 | 0.2393 | 29.84 | 29.78 |
| Slate green silundum | 0.2082 | 0.2308 | 0.2133 | 27.94 | in |
| | 0.2413 | 0.2633 | 0.2458 | 27.76 | $SiC_2O$ |
| | 0.2265 | 0.2488 | 0.2313 | 27.85 | 27.09 |

From the examination of the data in Tables V and VI as summarized in Table VII, it is evident that the percentage of carbon and the percentage of silicon in the steel-gray variety of silundum add up nearly to 100 per cent, indicating that the accepted formula

[1] Fitzgerald, *Loc. cit.*

[2] Ehmer and Vmend, New York

SiC is correct for this modification or variety. On the other hand the silicon and carbon in the slate-green variety of silundum add up to only 91.07 per cent. This variety evidently does not correspond to the formula SiC.

TABLE VII—SUMMARY OF ANALYSES

| | | Carborundum | Steel-gray silundum | Slate-green silundum |
|---|---|---|---|---|
| PER CENT FOUND | Si | | 69.53 | 63.22 |
| | C | 29.39 | 29.89 | 27.85 |
| TOTAL | | | 99.42 | 91.07 |
| | | | Silicon carbide | $Si_4C_4O$ |
| PER CENT THEORETICAL | Si | | 70.22 | 63.88 |
| | C | 29.78 | 29.78 | 27.09 |
| TOTAL | | | 100.00 | 90.97 |

It may be assumed from the careful method of preparation, in which only pure silica, sugar-carbon, and graphite were used, that the compound can contain only silicon, carbon, and oxygen. Since a temperature of approximately 1600° C. must be attained for the reaction to begin, practically all the air is expelled from the covered crucible; and further, since carbon monoxide gas is formed by the reaction and sweeps out the last traces of air, the reaction product can consist only of carbon, silicon, and oxygen, and their compounds. The remaining 8.93 per cent may legitimately be assumed to be oxygen. The percentage of oxygen corresponding to the formula $Si_4C_4O$ is 9.03 per cent; oxygen by difference is 8.93 per cent, which is good agreement.

Attempts were made to determine the oxygen content of the slate-green variety directly. The sample was placed with a pure metal, such as lead, steel, or copper in a vitrified clay boat in a combustion tube of a platinum-wound electric furnace, in which a temperature of 1300° C. can be easily attained. The air in the apparatus was displaced by extremely carefully purified nitrogen, prepared from ammonium nitrite. The idea in view was that the molten metal would dissolve the substance and carbon monoxide or carbon dioxide might be liberated. Arrangement was made for the monoxide to be oxidized to dioxide by passing through a hot tube containing cupric oxide. Owing to the fact that the sample in each case floated on the surface of the molten metal, no reaction occurred, as evidenced by the fact that the KOH absorption apparatus did not gain in weight.

As regards the relationship of silundum to carborundum, results obtained in this paper indicate that the steel-gray variety is a form of carborundum. The following facts may be mentioned:

1—Silundum has the same chemical composition as carborundum.

2—Their chemical properties are similar.

3—The temperatures of formation and decomposition are practically the same.

4—Some of the physical properties measured vary from those given in the literature.[1] This difference most likely is due to the fact that the other workers used different methods for their measurements.

SUMMARY

I—Two distinct varieties of silundum were prepared.

1—The slate-green variety: formula $Si_4C_4O$.

2—The steel-gray variety: formula SiC.

II—Experiments were made to determine the effect of varying the temperature, duration of heating, and composition of charge.

III—The temperatures of formation and decomposition of the two varieties of silundum were determined.

IV—The physical and chemical properties of both forms of silundum were investigated.

V—Results obtained in this investigation tend to show that the steel-gray variety of silundum is a variety of carborundum.

VI—A quantitative method for carbon determination in carborundum-like substances has been devised.

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[1] Pamphlet, "Chemical and Physical Properties of Carborundum," published by The Carborundum Co., Niagara Falls, N. Y., 1913.

## THE CONSTITUTION OF CHINESE WOOD OIL VARNISHES

By E. E WARE AND C. L. SCHUMANN[1]

Received April 19, 1915

The modern varnish operator is well acquainted with the general characteristics of Chinese wood oil, particularly those developed during the heat treatment necessary to the manufacture of high-grade rosin varnishes. He is, however, sometimes puzzled to account for the irregularities exhibited by the different shipments of raw oil, with which he is supplied. There has always been considerable difficulty in determining whether the peculiarities of the particular oil in question are due to unavoidable irregularities of the oil or to an adulteration that has not made itself manifest during the laboratory examination of the shipment.

The past difficulty in the detection of tung oil adulteration is being overcome, due to the development of methods of examination that will detect comparatively small amounts of added material. The 1915 report of Committee D1, American Society for Testing Materials, will, no doubt, do much toward standardizing the analytical methods for this oil, and by so doing, will be of considerable assistance to the varnish maker in the regulation of his product.

The most characteristic property exhibited by chinawood oil is its rapid bodying at temperatures considerably below those used for other oils. This increase in viscosity continues to the point of complete solidification, even at a temperature as low as 150° C. The length of time necessary for complete solidification depends upon the temperature and ranges from 30 hours heating at 150°, to 10 minutes at 280°. This solid material, particularly when formed at high temperatures, is a non-tacky, resilient body, practically insoluble in the ordinary solvents. It is saponified only with difficulty, and exhibits other characteristics that denote a complete change in the original glyceride. Although insoluble in most solvents, this material is completely soluble in a number of the organic acids, including rosin.

The presence of air has a decided effect upon the rate of solidification, although, as has been demon-

[1] Holder of Acme White Lead & Color Company Fellowship.

strated at different times,[1] air is not essential to solidification, which takes place perfectly well in a sealed vessel, though a longer time is required for the formation of the completely solid product. The statement of Schapringer that the effect of oxygen is entirely catalytic, and that no oxy-compounds are formed is difficult to verify by experiment. In all cases studied by the authors there have been progressively increasing amounts of oxidized materials formed, whenever wood oil or wood oil mixtures have been heated in the air. Also, if the action of oxygen be entirely catalytic, blowing air through the heated mass would hardly show such a decided effect on the rate of solidification in comparison to the rate during unagitated open air cooking. At 165° C., oil in an open dish will solidify in from 20 to 24 hours, while at the same temperature blown oil will solidify in 4 hours.

Various attempts have been made to prevent or control this solidification at high temperatures, for it is quite generally agreed that chinawood oil should impart the same superior quality to gum varnishes that it has given to rosin-chinawood varnishes as compared to rosin-linseed varnishes. The high cooking temperature of gum varnish has discouraged any extensive use of chinawood oil in this product, as the temperature is beyond the range to which the oil may be heated without solidification, and the fossil gums do not possess the solvent power for the solid material that is shown by rosin.

Several patents have been taken out covering processes to prevent solidification. One, evidently recognizing the very decided accelerating effect of oxy-acids on the time for solidification, recommends the introduction of a strongly reducing metal.[2] Another, possibly in an attempt to make use of the solvent power of free fatty acid, superheats the oil to a temperature of partial decomposition, after which it does not solidify even when heated for a long time.[3]

Investigators are pretty well agreed that the solidification of wood oil comes as a more or less direct result of the polymerization of the glyceride of elaeomargaric acid, which is the major constituent of the raw oil. This polymerization takes place through a joining at the unsaturated linkings. This, however, is not accompanied by a complete saturation, for a study of the iodine absorption of the raw and heat-treated products shows a difference of only about one-third. The polymerization is not reversed by saponification and subsequent acidification. Inasmuch as the polymerized glyceride is insoluble in the solvents suitable for molecular weight determinations, the best evidence we have that polymerization has really been effected is that the fatty acid from the solidified product has approximately double the molecular weight of the acid from the raw oil.

Morrell[4] has studied the bodying of linseed and poppyseed oils, and has shown that there occurs a similar heat polymerization with these oils, but that there is no solidification, and that the polymerization is by no means complete.

Various explanations have been offered for the solidification of chinawood oil when subjected to this heat treatment. Some experimenters believe that the solid is a uniform product of a chemical reaction which takes place at a rate dependent upon the temperature of heating and goes to completion under the proper conditions. Others take the stand that the solidification is really the development of a colloidal gel, and is not necessarily a product of complete polymerization.

Wolff[1] claims to be able to extract the unpolymerized oil from the dry polymerized product, and he shows in his experiments that the extracted material has not increased in molecular weight, and that the polymerized material constitutes only a minor portion of the gel.

Schapringer[2] says that the solid is a final product of a double reaction, and that the polymer is well developed in the primary reaction, but remains soluble until the second reaction starts, when there is a sudden exothermic formation of the gel.

The authors are led to believe from their experiments, that the solidification is due to the formation of a colloidal gel, and although, in the case of heated oils, a direct result of the presence of the polymer, the gel formation does not necessarily accompany the polymerization. The methods for control of solidification are simply means for hindering the gel formation, and exert comparatively little effect upon the polymerization.

A somewhat similar colloidal gel makes its appearance when the oil is treated with a solution of sulfur chloride or iodine. The time for gel formation may be regulated by adjusting the strength of solution used. In the case of the iodine-chinawood gel, the solidification may be entirely prevented by the introduction of a comparatively small amount of alcohol. This does not interfere with the formation of the iodine addition products, but acts to keep the colloid in solution.

The decomposition products formed during superheating of the oil must act similarly toward the oil in preventing solidification during subsequent heating. It is possible, by heating chinawood oil to 350° C. for only a short time, to prevent solidification from heat, even though the oil may be subjected to heating at the ordinary solidification temperatures for long periods. This still liquid product of heat treatment exhibits most of the characteristics of regularly polymerized oil. It contains a large amount of glyceride of high molecular weight, together with some free acid and a considerable quantity of unsaponifiable matter. This unsaponifiable material must exert some influence in preventing the natural solidification of the oil, for it seems hardly possible that the small amount of free acid

Jenkins, *J. Soc. Chem. Ind.*, **16** (1897), 195.
[2] German Patent 219,715, 1910.
[3] German Patent 211,405, 1908.
[4] *J. Soc. Chem. Ind.*, **34** (1915), 105.

[1] *Farben Zeitung*, **18** (1913), 1171.
Dissertation Translated Armitage and Stevens "Chinawood Oil"

present should act in any different manner from the same amount of free acid added to the original oil. It takes considerably more added fatty acid to prevent gel formation than has been shown in any of the superheated products with which the authors have worked.

Undoubtedly the effect of rosin upon heated oil is also one of solution or gel prevention rather than one of suspension of reaction. It should, then, be possible to show the progress of polymerization as influenced by time, temperature, and other conditions, and entirely independent of the rosin present. There might also be other reagents that would exhibit the same ability to control. The development of a nonpolymerizing wood oil will probably be along these lines.

To keep the finished product light in color, and to avoid undue loss from decomposition and volatilization of the gum, it is common practice, in varnish manufacture, to subject the oil to a preliminary heat treatment, to bring it to a body at which the final cook may be comparatively short. In the case of chinawood oil, the polymerization during this preliminary heating must be considerable, and inasmuch as this polymerization reaction is not ordinarily considered to be reversible, the function of rosin in these mixtures must be one of gel prevention.

In the experimental work, of which this paper is a preliminary discussion, the heating was carried out on the mixtures rather than on the individual constituents. The matter of color was of little consequence, and in order to get a more uniform set of results it was thought advisable to permit the rosin to exert its influence during the whole time of heating.

The first problem in the study of the polymerization of chinawood oil in the presence of rosin was the development of a satisfactory method of separation of the various possible constituents of the final mixture.

An attempt was made to use a modification of the Twitchell separation, by forming the ethyl esters of the fatty acids, and their subsequent separation from the rosin and from each other. This method gave a more or less satisfactory separation of the oils from the rosin, but the esters of the polymerized and unpolymerized oils did not show sufficiently pronounced differences upon which to base a method for their separation.

A modification of the method suggested by the authors[1] for the separation of raw chinawood oil from adulterating oils, served the purpose quite well.

The sodium soaps of the fatty acids of both the raw and heat-treated oils are insoluble in absolute alcohol, while sodium resinate is soluble in that menstruum. If proper precautions be taken for the control of temperature and concentration, the soaps of the fatty acids precipitate in a sufficiently granular form to permit of ready filtration and washing.

The subsequently freed fatty acids may be dissolved in warm alcohol of about 80 per cent concentration, from which the comparatively insoluble elaeomargaric acid may be crystallized by cooling. These characteristic crystals of elaeomargaric acid may be filtered and weighed, or the residue acids may be weighed and the elaeomargaric acid computed by difference. The oxy-acid present may be separated from the residue by precipitation from petroleum ether. In this way it is possible to get an estimation of the total fatty acid, the unpolymerized acid, the oxy-acid, the polymerized acid and the unsaponifiable.

An extensive study of chinawood-rosin heat-treated mixtures, the results of which are now being tabulated, demonstrates quite conclusively that rosin exerts no inhibiting effect upon the polymerization of chinawood oil, either at high or at low temperatures.

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[1] THIS JOURNAL, 6 (1914), 806

## STUDIES ON THE PRESSURE DISTILLATION OF PETROLEUM HYDROCARBONS

By A. P. BJERREGAARD

Received March 26, 1915

The investigation here reported upon was carried out during the summer of 1914 for the purpose of developing, if possible, a feasible and safe process for the production on a commercial scale of light gravity hydrocarbons, such as gasolines and naphthas, from the heavier and less valuable fractions of petroleum. It has been known for many years that these heavier hydrocarbons, on being subjected to heat and pressure, undergo a decomposition or breaking down into lighter products. This decomposition, whether under pressure or not, has received the name "cracking" in the petroleum industry. It is not the purpose here to go into the history of the process, further than to say that an apparatus somewhat similar to that herein employed was described in U. S. Patents Nos. 342,564 and 342,565, dated May 25, 1886, issued to Geo. L. Benton. In those early days, gasoline was an undesirable by-product, and Benton's process was intended to increase the kerosene fraction. What it actually accomplished is not recorded, so far as I am aware.

### APPARATUS

The apparatus which was employed (see Fig. 1) consisted of a reaction coil built of one inch double extra strong iron pipe, about 63 ft. long, interior diameter 0.60 in. with walls 0.36 in. thick. This coil was made up of five lengths, each 12 ft. long, with the necessary cross pieces at the ends, each 9 in. long, to make one continuous coil. Extra strong unions were used in each cross piece, and at the ends of each 12 ft. length, so that the whole could readily be opened up for inspection and cleaning. This coil was enclosed in a furnace constructed of fire-brick, asbestos and sheet-iron. It was heated by fourteen large Bunsen burners, each consisting of a horizontally disposed slotted piece of 2 in. pipe, 3 ft. long, fitted at one end with gas and air inlets, and closed at the other end. These burners were arranged under the reaction coil so that the flat sheets of flame issuing from them impinged lengthwise onto the pipes of the reaction coil. Each burner was controlled by a separate gas valve. The fuel was natural gas. Fig. 2 is a general view of part of the furnace, showing some of the gas-controlling

valves. The oil to be subjected to the pressure-cracking process was forced into one end of the coil by means of a hydraulic pump, capable of easily developing a pressure of 4,000 lbs. per sq. in. A pressure gauge reading to 2,000 lbs. was attached to the pipe leading from the pump to the coil. At the other end of the reaction coil was a pressure-release valve controlled by a spring. Various forms of valves were tried. Finally, the one illustrated in Fig. it to flow into an appropriate receptacle. The hydraulic pump was the smallest that could be bought, but was much too large for the purpose intended. It was necessary, therefore, to run it extremely slowly. This was accomplished by a system of pulleys and gears. By varying the sizes of the pulleys, different speeds could be given to the pump whereby the oil could be fed to the reaction coil at different rates: an electric motor was the driving force: Fig. 4 shows

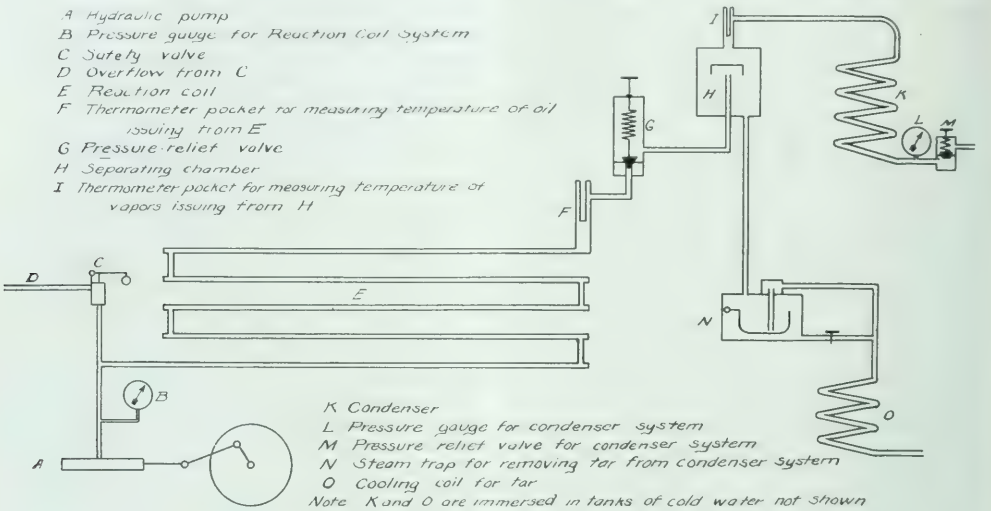



FIG. 1 DIAGRAM SHOWING ARRANGEMENT OF REACTION COIL AND AUXILIARY APPARATUS

3 was evolved, and this appears to be satisfactory. After leaving the pressure-release valve, the products of reaction passed into a separatory chamber, kept hot enough to allow the lighter vapors, which might be present, to pass out through an opening in the top into a condenser, while the tar, etc., passed out through the bottom. A slight pressure (about 20 to 30 lbs., never more than 40 lbs. per sq. in.) was maintained in the separatory chamber and condenser to facilitate the liquefaction of the most volatile constituents. A brass pressure-relief valve was attached to the lower end of the condenser to permit the condensed vapors and the permanent gases to escape. The condenser was a coil of 1-in. pipe immersed in a tank of water. The pressure in the cooling system described necessitated the use of a steam trap for the issuing stream of tar; this was of the ordinary floating bucket pattern, and performed its duty excellently. The hot tar was passed through a coil of pipe immersed in a tank of water to cool it before finally allowing

the general arrangement of this part of the apparatus. By means of the separating chamber *H* (Fig. 1), the crude mixture of reaction products was separated into two parts, and collected separately. The lighter here called *transformation distillate*, together with whatever permanent gases were produced, flowed from the condenser *K* (Fig. 1), through the valve *M*, and the heavier parts, here called *tar*, flowed from the steam trap *N*, and cooling coil *O*. The transformation distillates were all yellow in color and when re-

TABLE I DESCRIPTION OF OILS USED IN EXPERIMENTS

| Kind of oil | Source of oil | Description of oil | Color of oil | Flash test | Fire test | Begins to boil | Sp. gr. | Viscosity (Saybolt) | Cold test solid at | Amount of distillate |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Ill. crude | Ordinary 300 oil | Nearly white | 110° C. | 135° C. | 210° C. | 0.852 | 38 | —5° C. | |
| B | Ill. crude | Unpressed acid refined, neutral | Pale yellow | 155° C. | 175° C. | About 300° | 0.873 | 65 | 10° C. | Little below 320° C. |
| C | Ill. crude | Unrefined heavy distillate | Dark brown | | | About 300° | 0.880 | Very waxy | | Little below 330° C. |
| D | Pa. crude | Mixture of components from end of kerosene to heaviest distilled over in making cylinder stocks | Light brown | | | 260° C. | | Very waxy | | 10% below 310° C. |
| E | Ill. crude | Refined kerosene | Water white | 70° C. | | 170° C. | 0.820 | | | 31% up to 220° C. |
| F | Pa. crude | Refined kerosene | Water white | 65° C. | | 155° C. | 0.788 | | | 50% up to 220° C. |
| Tar | The tar produced in experiments 2708 and 2712 (see Table II) | | | | | | | | | |

distilled the first fractions were colorless; usually by about 150° C. the fractions began to be slightly yellow and by 200° very distinctly yellow.

The tars were all deep brownish red by transmitted light and they all had a dense green fluorescence, similar to that of Pennsylvania crude oil. No effort was made to ascertain the nature of the substances which imparted these characteristics to the tar.[1] When redistilled, the distillates from the tar were always yellow.

[1] See Brooks and Bacon, THIS JOURNAL, **6** 1914 623

On account of the frequent stoppages by the coke deposits described further on in this report, the 1-in. pipe was removed after most of the experiments herein were performed, and a piece of $2^1/_2$-in. double extra strong pipe, 12 ft. long, was substituted; its internal diameter was 1.77 in., its walls 0.55 in. thick. Only one trial was made in this, namely, No. 2750.

The various oils used in the experiments are described in Table I. All viscosity tests mentioned were made with the old style Saybolt viscosimeter. All flash and fire tests were made in the open cup.

TABLE II—RESULTS OF EXPERIMENTS

| No. | Kind of oil | Rate of feed Gals. per hr. | Average pressure lbs. per sq. in. | Average temp. ° C. | Per cent yield of fraction up to 150° C. | Per cent yield of fraction 150 to 220° C. | Total yield to 220° Per cent | Per cent loss |
|---|---|---|---|---|---|---|---|---|
| A—HIGH BOILING POINT OILS | | | | | | | | |
| 2701 | A | 3.7 | 275 | 350 | 23.0 | 17.3 | 40.3 | |
| 2717 | C | 3.7 | 400 | 350 | 24.0 | 8.6(a) | 32.6 | |
| 2750(b) | D | 3.7 | 450 | 440 | 18.5 | 15.0 | 33.5 | 7.8 |
| 2699 | A | 3.7 | 700 | 340 | 21.4 | 10.4 | 31.8 | |
| 2729 | D | 3.7 | 900 | 360 | 17.7 | 13.4 | 31.1 | 16.8 |
| 2702 | A | 3.7 | 900 | 340 | 23.3 | 11.2(a) | 34.5 | 15.7 |
| 2730 | D | 3.7 | 1000 | 395 | 27.9 | 14.4 | 42.3 | 15.0 |
| 2716 | C | 11.5 | 400 | 433 | 4.8 | 1.5(a) | 6.3 | |
| 2715 | Tar | 11.5 | 550 | 430 | 4.5 | 1.7(a) | 6.2 | |
| 2725 | D | 11.5 | 875 | 430 | 3.4 | 8.6 | 12.0 | |
| 2712 | B | 11.5 | 1300 | 430 | 6.7 | 3.8(a) | 10.5 | 1.6 |
| 2708 | A | 11.5 | 1375 | 430 | 8.6 | 5.4(a) | 14.0 | |
| 2711 | B | 11.5 | 1400 | 430 | 8.2 | 3.9(a) | 12.1 | 1.9 |
| B—NO YIELD OF LIGHT HYDROCARBONS | | | | | | | | |
| 2706A | A | 12.25 | 800 | 355 | 0 | 0 | 0 | |
| 2706B | A | 12.25 | 1400 | 360 | 0 | 0 | 0 | |
| C—KEROSENES | | | | | | | | |
| 2732 | F | 3.7 | 1000 | 360 | 24.8 | 21.5 | 46.3 | 29.6 |
| 2736 | F | 3.7 | 775 | 365 | 22.0 | 33.6 | 55.6 | 18.4 |
| 2739 | F | 3.7 | 775 | 365 | 10.0 | 42.0 | 52.0 | 11.4 |
| 2728 | E | 3.7 | 900 | 360 | 15.7 | 36.1 | 51.8 | 10.2 |
| 2727 | E | 11.5 | 875 | 435 | 3.3 | 31.5 | 34.8 | 1.9 |

(a) Tar not examined for low boiling components.
(b) $2^1/_2$ in. reaction coil.

Table II gives a summary of the experiments tried, together with a brief statement of the results obtained.

It will be noticed that three rates of feed were employed, and that there is a sharp distinction between the temperatures used with the two speeds of Table IIA. At the faster rate, it was found necessary greatly to increase the temperature in order to develop any "cracking." This is plainly shown by comparing Table IIB with A. Again, for some reason not clear, the larger sized pipe used in No. 2750 required the higher temperature, although the speed was set at the slower rate. It is also noticeable that the yields of low boiling point hydrocarbons and the gas loss was very much greater at the slowest speed. Neither the kind of oil nor the pressure seems to have any pronounced influence on the yield of low boiling hydrocarbons in the trials at the slower rate of feed. But at the higher rate, there seems to be a little better yield at the greater pressures. Even once-run tar when re-run yielded the same results as fresh oil run under the same conditions—compare Nos. 2715 with 2716.

In respect to the apparent large yields from the kerosenes (Table IIC), it is to be noted that the oil used in the first three cases contained before use 50 per cent boiling below 220°, while the other oil contained 31 per cent.

The percentages of yields in all cases (except those where the tar was not examined) is the sum of what was found in both the transformation distillate and the tar. The latter rarely contained anything boiling below 150°.

The figures in Table II show plainly that the time factor is a most important one, and that the yield is at least roughly proportional to the time the oil is subjected to the influence of heat and pressure, since the slower the rate of feed of the raw material, the longer the oil is in the reaction coil.

In two experiments an attempt was made to apply catalyzers, or at least to see if the substances employed would have any effect on the reactions involved. In No. 2736, one pound of highly magnesium calcium hydroxide to 50 gals. oil was used. In No. 2739 zinc oxide was similarly used. Neither increased the yield of gasoline; indeed, both appeared to decrease both that and the gas loss, the zinc oxide more so than the lime. The larger amounts of fraction 150°–220° in these two

FIG. 2—CONDENSER IN FOREGROUND, WALL OF FURNACE TO RIGHT WITH GAS SUPPLY COCKS AND LARGE ROUND LIGHTING-UP DOORS. ASBESTOS COVERED PIPE IS FOR LEADING THE HOT TAR FROM THE SEPARATING CHAMBER (NEAR TOP) TO THE STEAM TRAP

trials also indicate less cracking action, since there already was 50 per cent of this fraction present in the raw material.

A dense deposit of so-called coke formed on the inner surfaces of the pipes in the reaction coil. Because of the stoppage caused by this coke plugging up the pipes, prolonged use of the pipes was impossible. This carbon is quite hard, moderately brittle and breaks with a glossy conchoidal fracture like gilsonite or anthracite. Carbon bisulfide extracts only a very small part of it, forming a deep brownish red solution having a deep green fluorescence. That which is insoluble in carbon bisulfide is heavier in gravity than that liquid; it is insoluble in boiling aqua regia and almost incombustible when ignited on platinum foil. The aqua regia extract gives faint

reactions for iron. The carbon adheres with great tenacity to the iron of the pipes.

The carbon set free not only accumulated in the form of coke, but some seemed to be forced into combination with or into solid solution in the iron of the pipes. At any rate, whatever may be the cause of it, the iron became brittle so that when after about 15 runs an attempt was made to unscrew a fitting from one of the pipes, the pipe broke off with a crystalline fracture. But little torsion had been applied before the break took place. Shortly after that, one of the double extra strong 1-in. pipes burst during an experiment, at a time when only 400 lbs. pressure was being applied. There was no evidence that this part of the pipe had been greatly overheated and thus weakened. It did not look burnt, nor was it swelled as though it had been soft; on the contrary, a scarcely perceptible crack about $1^1/_2$ in. long opened up. The coil was always tested before each run to 2,000 lbs. pressure, cold. According to U. S. Patents 822,460 and 1,013,191, dated June 5, 1906, and January 2, 1912, respectively, issued to A. W. Machlet, iron articles are case-hardened by subjecting them to the action of light petroleum hydrocarbon vapors under heat and pressure. A similar action must have gone on in these trials, but penetrating into the iron of the pipes to a much greater depth under the influence of a very much longer time of exposure.

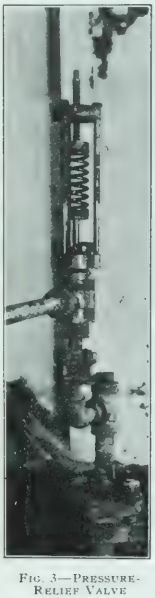


FIG. 3—PRESSURE-RELIEF VALVE

In several of these runs, measurements were made of yields during the run for the purpose of finding out whether the rate of production of transformation distillate was uniform throughout the run. It was found that in every case there was a distinct falling off in rate during the time of the run. This is attributed to the partial closing up of the pipe by the coke formed, causing a more rapid flow of the oil through the reaction coil and thus diminishing the time during which the oil was acted upon by the heat and pressure.

The yellow color of the transformation distillate is not removed by treatment with concentrated sulfuric acid in the usual petroleum refining process. Considerable heat is generated when these distillates are shaken with the acid. They become very dark, but after removing the acid and washing with water, the yellow color is restored. On now distilling the liquid, it passes over almost white even up to 220°.

Mercurous nitrate solution added to the yellow transformation distillate causes the formation of an abundant bright yellow precipitate; indeed with sufficient mercurous solution the whole mass becomes a yellow paste; large proportions of olefines must, therefore, be present. Ammoniacal silver nitrate was not reduced and gave no precipitate; acetylenes are, therefore, absent. Iodine and bromine are freely absorbed from their aqueous solutions by transformation distillates; this greatly modifies their odor, but not their color.

In order to find out just how transformation distillate would act under the usual refinery process for producing ordinary gasoline, $24^1/_2$ gals. were distilled with live open steam from a laboratory still of about 50 gals. total capacity, no other heat being applied. The first 39 per cent that came over was colorless and had sp. gr. 0.721 (64.6° Bé.); it left a residue of 5.2 per cent at 150° C; it was, therefore, a good gasoline. The next 12.3 per cent that came over was faint yellow: it had sp. gr. 0.761 (54.5° Bé.) and distilled between 90° and 200° C., and, except for the color, was a good naphtha. The next 17.4 per cent that came over was distinctly yellow, had sp. gr. 0.784, and distilled between 130° and 220° C.; its flash point was 36° C. The residue left in the still, amounting to 41.5 per cent (by difference) of the charge, was dark yellow, sp. gr. 0.835, and distilled between 180° and 320° C.

In another trial 17 gals. were similarly distilled.

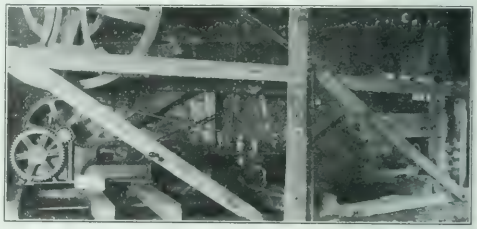


FIG. 4—GENERAL VIEW OF HYDRAULIC PUMP (TO LEFT), ELECTRIC MOTOR (TO RIGHT) AND PULLEY, SPROCKET AND GEAR ARRANGEMENT FOR OPERATING THE PUMP SLOWLY ENOUGH

The first fraction, 50 per cent of the whole, was white, had sp. gr. 0.720 (65.0° Bé.), and distilled between 40° and 170° C. The second fraction, 25 per cent of the whole, was yellow in color, sp. gr. 0.771, and distilled between 110° and 210° C. The residue left in the still was deep yellow, sp. gr. 0.804, and distilled between 130° and 250° C.

The transformation distillate used in both cases had not been treated in any way with chemicals to decolorize or otherwise change it. These distillations showed that transformation distillate behaves perfectly normally in the usual gasoline distilling process.

Search was made for aromatic compounds in the transformation distillate by an effort to isolate the xylenes. The method employed was as follows: The fraction of boiling point 130° to 220° obtained in steam-distilling the transformation distillate was fractionated in a copper still-head still and the fractions up to 140° and 140° to 150° collected separately. The residue left in the steam still was subjected to the same process, and the corresponding fractions were mixed. Lots of 1600 cc. each, of these fractions,

were then further fractionated from a 2000 cc. round-bottomed flask provided with a glass 12-bulb pear still-head and an Anschütz normal thermometer. The fractions 135° to 145° were collected and mixed. A total of 1170 cc. were obtained originating from the 24½ gals. transformation distillate. This was again fractionated, as before, collecting this time between 138.5° and 142.5°. Of this last fraction, only 125 cc. were obtained. A little of this was treated with concentrated nitric acid, first cold, finally boiling, but it yielded no nitro compounds. Hence, no xylene is present. Since xylene is absent, it is assumed that no aromatic hydrocarbons are present.

Several distillations were made of the tars obtained in these experiments with the object in view of isolating any viscous hydrocarbons of value as lubricating oils that might be present. This was always done with live open steam, with the simultaneous application of fire heat to the bottom of the still in the manner usual in the petroleum industry. In one case, 30 gals. of tar were subjected to this treatment. It is unnecessary to go into details about these trials, since nothing of value was found. The high heat and great pressure seems not only to have broken down whatever viscous hydrocarbons were originally present, but also to have prevented the formation of others, either by balanced reactions or otherwise. The original tars were all of heavier gravity than the oils from which they were made, of good cold test, and very thin in viscosity. All the residual oils left after steam distillation were similar, but the cold test was not so good; that is to say, there was present sufficient crystallizable paraffine to render the oil more susceptible to cold. All that is said above applies equally to tars derived from light original oils—namely, 300 oil and kerosene, and to those from heavy, waxy original oils—namely, wax distillate, etc. The original crystallizable paraffine, when present, was almost totally destroyed by the heat and pressure and so were all viscous components.

Credit is due to my son, James A. Bjerregaard, for constructing and operating this apparatus. My thanks are due to the Canfield Oil Company, of Cleveland, Ohio, for permission to publish this report.

CLEVELAND, OHIO

## THE TEMPERATURE COEFFICIENT OF EXPANSION OF PETROLEUM RESIDUUMS

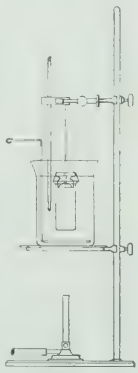
By H. Rossbacher

Received March 29, 1915

In the purchase of residuum oil the measurement of volume is usually made at an elevated temperature and the volume is then reduced to some standard temperature, usually 60° F. Engler[1] has shown that this coefficient is not a constant for all ranges of temperature but must be determined for ranges closely approximating those to which it is to be applied. Even for a defined temperature range the value will vary with the consistency of the material and the type of crude petroleum from which it is prepared. A closer attention to this value might prove of commercial advantage in many cases. With this idea, the following description is given of an easily applied method for determining the temperature coefficient of expansion of a petroleum residuum over any desired temperature range.

[1] "Das Erdoel," Vol. I, p. 95.

DESCRIPTION—To consider the most complicated case, it is assumed that the sample is semi-solid at the standard temperature. When the sample is sufficiently fluid to allow the seating of the stopper at this temperature, the following operations and calculations can be somewhat simplified. The specific gravity at the standard temperature is determined in a Hubbard pycnometer.[1] The pycnometer is then filled with the sample, warmed sufficiently to allow the stopper to be seated, and suspended in a wire sling in a glycerine bath, the top of the stopper projecting slightly from the surface of the glycerine. A thermometer is placed in the bath with its bulb opposite the middle of the pycnometer. The bath is heated slowly, with stirring, the stopper being kept firmly seated and wiped clean as the residuum expands. When the desired temperature is reached it is kept constant until the absence of further exudation of the sample from the capillary indicates that the sample has reached the temperature of the bath. The pycnometer is then removed, wiped clean, allowed to cool and weighed.



### CALCULATION

Let $a$ = Weight of pycnometer, empty.
$b$ = Weight of pycnometer, + water at standard temperature.
$c$ = Weight of pycnometer + sample at standard temperature.
$d$ = Weight of pycnometer + sample + water at standard temperature.
$e$ = Weight of pycnometer + sample at elevated temperature.
$f$ = Coefficient of cubical expansion of pycnometer, assumed 0.0000156 per °F. in this case.[1]

[1] "Chemiker Kalendar," Vol. II (1912), p. 89.

From values $a$, $b$ and $c$, calculate $W_s$, the weight of sample in the pycnometer at the standard temperature. The specific gravity of water at $T_s$ may be taken as unity for the purposes of this calculation. From $a$ and $b$ find $V_s$, the volume of the pycnometer at the standard temperature. Applying $f$, find the volume at the elevated temperature, $V_e$, in terms of $V_s$.

$$V_e = \frac{1 + 3T_e(f)V_s}{1 + 3T_s(f)}$$

From $a$ and $e$ find $W_e$, the weight of sample in the pycnometer at $T_e$. $\frac{W_e}{V_e} = W_{es}$, weight at $T_s$ for volume corresponding to $V_s$. $\frac{W_{es} - W_s}{W_s} = I_e$, the loss in weight of $V_s$ in increasing $T_e - T_s$ degrees in temperature.

$\frac{I_e}{T_e - T_s} = m$, coefficient of expansion in the formula

$$V_e = V_s[1 + m(T_e - T_s)]$$

Some results obtained by this method are of interest in illustrating the effect of temperature range on the coefficient.

[1] "Dust Preventives and Road Binders," pp. 329–30.

"STANOLITE"

| Specific Gravity | Coefficient of Expansion per °F. |
|---|---|
| 60–60° F | 60–212° F | 0.000364 |
| 1.0957 | 60–264° F. | 0.000378 |
| 77–77° F | 77–212° F | 0.000337 |
| 1.0887 | 77–264° F. | 0.000343 |

By Weiss' method of calculation[1] the coefficient of expansion for the range 60–77° F. on this sample is 0.000412.

A sample of Mexican residuum having a specific gravity of 1.0104 at 77/77° F. gave the coefficient 0.00032 for the range 77–160° F.

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## RELATIONS AMONG THE PHYSICAL CONSTANTS OF THE PETROLEUM DISTILLATES[2]

By Walter F. Rittman and Gustav Egloff

Received January 4, 1915

In the industrial study of petroleum and petroleum products strictly chemical methods of identification are of secondary importance. The number of reactions in use is limited, and these processes are not particularly convenient and satisfactory. They fail to give the sort of information most needed. For instance, the sulfonation test for olefines gives the same results whether the hydrocarbons have a boiling point of 100° or 300°, and indicates little regarding the commercial use or possibilities of an oil. Likewise a liquid sulfur dioxide extraction does not aid in differentiating a gasoline from a kerosene.

The important information in the study of petroleum distillates is obtained from determinations of various physical constants. In view of the convenience with which they can be measured, and the wide utility of these constants, it has been thought desirable to study relations existing among them. The work described in this communication deals with a comprehensive series of measurements and furnishes data which are helpful in indicating how the results of various experiments may be interpreted.

The two processes most universally employed and best understood are distillation and measurement of specific gravity. Distillation figures are more or less relative, depending upon the method used.[3] Gravity measurements are absolute and agree within the limits of experimental error no matter what device is employed to secure them.

Viscosity coefficients for crude oils and refined products are commonly determined. Many chemists measure refractive indices, though the use of this valuable method of identification is rather limited. Other physical constants such as surface tension, capillary rise and molecular weight have been determined in only a limited number of cases and their practical applications have not been given extensive consideration by petroleum technologists.

For the purpose of determining possible simple relationships, measurements were made of the following series of constants:

| | |
|---|---|
| A—Distillation range | E—Surface tension |
| B—Specific gravity | F—Capillary constant |
| C—Refractive index | G—Molecular weight |
| D—Viscosity | H—Ultimate analysis |

### SAMPLES AND DETERMINATIONS

As the present work deals with a comparison of constants, rather than oils, it was not considered necessary to secure an absolutely comprehensive series of samples. Representative oils from a number of different fields were obtained, and the selection was made with the view of including crude petroleums of different types.

The list includes five carefully selected samples of California crude oils, five from Oklahoma, four from Pennsylvania, two from Russia and one from Mexico. From the works of Mabery and other investigators, it is known that wide differences exist among the types of hydrocarbons found in oils from the different fields. Table I gives the sources and physical constants of the oils studied.

Table I Sources and Physical Constants of Crude Oil Samples

| No | Field | District | Sampled | Location | State | County | Lease | Well No. | Physical Constants of Crude Petroleums Arranged in Order of Their Specific Gravities | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Sample | Sp. Gr. | Viscosities Spec. | Viscosities Sec. | Surf. Tens | Cap Const |
| 269 | Cal. | Piru | 12/ 6/07 | T3N, R18W | Cal. | Ventura | Union Oil Co | 15 | | | | | | |
| 273 | Cal. | Piru | 12/ 4/07 | T4N, R18W | Cal. | Ventura | Modella, 7, 19, 21, 22, 28, 29 | | | | | | | |
| 587 | Cal. | Midway | 10/ 8/10 | T31S, R22E | Cal. | Kern | Manchuria, Midway | 1 | 815 | 0.799 | 1.30 | 67.5 | 24.07 | 6.17 |
| 591 | Cal. | Midway | 10/18/10 | T31S, R22E | Cal. | Kern | Bear Creek | 8 | 764 | 0.800 | 1.29 | 67 | 25.12 | 6.44 |
| Heald | | | | | | | | | 816 | 0.808 | 1.32 | 68.5 | 24.81 | 6.30 |
| 764 | Pa. | J. S. Sloan | 9/ 7/11 | Emlenton | Pa. | Venango | Boulder Sand: 1195 ft. | 9 | 765 | 0.816 | 1.40 | 73 | 25.44 | 6.38 |
| 765 | Pa. | Farm | 9/7/11 | Emlenton | Pa. | Venango | Second Sand: 1050 ft. | 8 | 1336 | 0.825 | 1.44 | 75 | 24.78 | 6.15 |
| 815 | Pa. | Branden | 9/21/11 | Pleasantville | Pa. | | First Sand: 580 ft. | 11 | 1339 | 0.838 | 1.71 | 89 | 26.19 | 6.40 |
| 816 | Pa. | Farm | 9/21/11 | Pleasantville | Pa. | | Second Sand: 650 ft. | 6 | 1280 | 0.846 | 1.70 | 88.5 | 25.03 | 6.06 |
| 1280 | Okla. | Collinsville | May/13 | T22N, R15E | Okla. | | Claremore Pool | | Heald | 0.865 | 2.77 | 144 | 26.59 | 6.30 |
| 1281 | Okla. | Collinsville | May/13 | T22N, R15E | Okla. | | Sellers Lease, Claremore Pool | 1 | 1281 | 0.870 | 3.35 | 174 | 26.59 | 6.26 |
| 1336 | Okla. | Collinsville | 5/24/13 | T14N, R18E | Okla. | | G. Callahan Lease, Muskogee Pool | 3 | 269 | 0.876 | 2.31 | 120 | 25.70 | 6.00 |
| 1339 | Okla. | Collinsville | 5/24/13 | T14N, R18E | Okla. | | Stevens Lease, Muskogee Pool | 1 | R. R. | 0.876 | 2.61 | 136 | 25.58 | 6.43 |
| S. Maria | | | | | | | | | R. M. | 0.878 | 3.22 | 167.5 | 27.82 | 6.49 |
| R. R. | Russian—Provided by the kindness of C. I. Robinson of the Standard Oil Co. of N. J. | | | | | | | | 273 | 0.891 | 3.11 | 110 | 26.08 | 5.99 |
| R. M. | Russian—Provided by the kindness of Prof. C. F. Mabery, The Case School, Cleveland, O. | | | | | | | | S. M. | 0.901 | 4.92 | 256 | 26.13 | 5.94 |
| Mex. | Mexican—Provided by the kindness of Dr. D. T. Day, U. S. Bureau of Mines, Washington, D. C. | | | | | | | | | | | | | |

The conversion factors from Engler[1] to Redwood and Saybolt are:

$$T_R = 192.2K\left(1 + \sqrt{1 + \frac{0.01024}{K^2}}\right)$$

[1] John Morris Weiss, "The Coefficient of Expansion of Tar," *J. Franklin Inst.*, Sept., 1911.

[2] Published with the permission of the Director of the Bureau of Mines. See Rittman and Dean, This Journal, **7** (1915), 185.

[1] *Chem. Rev. Fett-Harz Ind.*, **19** 30, 33; 44 to 49.

$$T_s = 228.7K\left(1 + \sqrt{1 + \frac{0.01300}{K^2}}\right)$$

$$K = 0.08010E - \frac{0.07013}{E}$$

The values calculated from the formulas agree with those actually observed within 4 per cent by Redwood and 2 per cent by Saybolt. By dividing the readings for Redwood and Saybolt instruments by the respective readings for water, comparative accuracy for these instruments is increased.

DISTILLATIONS were conducted according to a method which was designed to give a high degree of separation. In accordance with the results of some recent investigations conducted under the direction of one of the authors,[1] a Hempel column of definite height was provisionally adopted as standard for this set of experiments. The degree of efficiency attained was approximately that of the standard creosote flask[2] of the Forestry Division of the Department of Agriculture. The flasks here used were of the following dimensions:

| | | | |
|---|---|---|---|
| Initial charge | 400 cc. | Height from bulb to outlet | 6 in. |
| Capacity of bulb | 500 cc. | Height from outlet to top | 1½ in. |
| Cuts at 50° intervals 100 to 300° C. | | Diameter of neck of bulb | ⅝ in. |
| Fractionating column: 5 in. aluminum beads (between ¼ and ⅜ in.) | | | |

The results of distillation, shown in Table II, need no discussion in the present connection. The Kern River and Mexican Oils were emulsified and frothed badly, and to overcome this difficulty it was necessary to apply heat to the neck of the flask, which obviously altered the effect of the fractionating column.

a cut is selected, it will be noted that densities of Pennsylvania products are least and those of California and Russian greatest. This is in accord with observations of other investigators and is a striking evidence of the difference among the hydrocarbons contained in petroleums from different fields. Pennsylvania oils contain paraffins which have a low gravity for a given boiling point: California and Russian oils contain cyclic compounds which are heavier for the same boiling point: Oklahoma oils, containing both types of hydrocarbons, give intermediate gravity values.

REFRACTIVE INDICES were measured by means of a Pulfrich Refractometer. Determinations were made at room temperature, maintained at 20° C.

The use of refractive index as a means of identification of oils is to be recommended. The method is simple, rapid, and only a few drops of liquid are necessary for a determination. Comparatively little has been done in the use of refractive index by petroleum technologists, despite its wide utility in identifying essential oils. The property is an additive one and within certain limits we can assign to each atom in the molecule a certain share in the refractive index of the molecule.

The above property is emphasized by the present experiments. The values increase in the ascending order with increase of specific gravity of a series of oils: this is clearly shown when the oil is graphed against specific gravity and refractive index.

TABLE II—RESULTS OF FRACTIONAL DISTILLATIONS OF PETROLEUM OILS AND CONSTANTS OF VARIOUS DISTILLATION CUTS

| Source | Cal. | Cal. | Cal. | Cal. | Cal. | Pa. | Pa. | Pa. | Pa. | Okla. | Okla. | Okla. | Okla. | Okla. | Russian | | Mexican |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | 269 | 273 | 587 | 591 | S. M. | 764 | 765 | 815 | 816 | 1280 | 1281 | 1336 | 1339 | Heald | R R | R. M. | |
| Temp. | | | | | | | | VOLUME—PERCENTAGES | | | | | | | | | |
| To 100° | 8.00 | 5.25 | 0.38 | ... | 6.75 | 5.19 | 6.25 | 6.25 | 8.25 | 3.25 | 0.31 | 8.38 | 5.50 | 5.00 | 0.62 | 1.12 | ... |
| 100–150° | 10.50 | 15.50 | 0.50 | ... | 13.25 | 7.38 | 13.75 | 6.63 | 14.25 | 14.25 | 3.38 | 12.50 | 12.25 | 8.62 | 11.13 | 7.38 | 1.12 |
| 150–200° | 8.25 | 10.25 | 1.50 | 1.25 | 8.62 | 6.06 | 11.50 | 6.00 | 12.75 | 10.38 | 10.75 | 11.12 | 9.50 | 7.38 | 11.50 | 8.62 | 2.50 |
| 200–250° | 11.00 | 12.63 | 5.25 | 5.25 | 11.12 | 6.12 | 11.50 | 5.25 | 11.75 | 13.88 | 14.12 | 11.12 | 11.75 | 10.25 | 13.75 | 12.75 | 8.25 |
| 250–300° | 11.25 | 12.00 | 16.00 | 10.63 | 15.00 | 6.19 | 12.50 | 5.75 | 11.75 | 14.88 | 16.75 | 12.63 | 15.00 | 17.00 | 15.25 | 15.62 | 25.75 |
| | | | | | | | | SPECIFIC GRAVITIES | | | | | | | | | |
| To 100° | 0.688 | 0.706 | . | ... | 0.706 | 0.686 | 0.682 | 0.671 | 0.686 | 0.705 | ... | 0.680 | 0.689 | 0.690 | ... | 0.733 | ... |
| 100–150° | 0.756 | 0.762 | ... | ... | 0.762 | 0.736 | 0.748 | 0.737 | 0.740 | 0.746 | 0.757 | 0.749 | 0.752 | 0.754 | 0.767 | 0.769 | 0.759 |
| 150–200° | 0.792 | 0.805 | 0.820 | 0.826 | 0.806 | 0.766 | 0.780 | 0.767 | 0.771 | 0.781 | 0.785 | 0.783 | 0.785 | 0.791 | 0.804 | 0.806 | 0.798 |
| 200–250° | 0.825 | 0.851 | 0.858 | 0.860 | 0.846 | 0.789 | 0.799 | 0.792 | 0.793 | 0.814 | 0.815 | 0.809 | 0.812 | 0.818 | 0.836 | 0.836 | 0.843 |
| 250–300° | 0.855 | 0.891 | 0.887 | 0.890 | 0.878 | 0.812 | 0.818 | 0.815 | 0.813 | 0.839 | 0.839 | 0.831 | 0.836 | 0.839 | 0.861 | 0.861 | 0.871 |
| | | | | | | | | INDICES OF REFRACTION | | | | | | | | | |
| To 100° | 1.386 | 1.390 | 1.423 | . . | 1.392 | 1.385 | 1.385 | 1.375 | 1.386 | 1.389 | 1.409 | 1.385 | 1.387 | 1.388 | 1.401 | 1.403 | . . |
| 100–150° | 1.418 | 1.419 | 1.434 | . . | 1.420 | 1.407 | 1.416 | 1.408 | 1.410 | 1.413 | 1.419 | 1.416 | 1.417 | 1.418 | 1.421 | 1.423 | 1.419 |
| 150–200° | 1.436 | 1.440 | 1.445 | 1.448 | 1.444 | 1.425 | 1.430 | 1.426 | 1.427 | 1.431 | 1.435 | 1.432 | 1.434 | 1.435 | 1.439 | 1.441 | 1.439 |
| 200–250° | 1.455 | 1.465 | 1.465 | 1.465 | 1.465 | 1.437 | 1.443 | 1.438 | 1.439 | 1.449 | 1.450 | 1.448 | 1.448 | 1.451 | 1.457 | 1.457 | 1.464 |
| 250–300° | 1.472 | 1.493 | 1.484 | 1.484 | 1.483 | 1.449 | 1.452 | 1.449 | 1.449 | 1.464 | 1.464 | 1.459 | 1.461 | 1.465 | 1.472 | 1.474 | 1.481 |
| | | | | | | | | SURFACE TENSIONS | | | | | | | | | |
| To 100° | 19.54 | 18.92 | | . | 20.78 | 18.81 | 18.87 | 19.11 | 19.53 | 19.99 | | 19.85 | 18.92 | 19.71 | ... | 21.19 | . . |
| 100–150° | 22.12 | 22.33 | | . | 22.47 | 20.95 | 21.87 | 21.67 | 20.98 | 22.05 | 22.69 | 22.09 | 21.53 | 22.34 | 22.75 | 22.80 | |
| 150–200° | 22.70 | 24.55 | 25.25 | 25.36 | 25.31 | 23.29 | 24.00 | 23.75 | 22.64 | 24.25 | 24.35 | 24.07 | 22.91 | 23.98 | 24.85 | 24.93 | 24.62 |
| 200–250° | 23.47 | 26.43 | 28.62 | 27.22 | 26.28 | 25.04 | 25.29 | 25.42 | 23.67 | 26.13 | 26.12 | 25.61 | 23.91 | 24.99 | 26.50 | 26.71 | 26.36 |
| 250–300° | 23.81 | 28.18 | 29.51 | 28.03 | 28.04 | 26.47 | 26.84 | 26.80 | 24.48 | 27.48 | 27.37 | 27.02 | 24.45 | 26.01 | 27.15 | 28.01 | 27.26 |
| | | | | | | | | CAPILLARY CONSTANTS OR SPECIFIC COHESIONS | | | | | | | | | |
| To 100° | 5.84 | 5.50 | | . . | 6.04 | 5.64 | 5.69 | 5.86 | 5.84 | 5.82 | | 6.00 | 5.64 | 5.86 | | 5.93 | |
| 100–150° | 6.00 | 6.01 | | ... | 6.06 | 5.84 | 6.13 | 6.03 | 5.81 | 6.06 | 6.15 | 6.05 | 5.88 | 6.07 | 6.08 | 6.08 | |
| 150–200° | 5.87 | 6.25 | 6.30 | 6.29 | 6.44 | 6.23 | 6.46 | 6.38 | 6.02 | 6.32 | 6.36 | 6.31 | 5.99 | 6.21 | 6.34 | 6.34 | 6.33 |
| 200–250° | 5.82 | 6.36 | 6.83 | 6.48 | 6.36 | 6.51 | 6.61 | 6.58 | 6.12 | 6.57 | 6.56 | 6.49 | 6.03 | 6.26 | 6.49 | 6.55 | 6.39 |
| 250–300° | 5.71 | 6.47 | 6.81 | 6.45 | 6.54 | 6.68 | 6.79 | 6.73 | 6.16 | 6.71 | 6.68 | 6.66 | 5.99 | 6.34 | 6.46 | 6.67 | 6.41 |
| | | | | | | | | CRYOSCOPIC MOLECULAR WEIGHTS | | | | | | | | | |
| 150–200° | 133.3 | 125.8 | 131.4 | 142.9 | 125.9 | 137.6 | 171.7 | 139.8 | 130.3 | 132.2 | 138.3 | 130.6 | 130.7 | 127.8 | 127.6 | 119.1 | 142.7 |
| 200–250° | 166.7 | 152.7 | 151.5 | 179.2 | 140.0 | 164.5 | 159.4 | 167.3 | 149.0 | 158.4 | 170.1 | 165.9 | 153.9 | 159.8 | 146.4 | 140.7 | 178.3 |
| 250–300° | 191.6 | 173.2 | 181.8 | 193.9 | 179.6 | 202.6 | 184.2 | 205.8 | 180.9 | 195.7 | 212.3 | 214.3 | 190.6 | 192.5 | 171.3 | 180.5 | 197.7 |

SPECIFIC GRAVITY determinations were made at 15° C. by the use of a special small Westphal Balance with a plummet of 1 cc. displacement.

A study of the specific gravities shown in Table II brings out one fact, which, though well known, is worthy of comment. If for any given temperature

SURFACE TENSION—Up to the time of beginning this research but little attention has been given to the determination of surface tension and capillary constants of petroleum and its products. This phenomenon is important to the geologist[1] as well as to the chemist.

Surface tension is a direct result of unbalanced inter-molecular forces at the boundary between the liquid and gas phase, and is manifested by the apparent

[1] *Loc. cit.*

[2] Dean and Bateman, *Bull.* **112**, Forest Service of the U. S. Department of Agriculture.

[1] *Bull. Am. Inst. Min. Eng.*, **1914**, p. 2365

formation of an elastic skin. The familiar experiment of floating a greasy steel needle on water is the simplest and most impressive way of demonstrating the existence of a tension along the surface of a liquid. Two common resulting effects are the tendency of all liquids to form spherical drops whenever possible and the rise in tubes of all liquids which are able to wet the material of which the tube is composed.

Surface tension measurements were made by the use of the Morgan[1] drop weight apparatus. The method evolved by Morgan[2] and his co-workers is simple, rapid and highly accurate. It has in addition the advantage of being particularly adapted to liquids which are mixtures of several constituents of different volatilities—whereas the capillary rise method fails utterly under these conditions.

The method gives directly and accurately the weight of the drop of the liquid. From this the value of surface tension can be calculated by the following relation:[3]

$\gamma$ = Surface Tension (dynes per cm.) = KW
where K = The constant for the apparatus used and W = Weight of a drop in milligrams.

It will be noted from the results shown in Table II that surface tension is apparently an additive property as far as the distillation cuts of any one oil are concerned, but that additivity vanishes when the relations of different petroleums are considered. An explanation is not difficult to find, for it has been demonstrated by Morgan[4] that small additions of certain substances influence greatly the surface tension of a solvent. Thus in the presence of 1 per cent of amyl alcohol the surface tension of water decreases 48 per cent, while 1 per cent of phenol[5] in water produces a 17 per cent depression of surface tension.

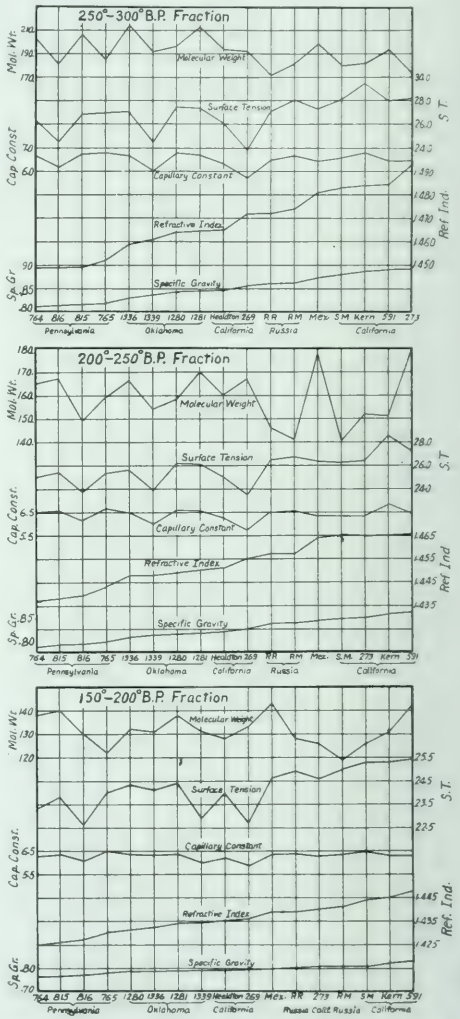
All this indicates the possible occurrence in crude petroleum of small quantities of substances which have a large influence on surface tension and which are distributed throughout the various cuts of a distillation. On this basis it is easy to understand why the apparent additive nature of this constant vanishes when relations of different original oils are considered. With pure hydrocarbons, of homologous series, surface tension is an additive property.

That phenols, cresols, mercaptans and other sulfur and oxygen compounds exist in crude petroleums has been clearly shown by the work of Markownikoff and Ogloblin,[6] Pebal and Freund,[7] Hall,[8] Thiele,[9] and Mabery.[10]

The above mentioned observations on surface tension have indicated interesting possibilities for research. It is hoped that in the near future investigations along these lines may be conducted and knowledge of more specific character obtained.

[1] *J. Am. Chem. Soc.*, **32** (1911), 349.
[2] *Z. physik. Chem.*, **1915**; *Jour. Am. Chem. Soc.*, **1911**-**1915** (résumé).
[3] *J. Am. Chem. Soc.*, **33** (1911), 658.
[4] *Ibid.*, **35** (1913), 1860.
[5] Results on phenol not published. Morgan and Egloff.
[6] *Ber.*, **16** (1883), 1873; *Chem. Ztg.*, **1881**, p. 609.
[7] Liebig's *Ann.*, **115** (1860), 19.
[8] *J. Soc. Chem. Ind.*, **1907**, p. 1223.
[9] *Chem. Ztg.*, **175** (1901), 433.
[10] *Proc. Am. Acad.*, **36** (1901), 255; **40** (1904), 348.

CAPILLARY CONSTANT OR SPECIFIC COHESION—The capillary constant is a derived function of surface tension and specific gravity. It has been largely used in the past and many values in the literature are expressed in terms of this constant. For purposes of comparison the surface tension values obtained by the drop weight method have been converted into




RELATIONS AMONG PHYSICAL CONSTANTS OF PETROLEUM DISTILLATES

capillary constants. Transformations were made by the use of the following formula:[1]

$$a^2 = \frac{2\gamma}{g.Sd}$$

$a^2$ = Capillary Constant $\gamma$ = Surface Tension
$d$ = Specific Gravity

[1] Morgan, "Principles of Physical Chemistry," **1914**, p. 100.

Values of *d* for 20° were calculated (see Table II) from those measured at 15° by conversion figures given by Markownikoff-Ogloblin[1] for American oils, and by Mendelejeff[2] for Russian.

CRYOSCOPIC "MOLECULAR WEIGHT"—The average "molecular weights" of the 50° cuts between 150° and 300° were determined by the cryoscopic method, using benzol as a solvent. No measurements were made on fractions boiling below 150° because of the possible presence of benzol in these distillates.

The concentration of solute was kept practically constant and to eliminate possible variations due to association so as to make all determinations comparable. The values of solute were between 0.12 to 0.15 of a gm., whereas the solvent weighed from 13 to 18 gms. The temperature readings were made with a Reichsanstalt certified Beckmann thermometer. The solvent used was Kahlbaum's thiophen-free, recrystallized benzol. The benzol was further purified by the method advocated by Richards[3] and Shipley for freezing point in thermometry.

Every experimental precaution was taken to eliminate errors due to impurity of solvent, weighing vessels and thermometer. The average "molecular weights" as determined are given in Table II.

It appeared from these experiments that "molecular weights" did not exhibit an agreement with the values for specific gravity and refractive index. Neither was there any agreement between "molecular weights" and surface tension or capillary constant.

It also appeared that "molecular weights" were lower than would be indicated from calculations concerning hydrocarbons boiling between the given temperature limits. This discrepancy is probably due to the fact that the actual average boiling temperature of a cut obtained on distilling a crude oil is lower than the average indicated by the given limits.

ULTIMATE ANALYSIS—Eight samples of distillates of b. p. 200–250° were analyzed for the carbon and hydrogen content. The results appear in Table III and indicate for a number of American oils, practically pure hydrocarbons with small amounts of oxygen, nitrogen or sulfur compounds, whereas one Russian and the Mexican oil show a relatively high per cent of oxygen, nitrogen or sulfur compounds, which might bear out the statement as to small amounts of certain extraneous substances greatly changing the surface tensions of pure hydrocarbons.

TABLE III—ULTIMATE ANALYSES OF CERTAIN 200–250° B. P. FRACTIONS

| Sample No. | 269 | 1281 | 816 | Kern S. M. | Mex. R. M. | R. R. |
|---|---|---|---|---|---|---|
| Per cent hydrogen.. | 13.62 | 13.90 | 14.57 | 13.40 | 13.07 | 13.34 | 13.42 | 13.31 |
| Per cent carbon.... | 86.36 | 85.37 | 84.99 | 86.27 | 85.42 | 85.00 | 86.34 | 84.49 |

The relations existing among the various sets of constants are shown by two comparison tables. Table IV represents cuts boiling up to 100°, from 100–150°, from 150–200°, from 200–250°, and from 250–300°. Table V represents data on combined cuts up to 150°, generally classed by petroleum technologists as "naphtha," and combined cuts from 150–300°, generally classed as "kerosene."

Comparisons are best made by the use of the accompanying graphs plotted from the values for the last three series in Table IV. These are representative of the results of all the other tables and were selected because they include the most comprehensive lists of constants.

The graphs are plotted using as abscissas equidistant points, each representing a different oil. The oils are arranged in such order as to give an ascending curve for specific gravities. An inspection of the graphs shows that the only constant bearing any clear-cut relation to specific gravity is refractive index.

TABLE IV—PHYSICAL CONSTANTS OF DISTILLATION CUTS IN ORDER OF SPECIFIC GRAVITIES

FRACTION B. P. UP TO 100° C.

| SAMPLE | 815 | 1336 | 765 | 764 | 816 | 269 | 1339 | Heald | 1280 | 1281 | 273 | S. M. | R. R. | R M | 587 | 591 | Mex. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 0.670 | 0.680 | 0.682 | 0.686 | 0.686 | 0.688 | 0.689 | 0.690 | 0.705 | .. | 0.706 | 0.706 | .. | 0.733 | | | |
| Ref. ind. | 1.375 | 1.385 | 1.385 | 1.385 | 1.386 | 1.386 | 1.387 | 1.388 | 1.398 | .. | 1.390 | 1.392 | 1.401 | 1.403 | 1.423 | | |
| Sur. ten. | 19.11 | 19.85 | 18.87 | 18.81 | 19.53 | 19.54 | 18.92 | 19.71 | 19.99 | . | 18.92 | 20.78 | . | 21.19 | | | |
| Cap. const | 5.86 | 6.00 | 5.69 | 5.64 | 5.84 | 5.84 | 5.64 | 5.86 | 5.82 | . | 5.50 | 6.04 | . | 5.93 | | | |

FRACTION B. P. BETWEEN 100° AND 150°

| SAMPLE | 764 | 815 | 816 | 1280 | 765 | 1336 | 1339 | Heald | 269 | 1281 | Mex. | 273 | S. M. | R. R | R. M. | Kern | 591 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 0.736 | 0.737 | 0.740 | 0.746 | 0.748 | 0.749 | 0.752 | 0.754 | 0.756 | 0.757 | 0.759 | 0.762 | 0.762 | 0.767 | 0.769 | | |
| Ref. ind. | 1.407 | 1.408 | 1.410 | 1.1413 | 1.416 | 1.416 | 1.416 | 1.418 | 1.418 | 1.419 | 1.419 | 1.419 | 1.420 | 1.421 | 1.423 | 1.434 | |
| Sur. ten. | 21.95 | 21.67 | 20.98 | 22.05 | 21.87 | 22.09 | 21.53 | 22.34 | 22.12 | 22.69 | .. | 22.33 | 22.47 | 22.75 | 22.80 | | |
| Cap. const. | 5.84 | 6.03 | 5.81 | 6.06 | 6.13 | 6.05 | 5.88 | 6.07 | 6.00 | 6.15 | .. | 6.01 | 6.06 | 6.08 | 6.08 | | |

FRACTION B. P. BETWEEN 150° AND 200°

| SAMPLE | 764 | 815 | 816 | 765 | 1280 | 1336 | 1281 | 1339 | Heald | 269 | Mex. | R. R. | 273 | R. M. | S. M. | Kern | 591 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 0.766 | 0.767 | 0.771 | 0.780 | 0.781 | 0.783 | 0.785 | 0.785 | 0.791 | 0.792 | 0.798 | 0.804 | 0.805 | 0.806 | 0.806 | 0.820 | 0.826 |
| Ref. ind. | 1.425 | 1.426 | 1.427 | 1.430 | 1.431 | 1.432 | 1.434 | 1.434 | 1.435 | 1.436 | 1.439 | 1.439 | 1.440 | 1.441 | 1.444 | 1.445 | 1.448 |
| Sur. ten. | 23.29 | 23.75 | 22.64 | 24.00 | 24.25 | 24.07 | 24.35 | 22.91 | 23.98 | 22.70 | 24.62 | 24.85 | 24.55 | 24.93 | 25.31 | 25.25 | 25.36 |
| Cap. const. | 6.23 | 6.35 | 6.02 | 6.46 | 6.32 | 6.31 | 6.36 | 5.99 | 6.21 | 5.87 | 6.33 | 6.34 | 6.25 | 6.34 | 6.44 | 6.30 | 6.29 |
| Mol. wt. | 138 | 140 | 130 | 122 | 132 | 131 | 138 | 131 | 128 | 133 | 143 | 128 | 126 | 119 | 126 | 131 | 143 |

FRACTION B. P. BETWEEN 200° AND 250°

| SAMPLE | 764 | 815 | 816 | 765 | 1336 | 1339 | 1280 | 1281 | Heald | 269 | R. R. | R. M. | Mex. | S. M. | 273 | Kern | 591 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 0.789 | 0.792 | 0.793 | 0.799 | 0.809 | 0.812 | 0.814 | 0.815 | 0.818 | 0.825 | 0.836 | 0.836 | 0.843 | 0.846 | 0.851 | 0.858 | 0.860 |
| Ref. ind. | 1.437 | 1.438 | 1.439 | 1.443 | 1.448 | 1.448 | 1.449 | 1.450 | 1.451 | 1.455 | 1.457 | 1.457 | 1.464 | 1.465 | 1.465 | 1.465 | 1.465 |
| Sur. ten. | 25.04 | 25.42 | 23.67 | 25.29 | 25.61 | 23.91 | 26.13 | 26.12 | 24.00 | 23.47 | 26.50 | 26.71 | 26.36 | 26.28 | 26.43 | 28.62 | 27.22 |
| Cap. const. | 6.51 | 6.58 | 6.12 | 6.61 | 6.49 | 6.03 | 6.57 | 6.56 | 6.26 | 5.82 | 6.49 | 6.55 | 6.39 | 6.36 | 6.36 | 6.83 | 6.48 |
| Mol. wt. | 165 | 167 | 149 | 159 | 166 | 154 | 158 | 170 | 160 | 167 | 146 | 141 | 178 | 140 | 152 | 151 | 179 |

FRACTION B. P. BETWEEN 250° AND 300°

| SAMPLE | 764 | 816 | 815 | 765 | 1336 | 1339 | 1280 | 1281 | Heald | 269 | R. R. | R. M. | Mex. | S. M. | Kern | 591 | 273 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 0.812 | 0.813 | 0.815 | 0.818 | 0.831 | 0.836 | 0.839 | 0.813 | 0.839 | 0.855 | 0.861 | 0.861 | 0.871 | 0.878 | 0.887 | 0.890 | 0.891 |
| Ref. ind. | 1.449 | 1.449 | 1.449 | 1.452 | 1.459 | 1.461 | 1.464 | 1.464 | 1.465 | 1.472 | 1.472 | 1.474 | 1.481 | 1.483 | 1.484 | 1.484 | 1.493 |
| Sur. ten. | 26.47 | 24.48 | 26.80 | 26.84 | 27.02 | 24.45 | 27.48 | 27.37 | 26.01 | 23.81 | 27.15 | 28.01 | 27.26 | 28.04 | 29.51 | 28.03 | 28.18 |
| Cap. const. | 6.68 | 6.16 | 6.73 | 6.79 | 6.66 | 5.99 | 6.71 | 6.68 | 6.34 | 5.71 | 6.46 | 6.67 | 6.41 | 6.54 | 6.81 | 6.45 | 6.47 |
| Mol. wt. | 203 | 181 | 206 | 184 | 214 | 191 | 196 | 212 | 193 | 192 | 171 | 181 | 198 | 180 | 182 | 194 | 173 |

[1] *Ber.*, **16**, 1873.
[2] Rakusin, *Untersuch. d. Erdols.*
[3] *J. Am. Chem. Soc.*, **36** (1914), 1825.

The curve for surface tension is decidedly irregular but shows a tendency to slope upwards. This indicates that among petroleum hydrocarbons surface tension varies in the same direction as specific gravity. This constant is, however, so strongly affected by small variations in chemical composition that it is at present of little value as a means of identification. It is hoped, however, that later these irregularities may be understood well enough to furnish scientific as well as useful industrial information.

Capillary constant curves show the same irregularities as those of surface tension but lack the slope upward. This is to be expected when the method of derivation of this constant is considered.

In considering the "molecular-weight" graph, it appears that the agreement of this constant with

TABLE V—PHYSICAL CONSTANTS OF "NAPHTHA" AND "KEROSENE" CUTS OF OILS STUDIED

| NAPHTHA—B. P. UP TO 150° C. | | | | | KEROSENE B. P. 150° TO 300° | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Sp. gr. | Refr. index | Surf. tens. | Cap. const. | Sample No. | Sp. gr. | Refr. index | Surf. tens. | Cap. const. |
| 815 | 0.706 | 1.392 | 19.96 | 5.82 | 815 | 0.789 | 1.437 | 24.73 | 6.44 |
| 764 | 0.716 | 1.398 | 20.54 | 5.88 | 764 | 0.790 | 1.438 | 25.07 | 6.50 |
| 816 | 0.722 | 1.400 | 20.02 | 5.69 | 816 | 0.792 | 1.439 | 23.96 | 6.20 |
| 1336 | 0.726 | 1.402 | 20.52 | 5.79 | 765 | 0.795 | 1.440 | 24.66 | 6.43 |
| 765 | 0.731 | 1.405 | 19.34 | 5.57 | 1336 | 0.808 | 1.445 | 25.59 | 6.49 |
| 269 | 0.733 | 1.406 | 21.12 | 5.92 | 1281 | 0.811 | 1.448 | 26.80 | 6.66 |
| Heald | 0.734 | 1.406 | 20.38 | 5.69 | 1339 | 0.814 | 1.449 | 23.91 | 6.02 |
| 1339 | 0.736 | 1.407 | 19.41 | 5.41 | 1280 | 0.815 | 1.451 | 25.04 | 6.30 |
| 1280 | 0.741 | 1.410 | 20.28 | 5.61 | 269 | 0.820 | 1.452 | 23.18 | 5.77 |
| S. M. | 0.744 | 1.410 | 21.34 | 5.87 | Heald | 0.824 | 1.454 | 25.27 | 6.28 |
| 273 | 0.750 | 1.412 | 20.74 | 5.67 | R. R | 0.836 | 1.458 | 26.34 | 6.45 |
| R. M | 0.765 | 1.418 | 22.37 | 5.99 | R. M | 0.841 | 1.459 | 26.57 | 6.46 |
| | | | | | 273 | 0.842 | 1.463 | 25.50 | 6.20 |
| | | | | | S. M | 0.849 | 1.466 | 26.40 | 6.37 |
| | | | | | Mex. | 0.861 | 1.475 | 26.96 | 6.40 |
| | | | | | Kern | 0.878 | 1.476 | 27.79 | 6.48 |
| | | | | | 591 | 0.878 | 1.476 | 26.87 | 6.26 |

specific gravity, though theoretically to be expected, is conspicuous by its absence. No satisfactory explanation appears except that there is some inherent error in the method here employed for the determination of molecular weights. Present experience indicates that the measurement of this constant by the cryoscopic method with benzol as a solvent is of doubtful value in the identification of petroleum distillates. The experimental values are recorded with a full knowledge of their being "so-called Molecular Weights."

### CONCLUSIONS

I—The present series of experiments has tended to justify the methods of identification (distillation, specific gravity and refractive index) usually employed in petroleum testing laboratories.

II—Volatility and specific gravity are the two most important constants and a knowledge of these two is generally sufficient for the identification of an oil.

III—Refractive indices vary in the same direction as specific gravities. When only small quantities of distillates are available, determinations of the former are more convenient than measurements of specific gravities.

IV—Surface tension is a constant not yet of value. This is on account of our lack of knowledge regarding variations caused by the probable presence of small quantities of certain substances in crude petroleums. Surface tensions in general seem to increase with specific gravity when relations among petroleum hydrocarbons are considered.

V—Cryoscopic "molecular weights," as measured by the cryoscopic method with benzene as a solvent, are of questionable value in the study of mixtures of petroleum products.

The experimental work connected with the determinations reported in this paper was carried out in the laboratories of the Departments of Physical Chemistry and Industrial Chemistry of Columbia University, New York.

CHEMICAL SECTION OF PETROLEUM DIVISION
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## THE SPECIFICATION OF VULCANIZED RUBBER GUM BY VOLUME AND ITS DETERMINATION BY A NEW SOLUTION METHOD

By FRANK GOTTSCH

Received April 21, 1915

The following methods for the chemical analysis of rubber goods are those in use at Mt. Prospect Laboratory, Department of Water Supply, Gas and Electricity, City of New York. These methods contain certain matter original with the author, under the headings of "MINERAL FILLERS," "FOREIGN ALCOHOLIC POTASH EXTRACT," "VULCANIZED RUBBER GUM BY WEIGHT," and "VULCANIZED RUBBER GUM BY VOLUME." The method for "FREE SULFUR" is novel in the application of a well-known method for total sulfur to the free sulfur determination.

### METHODS OF TEST

SAMPLES—Samples shall be taken representative of the lots to be tested.

BLANKS—Blanks shall be run and deductions made according to the lots of reagents.

CHECKS—In the event of any determination not falling within the limits given in the specifications, a check test shall be made before the report is sent out.

PREPARATION OF SOFT RUBBER—Prepare a sample of not less than 25 grams, taking pieces from various parts of the original sample. The backing of fire hose shall be buffed off before grinding; in all other hose, separate samples of tube and cover shall be made, without removing the backing or friction compound. Other rubber goods built up with friction fabric shall have the rubber layers ground up without removal of the adhering rubber friction.

GRINDING—The sample shall be cut into small pieces and then run through the grinder, taking for analysis only such material as will pass a standard 20 mesh sieve. Care must be taken to see that the grinder does not become appreciably warm during the grinding. If the nature of the material is such that it gums together so that it will not pass through the sieve, as would be the case with undervulcanized samples, it will be sufficient to pass the material through the grinder twice and accept all the material for the final sample. Crude rubber shall be cut with scissors.

Pass a strong magnet through the sample to remove any metal from the grinders, mix thoroughly, and put in tightly stoppered bottles. Do not expose to sunlight or heat.

HARD RUBBER—Samples of this material shall be prepared for analysis by rasping.

REAGENTS—*Acetone* shall be distilled not more than 10 days before use over anhydrous potassium carbonate, using the fraction 56 to 57° C.

*Alcoholic potash* shall be of normal strength, made by dissolving the required amount of potassium hydroxide in absolute

alcohol the day before use, and allowing to settle. Only the clear solution shall be used.

*Barium chloride solution* shall be made by dissolving 100 grams of barium chloride in one liter of distilled water, and adding two or three drops of concentrated hydrochloric acid. If there is any insoluble matter or cloudiness, the solution shall be heated on the steam bath over night, and filtered through S. & S. 589 blue-ribbon filter paper.

*Turpentine* shall be redistilled.

*All reagents* shall be of C. P. quality

ANALYSIS

ACETONE EXTRACT—Place a two gram sample, which has been ground not more than 24 hours before, in an acetone extracted paper thimble, and insert in a glass syphon cup (E. & A. 1913, No. 2846) under a condenser (E. & A. 1913, No. 2848). Dry and weigh, by means of a wire loop, a clean 8 in. × 1¼ in. test tube weighing between 20 and 40 grams, pour in 50 cc. acetone, connect the apparatus, and extract continuously for 7 hours in such a manner that the drops of condensed solvent fall directly on to the ground rubber, and the syphon cup fills between 2½ and 3½ minutes, that the discharge of the syphon cup does not appreciably interrupt the boiling, that the condensed solvent filters rapidly through the paper thimble, and that no fine particles of rubber or fillers are carried over. If the solution in the cup is colored after seven hours' extraction, the extraction shall be continued for four hours the next day. Evaporate off the acetone from the tube in a slanting position over live steam, wipe off the outside with a clean linen cloth, and dry to constant weight in the water oven at 95 to 100° C., or until the weight increases, cooling in a desiccator. Calculate and record as "total acetone extract."

FREE SULFUR—Entirely transfer the residue from the tube to a 60 cc. iron or nickel crucible (E. & A. 1913, No. 2366) by acetone, chloroform, or benzol, evaporate off the solvents on the steam bath and add six grams of potassium carbonate and four grams of sodium peroxide. Mix by rotating the crucible, cover, heat at a low temperature over an asbestos shield to avoid sulfur fumes, until the mixture fuses, then bring to quiet fusion for 15 to 20 minutes. Avoid rapid heating and explosions. Rotate the melt while solidifying. When cool, put the crucible and cover into a casserole containing 200 cc. of water, add 5 to 10 cc. of bromine water, and boil until the melt is dissolved. Allow to settle, decant, filter and wash through a thick filter with hot water. Cool, acidify the filtrate with dilute hydrochloric acid, using Congo red paper, make up the volume to 400 cc., and precipitate boiling with 10 cc. of a 10 per cent solution of barium chloride, keeping the beaker covered with a watch glass. Allow the precipitate to stand over night, filter on an asbestos mat in a Gooch crucible, wash with hot water, ignite and weigh, cooling in a desiccator. Calculate to sulfur (factor 0.1372), and record as "free sulfur."

ORGANIC ACETONE EXTRACT—When waxy hydrocarbons are not to be determined, subtract the percentage of free sulfur from the percentage of total acetone extract above, and record the difference as "organic acetone extract."

MINERAL FILLERS—Extract a one gram sample as under "acetone extract" above for 4 hours and dry the rubber in the water oven at 95 to 100° C. until the odor of acetone is gone. Transfer the sample to a 100 cc. beaker, burn the thimble to ash, and add the residue to the beaker. Add 50 cc. of clear molten salol, and heat the beaker on the hot plate at a temperature of not less than 120° nor more than 150° C., stirring occasionally until the rubber is apparently dissolved. After settling a few minutes, carefully transfer the liquid to a 200 cc. beaker and examine the residue in the bottom of the smaller beaker for particles of undissolved rubber. If found, more salol is added and solution completed. Stir two cc. of a 1 per cent solution of soluble cotton in amyl acetate into the united warm liquids in the 200 cc. beaker, cool and add redistilled turpentine until a good "flock" has formed, adding at least 75 cc. of turpentine with constant stirring. Allow the liquid to stand until the flock has settled. The supernatant liquid is decanted and filtered by suction through an alundum crucible (Norton R. A. 84—B. P. 5204) placed in the Spencer holder (E. & A. 1913, No. 2384). Wash the flock by decantation with turpentine, filtering the latter, transfer the whole to the crucible, then dissolve carefully in a few cc. of acetone, and wash the fillers with acetone, being careful not to allow the fillers to cover up the sides of the crucible and so cause clogging. Wash thoroughly all beakers and crucible with acetone, using an acetone extracted policeman. Dry to constant weight at 105° to 110° C., cooling in a desiccator. Evaporate all the filtrates and washings, transfer to a weighed porcelain dish, burn off the organic matter, cool in a desiccator and weigh. Add this weight found to the fillers in the crucible, and calculate and record as "mineral fillers."

TOTAL SULFUR—Mix a five-tenths (0.5) gram sample with six (6) grams of potassium carbonate and four (4) grams of sodium peroxide and proceed exactly as under "free sulfur." Calculate the results in the same manner and record as "total sulfur."

FOREIGN ALCOHOLIC POTASH EXTRACT—When the presence of tar, pitch or asphalt is not indicated, spread out the rubber residue from the acetone extraction and dry in the water oven at 95° to 100° C., until the odor of acetone is no longer apparent. Transfer to a 100 cc. pressure flask (E. & A. 1913, No. 1064), fitted with washers previously extracted with alcoholic potash. Add 50 cc. of alcoholic potash, stopper and heat in an air oven kept between 105° and 110° C. for four hours. Cool the flask, filter and wash the residue with hot absolute alcohol until the washings are no longer colored. Make the filtrate strongly acid with concentrated hydrochloric acid to precipitate potassium chloride, allow to settle, filter and wash with hot chloroform into a small casserole. Place the casserole on the steam bath and evaporate until the odor of hydrochloric acid just disappears. Take up the residue with chloroform, filter and wash with hot chloroform into a beaker, evaporate the chloroform and examine the residue. If the residue is not oily or greasy to the touch, no report shall be made. If the residue is oily or greasy to the touch, it shall be washed with small portions of warm 88° Beaumé naphtha, filtered through a washed plug of cotton into a small weighed beaker, the naphtha evaporated, and the beaker dried in the water oven at 95° to 100° C. in 15-minute periods until the weight is constant, or increases, cooling in a desiccator. Calculate and record as "Foreign Alcoholic Potash Extract."

FOREIGN CHLOROFORM EXTRACT—If the compound is light in color, tar, pitch and asphalt shall be considered absent. If the compound is dark or black in color the residue after the acetone extract determination above, without removing the acetone, and before the alcoholic potash extraction is made, is extracted with chloroform for four hours in the same manner and by the same procedure as for the acetone extraction. If the chloroform extract is very dark in color, or the residue is tarry, from its calculated amount shall be subtracted 3 per cent of the weight of vulcanized rubber gum as determined below, and the balance recorded as "Foreign Chloroform Extract."

PRECAUTIONS—When the chloroform extraction is made the day after the acetone extraction, the rubber residue shall be covered with acetone over night. When the alcoholic potash extraction is made the day after either the acetone extraction or the chloroform extraction, the dried rubber residue shall be covered with the alcoholic potash over night.

CARBONACEOUS FOREIGN MATTER—Heat about a one gram sample with 30 cc. of concentrated nitric acid and 15 cc. water.

A black, insoluble residue indicates the presence of carbon as lampblack, graphite, etc. Examine the ground rubber under the microscope and observe the residue of fillers in the mineral fillers determination. If fibers or carbon are seen except as a trace proceed as follows:

The crucible containing the fillers is washed with hot dilute hydrochloric acid and hot water to decompose carbonates and sulfides, dried to constant weight at 105° to 110° C., and desiccated until cool. The crucible is then gently ignited to constant weight and the loss calculated and recorded as "Carbonaceous Foreign Matter," and shall be subtracted from the per cent of "mineral fillers" recorded above.

SPECIFIC GRAVITY—Make the determination on a strip or strips of not less than five grams weight. Weigh to 1 milligram in air, and then thoroughly wet with water, pressing and squeezing with the fingers under water to remove bubbles or films of air. Weigh to 1 milligram in water at 20° C. (taken as 1.00), calculate to 0.001, and record as "Specific Gravity."

## CALCULATIONS

VULCANIZED RUBBER GUM BY WEIGHT—Subtract the sum of the percentages of free sulfur, organic acetone extract, mineral fillers, and corrected foreign matter from 100 per cent and record the balance as "Vulcanized Rubber Gum by Weight."

The correction applied to the foreign chloroform extract reported shall be based on the vulcanized rubber gum calculated as above except that the value for foreign matter shall be taken uncorrected.

VULCANIZED RUBBER GUM BY VOLUME—Multiply the percentage by weight of vulcanized rubber gum by the specific gravity, recording the result to 0.01 per cent.

This product shall be that which is specified by the term "Vulcanized Rubber Gum by Volume."

RATIOS—Free sulfur, total sulfur, and organic acetone extract shall be separately calculated and recorded as percentages by weight of vulcanized rubber gum present.

## DISCUSSION

GENERAL—Deductions for blanks are always made. The grinder mentioned is a No. 0 Enterprise Coffee Mill, fitted with a ball-bearing washer on the crank end of the shaft.

If the alcoholic potash is made up the day before use, the difficulties concerning aldehyde or decomposition are avoided.

ACETONE EXTRACT—The acetone extractions are made on an electric hot plate (Simplex, 110 V., D. C., 4A.) taking a battery of six tubes. These are supported by Forg's brass tool holders bolted to an asbestos cylinder by stove bolts. The tubes rest directly on the plate. The condensers are supplied by independent syphons from a constant water level as shown in the illustration.

The hydraulic head is about six inches. Too great a head of too cold water will cool the distillate in the cup below the boiling point, as well as causing annoying condensation of dew during the summer months.

A great economy of space is secured. The whole arrangement as shown hardly occupies more than one square foot of space. By this apparatus the extractions are made under exactly the same conditions, heated at the same temperature, and cooled by the same volume of water at the same temperature.

The solvent is quickly evaporated from these tubes when placed in a slanting position in a wire frame on the steam bath, without danger of loss by spurting at the end. When placed nearly horizontal in the water oven, the vapor pours out rapidly and drying is quickly effected and constant or increasing weight always obtained after two half-hour periods.

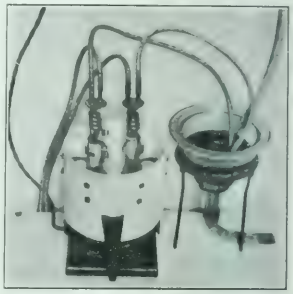
Duplicates show for example 2.99 per cent and 3.03 per cent. The blank approximates one milligram of total acetone extract.

FREE SULFUR—Waters and Tuttle[1] have shown that prolonged digestion with nitric acid gives low results in determination of total sulfur. F. W. Hinrichsen has shown that high results are caused by precipitation of barium resinates, which we have confirmed in dealing with high organic acetone extracts by nitric acid methods. We have used the following methods:

1—Nitric acid alone,
2—Nitric acid and bromine,
3—Nitric acid and chlorate
4—Bromine and water

All of these we have found have certain disadvantages and tendencies to error, due mainly to occlusion of sulfur with organic matter which has not been completely dissolved or to precipitation of barium resinates, when organic matter has been completely dissolved. These errors are sometimes very appreciable.

The method adopted for free sulfur is designed to absolutely remove the influence of organic matter by its complete destruction. Duplicates of free sulfur in a hose tube showed by this method 1.75 and 1.77 per cent as compared with 1.78 per cent obtained by oxidation with bromine and water as recommended by the Bureau of Standards, in Washington.



One-tenth of a gram of pure flowers of sulfur gave by the fusion method adopted 0.10006 gram. The blank approximates 2.5 milligrams of sulfur with a nickel crucible and 3.0 with an iron crucible, and is constant for a given crucible and lot of reagents. Nickel crucibles, although more expensive, offer an advantage over iron inasmuch as permanganate is sometimes formed from new iron crucibles.

MINERAL FILLERS—In the mineral fillers determination, the rubber compound is extracted with acetone to remove free sulfur and any fatty oils that may be present, both of which would combine with the metallic oxides and thus make the fillers too high and the vulcanized rubber gum by difference too low. Salol will dissolve soft rubber in less than an hour, vulcanite it from two to three hours. Many of the mineral fillers used in rubber compounding are in an extremely fine state of subdivision approaching the order of the wave lengths of light (the so-called "fume pigments" especially) and without a coagulant it is a prolonged operation to filter them off even through an

[1] THIS JOURNAL, 3 (1911), 734

alundum crucible. Such a coagulant is found in soluble cotton dissolved in amyl acetate. This is added to the warm liquid not only in order to secure thorough mixing but also on account of the fact that the cold, undiluted salol crystallizes on stirring. Cooling is necessary before addition of the turpentine, as the texture of the flock is coarser and the settling more rapid. The flock settles in about fifteen minutes. After washing by decantation and transferring with turpentine the flock is dissolved by carefully adding acetone. About 20 mg. of ash are recovered from the filtrates: the blank approximates 6 mg. Determinations made on compounds of known composition follow:

| Compound | Per Cent Fillers Used | Per Cent Fillers Found |
|---|---|---|
| Medium hard valve | 64.23 | 63.12 |
| Sheet rubber | 54.81 | 55.04 |
| Hard valve | 61.23 | 61.40 |
| Medium hard valve | 52.78 | 52.20 |
| Hose tube | 49.00 | 51.01 |
| Hose tube | 61.00 | 61.29 |

A sample of smoked Ceylon crepe with ash 0.98 per cent gave 1.21 per cent by the Mineral Fillers method. It would seem that any proteid matter present was almost entirely soluble.

For many years many investigators have endeavored to develop a satisfactory and accurate solution method for determination of the amount of rubber gum in rubber compounds. The method of determination by ashing at present in vogue is universally conceded to be inaccurate. Such fillers as carbonates, especially magnesium carbonate, lose carbon dioxide, sulfides such as antimony pentasulfide entirely volatilize, other sulfides change to oxides or sulfates, water of crystallization or of composition is lost. The above errors are avoided by the new method described.

Among the solvents tried by the author and found unsatisfactory before the discovery of the present solvent, *salol*, were the following: nitro-benzol, nitro-naphthalene, gum camphor, camphor oil, kerosene, paraffin and other mineral oils, turpineol, turpenol, terebene, fatty oils and acids such as palm oil, oleic acid, etc., methyl salicylate, thymol, menthol, amyl acetate, amyl alcohol, benzol, xylol, toluol, naphthalene, aniline and many others.

Even after complete solution of the vulcanized rubber gum difficulty was experienced in finding a suitable diluting agent which would not reprecipitate the rubber. Ether, chloroform and turpentine were the only satisfactory ones found among many tried. Of these only turpentine satisfactorily reprecipitates the soluble cotton used to form a flock suitable for filtration. The advent of the alundum crucible and later of the Spencer holder aided in the successful development of the method.

TOTAL SULFUR—In the total sulfur determination there is no danger of occlusion of silica in the barium sulfate precipitate if the cold dilute solution is acidified with dilute acid, as recommended by Hillebrand.[1]

FOREIGN MATTER—The methods for foreign matter are designed primarily to detect the presence of such. No limiting amounts are fixed on these extracts. The character only of such residues is taken into consideration in determining the presence of foreign material. Most of the tar or asphaltum will be in the acetone extract as well as free fatty oils from substitutes. As the methods of analysis are formulated for specifications to cover compounds made up of rubber, sulfur and mineral fillers only, an excessive organic acetone extract above the limit of the specification as well as the mere presence of foreign matter would condemn the goods. Nevertheless the analyst is expected to report on the amounts of such foreign matter, as well as the amount of vulcanized rubber gum present. However, the determination of the combined total amount of such foreign extracts is necessary in order to find the amount of vulcanized rubber gum present.

The chloroform extraction is not very satisfactory. Soft compounds swell up enormously and the asphaltum is not entirely extracted.

We are now working upon a method for the direct determination of tarry or asphaltic matter.

Saponification under pressure was selected in the method for oily foreign matter to decompose treated oils which are difficult to saponify in the ordinary way. The recovery of the extracted matter by chloroform, as described, is rapid, accurate and clean. The unpleasant, long and dangerous ether method, requiring a special room, is not necessary. A residue of rubber is always obtained due to the solubility of the rubber in alcohol, as previous extractions with absolute alcohol alone have shown. The amount thus extracted depends upon the quality of the new or old rubber used and the method of vulcanizing. This rubber residue is not soluble in 88° B. naphtha, while any fatty acids derived from oil substitutes are dissolved.

When necessary to ignite the alundum crucible containing the undissolved residue of fillers after treatment with hydrochloric acid to determine carbonaceous foreign matter, a loss of combined water in the mineral matter may occur and make the result for foreign matter too high and mineral fillers correspondingly low. This error will rarely amount to more than one per cent of the compound and will not of course affect the result for vulcanized rubber gum present as the sum of carbonaceous foreign matter and mineral fillers is unaltered.

VULCANIZED RUBBER GUM BY WEIGHT—Vulcanized rubber gum by weight as calculated by difference represents the pure gum (resin, ash, moisture and air free) plus its combined sulfur. It is this vulcanized rubber gum and not the uncured original rubber that gives rubber goods their specific and desirable properties. It is therefore entirely rational to specify this substance. The amount of resins or organic acetone extract found varies greatly with the kind of rubber used or may consist of added material, and is best reported by itself. Some will question how the results of the analysis will correspond to the materials compounded, especially the rubber, and will say that it

[1] "Analysis of Silicate and Carbonate Rocks," *Bulletin* **305**, U. S. Geol. Survey, p. 160, first paragraph, and p. 190, first paragraph.

is better to specify the amount of the original materials.

The experience of two years has shown proper correspondence of analysis to ingredients used, taking into account changes produced by process of manufacture and vulcanization, when adulterants have not been introduced. The manufacturer cannot take chances with materials of unknown composition under our methods.

In specifications reading "It shall contain," the best evidence that certain materials have been used in the compound is to have an inspector at the factory to see them put in. We think we are safe in saying that rubber manufacturers have had enough of this system. We believe that "It *shall show*" should be specified, that the methods of analysis and tests should be standardized and the specific items defined. This seems by far the better method and offers fewer opportunities for disputes.

SPECIFICATION OF VULCANIZED RUBBER GUM BY VOLUME—The physical properties of a rubber compound and the quality are more properly related to the percentage by volume of vulcanized rubber gum present than to the percentage by weight. The large majority of rubber goods are sold by bulk and used by bulk rather than by weight. This volume conception is necessary to an understanding of rubber mixings.

Now the specific gravity of this vulcanized rubber gum (resin-, ash-, and air-free) is very nearly unity. The specific gravity of the purest washed and dried raw rubber is greatly influenced by the mode of preparation in regard to minute air bubbles enclosed in the rubber, and varies from 0.90 to 0.95.

According to Philip E. Young, inventor of Young's Gravitometer, the best value for the pure air-free rubber gum is 0.98. With 30 per cent of combined sulfur without mineral fillers, the specific gravity of the vulcanized rubber gum has been shown to be 1.00 The variation in the specific gravity for various degrees of vulcanization is in any case a small one and for purposes of calculation the specific gravity of all vulcanized rubber gum may be taken as unity. By multiplying the percentage by weight of vulcanized rubber gum present by the specific gravity of the compound a product is obtained which represents the percentage by volume of vulcanized rubber gum present. This volume would be strictly correct if divided by the true specific gravity of the vulcanized rubber gum present. However, it is not intended to determine the true volume, but a factor obtained as specified. As this is very nearly the true volume of vulcanized rubber gum present it has been so called in the methods. No closer method for determining the true volume is possible, or necessary.

It will at once be seen that hard rubbers will show more vulcanized rubber gum by weight than the original rubber put in; and that for soft rubber of good quality that which is taken away and reported as organic acetone extract will about equalize the combined sulfur.

The minimum vulcanized rubber gum by volume that will give a sound article can hardly be less than 55 per cent if made up of rubber, sulfur and mineral fillers only. Less than this amount needs something to fill the pores between the particles of fillers in the way of resins, oils, waxes or asphaltum. As the percentage of vulcanized rubber gum by volume decreases in a compound made up of rubber, sulfur and mineral fillers only, the liability of decay by oxidation due to porosity becomes greater.

Every manufacturer knows that with a fixed percentage by weight of rubber put into a compound and made into an article with fixed dimensions, like a hose tube or valve, the lighter he can make the specific gravity, the more money he saves. This is due to a reduction in the volume of rubber present. By specifying a minimum percentage by volume of vulcanized rubber gum the choice of fillers is left entirely to the manufacturer, as it should be. Whether he uses light or heavy fillers is immaterial as long as the volume specified is obtained, and the chemical and physical requirements are met. For example, let us suppose a minimum of 75 per cent of vulcanized rubber gum by volume is specified. The manufacturer can meet this by a compound with a specific gravity of 1.22 showing 61.5 per cent vulcanized rubber gum by weight or by a compound with a specific gravity of 2.27 showing 33.0 per cent vulcanized rubber gum by weight, or by various combinations between these extremes. The same result can be obtained by fixing a minimum specific gravity and a minimum percentage by weight of vulcanized rubber gum present but the kind of fillers would then be limited to a few or a mixture of a few having a certain density.

The method specified permits any manufacturer to make as good a compound as he knows how, using good rubber and any fillers he thinks best. He will be on an equal basis of competition with any other manufacturer as far as the quality of the finished article is concerned. He must necessarily also deliver an equal weight of vulcanized rubber gum of quality required to meet the physical tests.

In the few cases where it is advisable to specify total sulfur it is no extra hardship for the manufacturer to specify total sulfur in all forms. It is impracticable to determine sulfur present as barium sulfate, when other forms of barium are present. As a rule, the other chemical and physical tests, including an ageing test, can be made adequate and sufficient to ensure the delivery of goods made up from new rubber. The amounts of sulfur and organic acetone extract are specified as percentages of the weight of vulcanized rubber gum present as they are functions of the amount of rubber present. The specification of fixed limits for these as percentages of the compound does not make due allowance for such corresponding variation of these constituents with the amount of rubber used.

The quality of the rubber used as well as the suitability of the fillers and the proper vulcanization are fixed by physical tests which will be described in an article to follow.

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## THE SPECIFIC ABSORPTION OF REAGENTS FOR GAS ANALYSIS

By R. P. Anderson

Received February 10, 1915

A knowledge of the absorbing power of the reagents that are commonly used in gas analysis for the gases absorbed by them and for the conditions under which they are ordinarily employed would be of considerable value to the gas analyst. Definite information of this nature is for the most part lacking. Hempel[1] has proposed the term "analytical absorbing power," a suitable expression for this property, but his method of determining it seems open to objection. According to his method, an excess of pure gas was placed in contact with 1 cc. of reagent over mercury and shaken with the reagent as long "als noch schnelle Absorption erfolgte, so dass in Laufe einer Minute mindestens mehrere Kubikzentimeter verschwanden." The decrease in volume thus obtained was divided by four and this value termed the analytical absorbing power. No attempt was made to determine the absolute absorbing power of the reagent, nor was the reagent required to remove the gas completely as it must in actual service. The rapidity with which a reagent absorbs a pure gas that is present in excess is quite different from that with which it completely removes the gas from its mixture with other gases. In the first case, the pressure that is exerted by the gas is presumably that of the atmosphere, while in the second case, the partial pressure of the gas becomes less and less until it equals zero or is so small as to be negligible for technical purposes. In general, as the pressure becomes less, the rapidity of the absorption decreases, the last traces of the gas being absorbed with difficulty, or not at all. It is evident, therefore, that the values that are obtained by Hempel's method have little bearing upon the efficiency of the various reagents for quantitative absorptions, and that they afford the analyst no certainty that his reagents may be used until they have absorbed the quantity of gas indicated by the analytical absorbing power now assigned to them without possibility of the incomplete removal of the constituents.

The determination of the volume of a gas which a certain reagent will absorb up to the point at which the gas is not completely removed from its mixture with other gases is needed by gas analysts. It is here proposed to express this value in cc. of gas per cc. of reagent and term it the *specific absorbing power*, or the *specific absorption*, of the reagent. The statement of the specific absorption of a reagent for a gas must contain the name of the apparatus that is employed, the method of its manipulation, and the temperature of the reagent, since these conditions affect the results. Also the volume of gas that is absorbed at a time may have an effect upon the specific absorption and for this reason the mixture to be employed in the determination of this value should contain an amount of the gas to be removed such as would most frequently be met with, and this amount should be given in stating the specific absorption of a reagent.

[1] "Gasanalytische Methoden," 4th Ed., p. 128.

For example, the specific absorption at room temperature of a certain solution of alkaline pyrogallol for oxygen, obtained by shaking a mixture of gases containing 21 per cent oxygen with the reagent for 3 minutes in the Hempel double pipette, was found to be 5. By this is meant that successive samples of a gas mixture of the above composition were analyzed for oxygen by pyrogallol in the manner above indicated until the reagent was no longer capable of removing all of the oxygen in the time allotted. The total amount of oxygen absorbed up to that point was found to be 5 times the volume of the reagent that was employed.

Determinations of specific absorption are being made in this laboratory in connection with investigations on the most desirable concentrations of the various reagents and the most desirable conditions for their use. The results on alkaline pyrogallol are given in the following article.

Cornell University, Ithaca, New York

## REAGENTS FOR USE IN GAS ANALYSIS
## I. ALKALINE PYROGALLOL

By R. P. Anderson

Received February 10, 1915

### HISTORICAL RÉSUMÉ AND INTRODUCTION

To Döbereiner[1] is attributed the discovery of the absorption of oxygen by an alkaline solution of pyrogallol. Liebig[2] was the first to utilize this reaction for the quantitative removal of oxygen from its mixture with other gases. He employed a solution of potassium hydroxide of 1.4 specific gravity and added to it one-half its volume of a solution of pyrogallol containing 1 g. to 5–6 cc. of water. Much later Weyl and Zeitler[3] studied the effect upon the absorbing power of the reagent of varying the concentration of the alkali. In their work, a definite volume of air was aspirated through a U-tube that contained broken glass and a measured volume of the alkaline solution of pyrogallol. The amount of oxygen that remained in the air after this treatment was determined by titration with a solution of sodium hyposulfite, using indigo as the indicator. Three solutions of potassium hydroxide, of specific gravities 1.025, 1.050 and 1.500, were employed, and the reagent was prepared by adding 0.25 g. of pyrogallol to 10 cc. of one of these solutions. The oxygen that was not absorbed under the arbitrary conditions of the experiments amounted to 1.56, 0.88 and 2.9 per cent for the solutions in which the specific gravity of the alkali was 1.025, 1.050 and 1.500, respectively. From these data the authors conclude that the solution of potassium hydroxide of specific gravity 1.050 gives the reagent with the highest absorbing power and they state also that the pyrogallol probably is quickly destroyed by the solution of potassium hydroxide of specific gravity 1.5. Wehl and Goth[4] performed similar experiments substituting sodium

[1] Gilbert's *Ann.*, **74** (1823), 410.
[2] Liebig's *Ann.*, **77** (1851), 107.
[3] *Ibid.*, **205** (1880), 255.
[4] *Ber.*, **14** (1881), 2659.

hydroxide and sodium carbonate for the potassium hydroxide.

Soon after Liebig's experiments, it was found[1] that carbon monoxide was formed under certain conditions on the oxidation of alkaline pyrogallol. Lewes[2] states that a solution prepared by adding 10 g. of pyrogallol to 150 cc. of a 20 per cent solution of sodium hydroxide must not be employed for the absorption of oxygen more than four or five times on account of the formation of carbon monoxide. Clowes[3] studied the behavior of alkaline pyrogallol with especial reference to the formation of carbon monoxide. He found that although a reagent containing 10 g. of pyrogallol and 24 g. of potassium hydroxide to 100 cc. of solution can be used in determining oxygen when it does not exceed 28 per cent of the total volume, carbon monoxide is formed on the analysis of richer mixtures. He recommends that the amount of potassium hydroxide be increased to 120 g. whenever gases that contain more than 28 per cent of oxygen are to be analyzed. An attempt to determine oxygen in a gas mixture containing 90 per cent of it, with the reagent containing only 24 g. of potassium hydroxide to 100 cc. of solution, resulted in the formation of 6 per cent carbon monoxide, while no more than a trace was formed when the stronger solution of alkali was employed. Berthelot[4] found, from a study of the various factors that might affect the formation of carbon monoxide, that alkali in large excess and pyrogallol sufficient to absorb four or five times the amount of oxygen present are necessary in order to prevent the formation of more than a negligible amount of this undesirable product of the reaction. He also investigated the behavior of the reagent when the potassium hydroxide was replaced by sodium hydroxide, barium hydroxide and ammonium hydroxide. The total amount of oxygen that was absorbed by the solution containing sodium hydroxide was found to be practically the same as with the use of potassium hydroxide, while the solution in which barium hydroxide was used gave a smaller absorption, and the one in which ammonium hydroxide was used gave a larger absorption. The effect of these substitutions upon the formation of carbon monoxide was small.

Benedict[5] found, from precise determinations of the oxygen content of the atmosphere, that the results that were obtained depended upon the concentration of the alkali that was employed. The average of 14 determinations made with Haldane's[6] solution containing 1 g. of pyrogallol to 10 cc. of potassium hydroxide, 1.55 specific gravity, was 20.956; the average of similar determinations made with a slightly modified Haldane reagent which contained somewhat less alkali than the original, was 20.938; and other solutions containing less alkali gave still lower results. Benedict suggests that the discrepancy in the results obtained from the various solutions may be due to the formation of carbon monoxide. Haldane states that the solution prepared according to his directions yields no carbon monoxide on the absorption of oxygen.

An inspection of the proportions of pyrogallol, potassium hydroxide, and water that have been recommended by various gas analysts for the preparation of alkaline pyrogallol shows that there is little uniformity as regards either the composition of the reagents or the terms in which their descriptions are couched. In the accompanying list, for purposes of comparison, an attempt has been made to standardize as far as possible the statement of the composition of the reagent by expressing with sufficient accuracy the amount of pyrogallol and of potassium hydroxide in 100 cc. of the solution:

| Author | Grams per 100 cc. of solution of Pyrogallol | KOH |
|---|---|---|
| Liebig[1] | 6 to 7 | 32* |
| Clowes[2] | *a* 10 | 24 |
| | *b* 10 | 120 |
| Winkler[3] | 5 | 22* |
| Hempel[3] | 5.5 | 84 |
| Berthelot[4] | 15 | 25 |
| Franzen[5] | 8 | 70 |
| Gill[6] | *a* 4.9 | 43 |
| | *b* 4.9 | 81 |
| Haldane[7] | 9.4 | 74* |
| Benedict[7] | 9.4 | 66* |

[1] *Loc. cit.*

[2] "Lehrbuch der technischen Gasanalyse," 1901 Ed., p. 81.

[3] "Methods of Gas Analysis," 1902 Ed., p. 149. In the fourth edition of this work (1913), Hempel recommends practically the same proportions as are given by Benedict.

[4] "Traité Pratique de L'Analyse des Gas," 1906 Ed., p. 185.

[5] "Gasanalytische Übungen," 1907 Ed., p. 4.

[6] "Gas and Fuel Analysis," 1912 Ed., p. 54.

[7] "The Composition of the Atmosphere," 1913 Ed., p. 80.

Four of the solutions were prepared by using potassium hydroxide of a definite specific gravity. The amount of *water-free* potassium hydroxide is given in these cases and is marked by an asterisk to distinguish it from the amounts used in the other solutions where ordinary potassium hydroxide of unknown water content was employed. The water content of potassium hydroxide that is sold in stick form varies between rather wide limits and the amount of alkali in Haldane's solution would ordinarily be found to exceed that recommended by any other authority with the possible exception of Clowes' stronger solution.

In view of the conflicting results that have been obtained by earlier investigators of alkaline pyrogallol, and because of the apparent lack of any effort to determine what constitutes the most desirable reagent from a consideration of the various determining factors, it was decided to attempt a systematic investigation of the reagent. A study of the effects upon the specific absorption[1] of the reagent of variations in the amounts of potassium hydroxide and pyrogallol was made the starting point of the experimental work and, in order to eliminate as much unnecessary work as possible, an apparatus was constructed in which the specific absorption of various solutions of alkaline pyrogallol could be easily determined.

[1] See preceding article, THIS JOURNAL, 7 (1915), 587.

[1] See Calvert, *Compt. rend.*, **57** (1863), 873; Cloez, *Ibid.*, p. 875; Boussingault, p. 885; and Poleck, *Z. anal. Chem.*, **8** (1869), 451.

[2] *J. Soc. Chem. Ind.*, **10** (1891), 407.

[3] *Chem. News*, **72** (1895), 288; *J. Soc. Chem. Ind.*, **15** (1896), 170; *Chem. News*, **74** (1896), 199.

[4] *Ann. chim. phys.*, [7] **15** (1898), 294; *Compt. rend.*, **126** (1898), 1066, 1459.

[5] "The Composition of the Atmosphere," p. 113.

[6] "Methods of Air Analysis," 1912 Ed., p. 13.

SPECIAL APPARATUS FOR EXPERIMENTAL WORK

In the apparatus in Fig. 1, artificial mixtures of oxygen and nitrogen were shaken with the alkaline pyrogallol over mercury and the readings were made under constant volume (approximately), *i. e.*, the amount of oxygen absorbed was determined by the change in the pressure that was exerted by the gas as indicated by the change in a manometer reading during the absorption. A new sample was not taken after each determination, nearly the same result being obtained by the addition of oxygen to take the place of that which had been previously absorbed.

The contact between the gas mixture containing oxygen and the alkaline pyrogallol was effected in the pipette *P* which connects by means of a long, enameled rubber tube with the leveling bulb *L*. The pipette is closed at the top by a two-way stopcock, *A*, by means of which connection may be made either

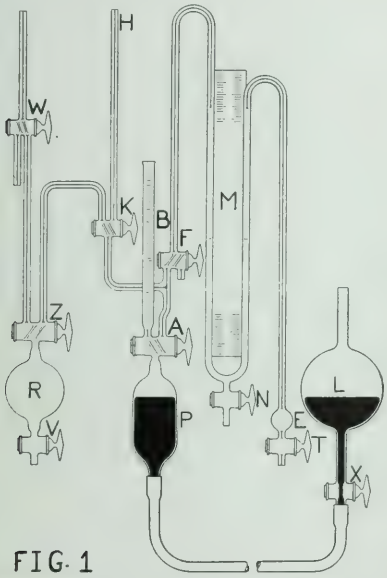



FIG. 1

with the burette *B* or with one arm of manometer *M* through stopcock *F*, and with the oxygen reservoir *R* through stopcocks *K* and *Z*. Reversal of the position of *K* permits connection of the pipette with the atmosphere at *H*. The other arm of the manometer bends downward and terminates in the enlargement[1] *E* and stopcock *T*.

To support the apparatus, a tall, narrow, rectangular iron frame was constructed of iron rods and clamps and the upper and lower ends of the pipette *P* were fastened to horizontal cross pieces near the bottom of the frame. In turn, the frame was suspended at a point about midway between the top and bottom (corresponding approximately to *K* on the apparatus) to a horizontal iron rod in such fashion that the apparatus might be rocked back and forth with the rod as an axis by means of a hot-air engine and the proper connections. A glass jar containing water was brought up around the apparatus[1] until *R*, *P* and *E* were covered, in order to maintain a uniform temperature in the separate compartments where gas was confined. The enameled rubber tubing passed from the pipette over the edge of the jar to the leveling bulb which was supported by a separate stand.

The apparatus was prepared for use by pouring mercury, sufficient in amount to fill the pipette *P*, into the leveling bulb *L*, drawing water into the manometer *M* through *N* by lowering *L* with *A* and *F* in the proper positions, and filling the reservoir *R* through *Z* and *W* with oxygen under pressure. The air in *R* was previously displaced by oxygen by opening *V* and allowing the oxygen to bubble through the water in the cell. After these operations were performed, the manipulation of the apparatus was carried out in the following fashion:

MANIPULATION OF THE APPARATUS

With *F* closed, mercury from the pipette was driven up to *H* by raising the leveling bulb. Connection was made at this point with a capillary tube, also filled with mercury, to a Hempel burette containing nitrogen from a phosphorus pipette, and 20 cc. of this gas was drawn into the pipette, following it with mercury from the burette over to *K*, which was thereupon closed. The proper amounts of solutions of pyrogallol and potassium hydroxide were then introduced separately into the pipette through the burette *B*. This was accomplished without danger of admission of air providing the mercury in the leveling bulb was at a slightly lower level than that in the pipette and care was taken in the manipulation of *A*. Connection with the manometer was next made by turning *A* and *F*, and the leveling bulb was then lowered until the water stood at some definite point on the scale near the upper end of the left-hand arm of the manometer. *X* was thereupon closed. At this point the engine that rocks the pipette back and forth was started in order to obtain a thorough mixture of the solutions of pyrogallol and potassium hydroxide in the pipette and to facilitate the absorption of the small amount of oxygen that was usually present in the space between *A* and the water in the manometer. This absorption of oxygen decreased the pressure in the pipette and necessitated the readjustment of the level of the water in the manometer. Oxygen was next admitted from the reservoir *R* into the pipette until the manometer reading indicated that the desired quantity[2] had been added. Shaking was started at this point and continued for 5 minutes, at the end of which time the motor was stopped, the manometer reading taken, oxygen added to the same manometer reading as before, and the shaking

[1] This enlargement was made of such size that a change of pressure of 1/4 atmosphere inside the pipette would produce as large a movement of the water in the manometer as was permissible.

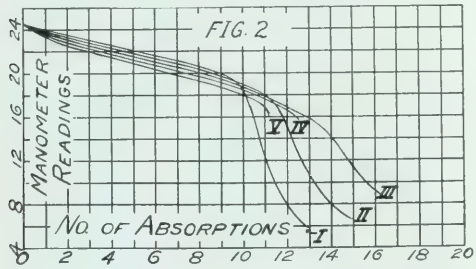
[1] To make the apparatus more compact, the capillary connections were bent so that *K* and *L* were situated behind *F*.

[2] This quantity was usually 5 cc., thus giving an artificial mixture containing 20 per cent of oxygen. The manometer reading that corresponded to the admission of 5 cc. of oxygen was obtained by running in 5 cc. of nitrogen without changing the level of the mercury in the pipette.

continued. This was repeated until the reagent became exhausted.

### EFFECT OF AMOUNT OF POTASSIUM HYDROXIDE ON THE SPECIFIC ABSORPTION OF THE REAGENT

Five solutions of potassium hydroxide were employed. These consisted of a solution (of specific gravity 1.55) containing about 1.5 parts of potassium hydroxide in stick form to 1 part of water, and four other solutions that were prepared from the first in the proportions of 4 volumes of alkali to 1 volume of water, 3 volumes to 2 volumes, 2 volumes to 3 volumes, and 1 volume to 4 volumes, respectively. The solution of pyrogallol was prepared by dissolving 1 part of pyrogallol in 1.5 parts of water: 0.43 cc. of this solution (containing 0.2 g. of pyrogallol) was employed in each case and to it was added 5 cc. of one of the solutions of alkali. The saturation of each reagent was carried out as previously outlined and the results are shown in Fig. 2 in which manometer readings that were obtained after the absorption of oxygen from its mixture with nitrogen are plotted against the number of samples from which the oxygen had been absorbed. Curve I was obtained from the




solution containing the most alkali, Curve II from the next weaker, etc.

Three or more determinations were made on each of the five solutions. Owing to difficulties in admitting to the pipette exactly the proper amount of reagent and in maintaining a uniform rate of shaking, duplicate manometer readings did not always agree as closely as seemed desirable, but sufficient determinations were made to establish with the necessary accuracy the relative positions of the curves corresponding to the different solutions with the exception of the latter portion of Curves IV and V. The different determinations failed to show definitely the positions of the breaks in these two curves. The break in Curve V falls at the left of the break in Curve IV and both lie between the breaks in Curves I and III. It was not deemed of sufficient importance to locate them more accurately.

The downward slope of the first portion of each of the curves is due to the presence of about one per cent of nitrogen in the oxygen. This caused a gradual decrease in the amount of oxygen that was added at a time, and a corresponding drop in the manometer reading. This fact proved to be of little consequence in the study of the various solutions since it did not obscure the sudden break which was obtained when the reagent became nearly exhausted, and consequently no effort was made to free the gas from the impurity.

It will be noted that the largest manometer readings were obtained with the solution that contained the most potassium hydroxide; in other words, the greater the amount of alkali, the larger the apparent oxygen content of the gas sample. To determine whether the amount of alkali present in Solution I was sufficient for the removal of all of the oxygen from a mixture of this nature, similar determinations were made with a solution containing still more potassium hydroxide[1] and the same amount of pyrogallol. As far as could be determined from the apparatus that was employed, the curve obtained from this solution occupied practically the same position as Curve I, thus showing that practically complete absorption is obtained with Solution I. The statement of Weyl and Zeitler[2] regarding the effect on pyrogallol of a concentrated solution of potassium hydroxide does not appear to be substantiated by these results. Further, the results which they give in support of the use of a solution containing alkali of specific gravity 1.05 show only that more rapid absorption is obtained with this solution, not that the absorption is complete or that the solution has a higher absorbing power than one containing more alkali.

The break in Curve I occurs at about the ninth absorption, in II at the eleventh, and in III at the thirteenth absorption. The reason for this apparent increase in specific absorption with decreasing content of alkali is no doubt due in part to the failure of the solutions showing this increase to absorb all of the oxygen from the mixtures with which they were treated as is shown by lower manometer readings. With still lower concentrations of alkali, as in Solutions IV and V, the break in the curve occurs before the break in III, indicating that in this case the break is due to insufficient alkali rather than to exhaustion of the pyrogallol. The remainders of Curves IV and V are not shown on account of the uncertainty of the positions of the breaks, but these portions are much more nearly vertical than is the case with the other curves.

### EFFECT OF AMOUNT OF PYROGALLOL ON THE SPECIFIC ABSORPTION OF THE REAGENT

Five solutions of pyrogallol were employed. These consisted of a solution containing 0.625 g. of pyrogallol per cc., which was obtained by dissolving pyrogallol in an equal weight of water, and four other solutions that were prepared from the first, containing 0.5, 0.375, 0.25, and 0.125 g. of pyrogallol per cc. It was desired to keep the concentration of potassium hydroxide in this series of experiments as high as in Solution I of the previous series[3] and, at the same time, introduce as much as possible of the solution of pyrogallol in order to obtain a wide variation of this constituent. Accordingly, a solution of potas-

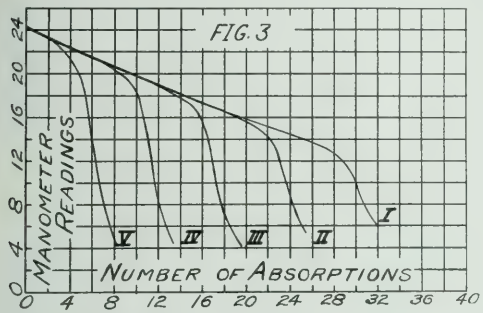
[1] The amount of potassium hydroxide was sufficient to place the solution in the zero position in the sequence 0, I, II, III, IV, V.

[2] *Loc. cit.*

[3] Solution I contained 5 cc. of a solution of KOH, sp. gr. 1.55 (4 g KOH), to about 5.4 cc. alkaline pyrogallol.

sium hydroxide was prepared of such strength that 4.45 cc. contained as much potassium hydroxide as 5 cc. of the alkali in Solution I, and was employed in this series of experiments in the proportion of 4.45 cc. of alkali to 1 cc. of one of the solutions of pyrogallol. The curves that were obtained from the treatment of these various solutions in the special apparatus are shown in Fig. 3, Solution I containing the most pyrogallol and Solution V the least.

From these curves it is evident that, within the limits of this series and with the amount of potassium hydroxide




that was employed, the specific absorption increases with the amount of pyrogallol which the reagent contains.

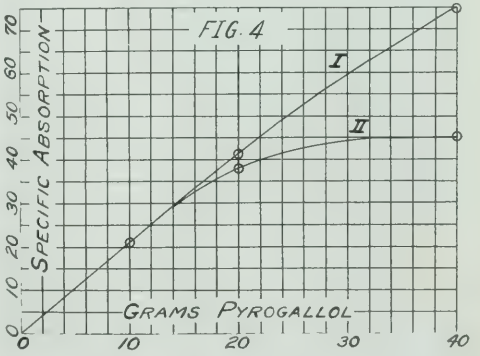
THE MAXIMUM SPECIFIC ABSORPTION OF ALKALINE PYROGALLOL

The two series of experiments that have been described show that a high concentration of potassium hydroxide in alkaline pyrogallol is necessary for the quantitative absorption of oxygen in gas-analytical work and a high concentration of pyrogallol is necessary to obtain a high specific absorption. Any effort to increase the specific absorption of the reagent by increasing the concentration of pyrogallol cannot be carried too far without danger of incomplete absorption as a result of the unavoidable decrease in the concentration of potassium hydroxide. In this connection, therefore, water, the third constituent of the reagent, is obviously undesirable in an amount larger than is necessary to prevent the reagent from crystallizing at ordinary temperatures.

To determine what proportions of pyrogallol, potassium hydroxide, and water give the maximum specific absorption for this reagent, a third series of experiments was performed. One set of solutions was prepared by dissolving 10, 20, 40 and 50 grams of pyrogallol in 100 cc. portions of a solution of potassium hydroxide, specific gravity 1.55, and a similar set was prepared using alkali of specific gravity 1.60, the necessary precautions being taken to prevent their deterioration through contact with the oxygen of the air. A definite amount of reagent (about 25 cc.) was transferred to a Hempel pipette for use with mercury without allowing oxygen to come into contact with it and was treated at room temperature[1] with 100 cc. samples of air[1] until the absorption of oxygen was no longer sufficiently complete for technical purposes[2] at the end of three minutes. The absorption was effected by gently rocking the pipette and stand backward and forward at the rate of two or three times a second, using the front edge of the base of the pipette stand as an axis.

The total volume of oxygen that had been absorbed, divided by the volume of the solution, gave the specific absorption of the particular reagent for the conditions under which the determinations were made. The values of the specific absorptions for the various amounts of pyrogallol in 100 cc. of alkali are shown in Fig. 4. Curve I was obtained from the solutions containing the alkali of specific gravity 1.60 and Curve II from those containing alkali of specific gravity 1.55.

In the case of Solution I, the specific absorption is approximately proportional to the amounts of pyrogallol to 100 cc. of alkali, and the lack of strict proportionality may be imputed to two causes. First, owing to the increase in volume that results when pyrogallol dissolves in a solution of potassium hydroxide, the concentration of pyrogallol in the various solutions is not proportional to the amount of pyrogallol that was employed, *e. g.*, the solution that was prepared by dissolving 20 g. of pyrogallol in 100 cc. of potassium hydroxide does not contain twice as much pyrogallol as the one prepared by dissolving 10 g. of pyrogallol in the same amount of alkali, and consequently the value that is obtained for the specific absorption of the stronger solution should be less than twice that of the weaker. Secondly, the concentration of the alkali is gradually lessened by the forma-




tion of carbon dioxide and water[3] during the oxidation of the pyrogallol, thus causing an earlier lack of complete absorption than would be expected from the amount of pyrogallol in the solution. The effect

[1] Hempel has shown that the absorption of oxygen by alkaline pyrogallol is much less rapid at temperatures below 15° C. than at room temperature. It was found that a temperature change from 20° to 24° C. caused little, if any, variation in the specific absorption of the reagent and no analyses were made if the room temperature fell outside these limits. Temperatures below 21° or above 23° were unusual.

[1] When it was known that the reagent was still capable of removing the oxygen from many samples of air before becoming exhausted, pure oxygen was added from a burette to lighten the routine work of the experiment. Care was taken that the heat of the reaction between the oxygen and the alkaline pyrogallol did not cause more than a slight rise in the temperature of the reagent.

[2] It was assumed that the absorption was complete as long as the apparent oxygen content of the sample amounted to 20.8 per cent or more.

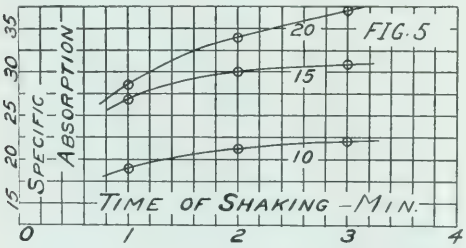
[3] See Berthelot, *Ann. chim. phys.*, [7] **16** (1898), 294.

of this gradual diminution in the amount of potassium hydroxide is especially noticeable in Curve II, where the specific absorption of a solution containing 40 g. of pyrogallol to 100 cc. of alkali, specific gravity 1.55, is but little more than that obtained from a solution containing one-half of that amount of pyrogallol.

The highest specific absorption that was obtained from the solutions of these two series is about 75 for the conditions that have already been stated. This probably does not actually represent the maximum specific absorption that might be obtained, but is no doubt a close approximation to it. The solutions that contained 50 g. of pyrogallol to 100 cc. of alkali failed to give an absorption sufficiently complete for technical use, even when new, and thus their specific absorption equals zero. This was no doubt due to the increase in volume which accompanied the solution of the pyrogallol and lowered the concentration of alkali beyond the lower limit for the production of complete absorption. It might be possible to increase the specific absorption by using a higher concentration of pyrogallol in a solution of potassium hydroxide of higher specific gravity or by preparing the solution by adding a minimum of water to a mixture of solid pyrogallol and solid potassium hydroxide, but such reagents would certainly never be actually employed on account of high viscosity and a tendency to foam on shaking, and consequently no attempt was made to determine more accurately the maximum specific absorption.

### EFFECT OF TIME OF SHAKING UPON THE SPECIFIC ABSORPTION OF THE REAGENT

The question as to the effect of the time of shaking upon the specific absorption of alkaline pyrogallol




next presented itself for consideration. Reagents were prepared containing 10, 15 and 20 grams of pyrogallol to 100 cc. of a solution of potassium hydroxide of specific gravity 1.55, and the specific absorption of each was determined in the manner described under the previous heading except for the time of shaking. This was made one minute for each reagent at the start, lengthened to two minutes when the absorption of oxygen was no longer practically complete for the shorter interval, and finally increased to three minutes for similar lack of complete absorption for the two-minute period. In this fashion, three values of the specific absorption corresponding to the three periods of shaking were obtained for each solution. In Fig. 5 these values are plotted against the time of shaking. The numbers below the curves represent the amounts of pyrogallol that were used in the preparation of the various solutions.

In the case of the reagent that contains the least amount of pyrogallol, the specific absorption for 1-minute shaking is nearly as large as that for 3-minute shaking, the difference amounting to only 3 units. The specific absorption for 1-minute shaking does not increase as rapidly as the value for 3-minute shaking when the amount of pyrogallol is made larger, as shown by the differences in the shapes of the curves for 10, 15 and 20 grams of pyrogallol to 100 cc. of a solution of potassium hydroxide. This behavior of the solutions indicates a less rapid absorption as the amount of pyrogallol is increased (at least for the condition of the reagent corresponding to incomplete absorption at the end of 1-minute shaking) and is probably due to the smaller excess of alkali.

### THE MOST DESIRABLE REAGENT FOR TECHNICAL USE AND ITS SPECIFIC ABSORPTION IN THE HEMPEL PIPETTE FOR USE WITH MERCURY

In ascertaining the desirability of a reagent for technical use, the ease of preparation, the convenience of manipulation, and the specific absorption must each be taken into consideration.

The reagents containing a solution of potassium hydroxide of 1.60 specific gravity are less simple to prepare and less convenient to manipulate than those containing alkali of 1.55 specific gravity. The greater difficulty of preparation is caused by the fact that a solution of potassium hydroxide of 1.60 sp. gr. crystallizes at ordinary temperatures (20° C.) and consequently must be heated for the preparation of the reagent.[1] This is not true of the solution of 1.55 specific gravity. The greater difficulty of manipulation is caused by the high viscosity of the solution that contains the greater amount of alkali. In the case of the reagents prepared from alkali of 1.60 specific gravity, the viscosity causes a comparatively thick film of the reagent to remain on the walls of the capillary tubing when a sample of gas is passed into the pipette, the film being of such thickness as to render opaque the bore of the capillary, even with only moderately large amounts of pyrogallol in the reagent. This opaque film makes it difficult to ascertain the position of the reagent in the capillary when the sample is drawn back into the burette.

The reagents that contain a high concentration of pyrogallol show a greater tendency to foam than those of low concentration. This tendency first becomes noticeable in regard to its effect upon the ease of manipulation in the case of those solutions that contain 20 grams of pyrogallol to 100 cc. of alkali and becomes decidedly objectionable in solutions containing twice as much pyrogallol.

Thus it is seen that high concentrations of potassium hydroxide and pyrogallol, the important factors in obtaining a reagent with a high specific absorption, are responsible for undesirable features such as diffi-

[1] The reagent itself is stable in liquid form at ordinary temperatures on account of the increase in volume that accompanies the solution of pyrogallol and also on account of the replacement of a part of the potassium hydroxide by water in the formation of potassium pyrogallate.

culty of preparation and manipulation. To eliminate these undesirable features necessitates limiting the specific gravity of the solution of potassium hydroxide to 1.55 and the amount of pyrogallol to less than 20 g. to 100 cc. of the alkali. This involves a sacrifice in specific absorption of about 40 units (see Fig. 4), but it is felt that the limits that have been mentioned should not be exceeded in choosing the most desirable reagent for technical use.

It was found that foaming, such as was noticed in the solution containing 20 grams of pyrogallol to 100 cc. of alkali of specific gravity 1.55, during the analysis of samples of air, disappeared almost entirely when only 15 grams of pyrogallol were employed. Further, the specific absorption of the latter reagent for 1-minute shaking is nearly as large as that of the more concentrated solution (see Fig. 5). It thus appears that the reagent prepared by dissolving 15 grams of pyrogallol in 100 cc. of a solution of potassium hydroxide of 1.55 specific gravity has practically the highest specific absorption that can be obtained in a solution satisfactory in other respects and that it is therefore the most desirable for technical use.[1] The volume of the solution obtained above is approximately 110 cc., and there are then 13.6 g. of pyrogallol and 71.5 g. of potassium hydroxide to 100 cc. of solution. The specific absorption of this reagent is about 27 when employed at room temperature in 25-cc. portions in a Hempel pipette over mercury and treated with 100-cc. samples of air with 1-minute shaking. The same reagent may be used still further to effect the absorption of oxygen from air if the analyst prefers a longer time of shaking to discarding the old and preparing a new reagent. The specific absorption for 2-minute shaking is about 30, and that for 3-minute shaking about 31. No material increase in the specific absorption of this solution can be effected by increasing the time of shaking beyond three minutes. Experiments have shown that the specific absorption that is obtained with a reagent prepared four months before the time when it was found to be no longer able to give complete absorption is as great as that obtained with one exhausted shortly after it was prepared. It thus appears that the proposed reagent is stable over an indefinite period of time, although conclusive results have not yet been obtained on this point.

The reagent that has been proposed has the disadvantage over using separate solutions of pyrogallol and potassium hydroxide that it must be prepared outside the pipette, thus allowing some oxidation, due to contact with the oxygen of the air, unless special precautions are introduced which would complicate its preparation. However, the specific absorption that may be obtained when pyrogallol is dissolved directly in a solution of potassium hydroxide of 1.55 specific gravity is greater than is possible when separate solutions of the two constituents are employed, and this fact more than offsets the deterioration that cannot readily be avoided in using the former method of preparing the reagent and in transferring it to a pipette.

When the specific absorption 31 has been reached, each molecule of pyrogallol in the reagent has then taken up about 2.3 atoms of oxygen. Berthelot[1] obtains 3 atoms of oxygen for each molecule of pyrogallol for complete saturation of the reagent.

Of the various solutions that have previously been employed for the absorption of oxygen (see Introduction), the one described by Haldane most closely resembles the one that has just been proposed. The specific absorption of a reagent prepared according to Haldane's directions is given on the lower curve of Fig. 5.

### THE SPECIFIC ABSORPTION OF THE PROPOSED REAGENT IN THE HEMPEL DOUBLE PIPETTE FOR LIQUID REAGENTS

Thirty grams of pyrogallol was weighed into an Erlenmeyer flask of 300 cc. capacity, and was dissolved in 200 cc. of a solution of potassium hydroxide of 1.55 specific gravity: 185 cc. of this solution was then transferred to a Hempel double pipette[2] for liquid reagents. Unnecessary deterioration of the reagent was avoided by stoppering the flask while the process of solution was taking place and by transferring it to the pipette as expeditiously as possible.

During the process of exhausting the reagent and determining the specific absorption of it for various periods of shaking with 100 cc. samples of air, the analysis of air was alternated with the admission of nearly pure oxygen from a calibrated gas holder. In other words, the greater portion of the oxygen necessary to exhaust the reagent was slowly admitted to the reagent from a gas holder in order to save time and labor, an occasional analysis of air being performed to make sure that the reagent was still giving complete absorption for a certain period of shaking. When the reagent was nearly exhausted (judging from the results obtained in the Hempel pipette for use with mercury) the successive additions of oxygen were made small to avoid more than a negligible error in the determinations of specific absorption. Undue heating of the reagent was prevented by playing a blast of air on the outside of the pipette and by controlling the rate at which the oxygen was admitted.[3] The specific absorption of the reagent at room temperature for 100 cc. samples of air was found to be 25.1 for 1-minute shaking, 29.4 for 2-minute shaking and 31.3 for 3-minute shaking.

Uniformity of procedure can readily be obtained with different pipettes except for the amount of reagent that is left in the first bulb of the pipette when the gas sample is introduced. This will vary with the size of the bulb and there is frequently a considerable variation in this particular in different pipettes. It seems likely, however, that any change in the specific

[1] At least, in the particular absorbing device in question. Other absorbing devices, with widely different methods of manipulation, might perhaps operate more successfully with a solution prepared in a different fashion.

[1] *Loc. cit.*

[2] A modified form was employed. See THIS JOURNAL, **6** (1914), 237.

[3] The effect of the rapid admission of oxygen without proper cooling is taken up in a later section. In each case after the admission of oxygen, the reagent was allowed to cool to room temperature before the analysis of a sample of air was attempted

absorption of the reagent due to this cause would be so small as to be negligible.

### THE EFFECT OF HIGH PERCENTAGES OF OXYGEN ON THE SPECIFIC ABSORPTION

The specific absorption of the proposed solution of alkaline pyrogallol was determined for the Hempel pipette for use with mercury and for the Hempel double pipette for liquid reagents, using mixtures containing about 90 per cent oxygen.

In the case of the Hempel pipette for use with mercury, 25 cc. of the proposed solution was employed and this was treated with 100-cc. gas samples containing about 90 per cent oxygen until the absorption failed to be complete for different times of shaking. The specific absorption under these conditions was found to be about 21 for 1-minute shaking and about 24 for 2- and 3-minute shakings. These results are only approximate since the amount of oxygen in each sample represents nearly four times the volume of the reagent.

In the case of the Hempel double pipette for liquid reagents, 185 cc. of the reagent was employed and this was treated with 100-cc. gas samples of a mixture containing about 90 per cent oxygen, alternated with admission of pure oxygen, until the absorption failed to be complete for different times of shaking. The specific absorption under these conditions was found to be zero for 1-minute shaking, 26.9 for 2-minute shaking, 29.9 for 3-minute shaking, 31.1 for 4-minute shaking, and 32.5 for 5-minute shaking.

The striking differences in the specific absorptions for the two forms of apparatus in the case of 1-minute shaking may be due, in a measure at least, to the following causes: (1) The heat of combination of oxygen and pyrogallol would cause a greater elevation of temperature when the volume of the reagent is 25 cc. than when it is 185 cc., which in turn would tend to increase the velocity of the reaction as Hempel has shown. (2) The shaking process would probably result in a more intimate contact of the gas and reagent when a small volume of the reagent is confined over mercury than when the reagent fills the pipette, due to the momentum of the mercury when the direction of its motion is suddenly changed.

### OTHER CONSIDERATIONS THAT MAY AFFECT THE SPECIFIC ABSORPTION UNDER WORKING CONDITIONS

Conditions which affect the specific absorption of alkaline pyrogallol, such as the composition of the reagent (concentrations of pyrogallol and potassium hydroxide) and the method of its manipulation (the apparatus employed, temperature of the reagent, time and character of shaking, and percentage of oxygen in the sample), have been taken into consideration in the previous discussion. Other factors that may influence the specific absorption under exceptional circumstances are the deleterious action of high temperature on the reagent, and the frequency with which analyses are made.

*The Deleterious Action of High Temperatures*—The effect of the temperature of the reagent upon the speed of absorption of oxygen has already been mentioned. At temperatures much above that of the room, this effect is also accompanied by a decrease in the specific absorption of the reagent, *i. e.*, the reagent becomes exhausted earlier than one that is employed only at ordinary temperatures.

This decrease in the specific absorption of the reagent was noticed particularly in the case of a reagent which was placed in a Hempel double pipette for liquid reagents and which was treated with oxygen in such fashion that its temperature rose to about 50° C. After the absorption of 1500 cc. of oxygen, this reagent removed the oxygen completely from a sample of air with 1-minute shaking, but after the absorption of an additional 2000 cc., it failed to remove the oxygen completely from a sample of air, even with 3-minute shaking. The total volume of oxygen up to this point would correspond to a specific absorption of about 19 while the specific absorption of another reagent prepared in the same manner and exhausted without allowing the temperature to rise much above that of the room, was, as before stated, 31.3 for 3-minute shaking. It seems probable that this decrease in specific absorption is the result of a change in the character of the reactions that take place between oxygen and pyrogallol as the reagent is heated, rather than the result of the direct action of heat upon the reagent. Whatever may be the cause, the drop in specific absorption caused by heating of the reagent would not be of importance under ordinary conditions unless many samples containing high percentages of oxygen were being analyzed in rapid succession.

*The Frequency with which Analyses Are Made*—It was found that the rapidity of the absorption of oxygen from a given sample depended upon whether or no the reagent had been used a short time before, the absorption taking place more rapidly when the reagent had been just previously used. This state of affairs was found to exist in the analysis of the gas samples containing about 90 per cent oxygen. As has previously been stated, the specific absorption of the proposed reagent in the Hempel double pipette was found to be zero for samples of the above composition for 1-minute shaking. After the reagent had been employed for a few analyses, however, it was found that complete absorption of the oxygen was obtained in one minute and this continued for a few absorptions, after which 2-minute shaking was again necessary for complete absorption. Further, when the reagent had been so far exhausted that 3-minute shaking was necessary for the complete absorption of oxygen from a 100 cc. sample, the reagent was allowed to stand for about 24 hours without being used; when the treatment of the reagent was resumed, it was found that complete absorption was not obtained with 3-minute shaking of the first sample, although it was in the second. This occurred a second time with the same reagent under similar conditions. The cause of this behavior of the reagent may be due to a slight rise in temperature caused by the first analysis or it may be due to the presence of some intermediate product of the reaction which hastens the absorption and which disappears on standing. At any rate, it

is of importance only when the reagent has nearly lost its ability to absorb oxygen completely from a sample under the condition of its use, and then only when it has not been used previously for several hours.

### THE FORMATION OF CARBON MONOXIDE ON THE OXIDATION OF ALKALINE PYROGALLOL

No systematic study of the conditions that affect the formation of carbon monoxide was attempted. However, samples of air that were placed in contact with the proposed reagent after it was no longer capable of removing the oxygen completely during several minutes' shaking were examined for carbon monoxide and none was found. In each case, shaking the same sample with a solution of alkaline pyrogallol, still in good condition, resulted in the indication of the proper percentage of oxygen, and subsequent treatment with an acid solution of cuprous chloride, freshly prepared, had no effect upon the volume of the sample. It is therefore evident that the formation of carbon monoxide attendant upon the use of the reagent that has been proposed is not sufficient in amount to be objectionable, even when the reagent is almost exhausted.

### THE USE OF POTASSIUM HYDROXIDE PURIFIED BY ALCOHOL

Hempel[1] has called attention to the fact that potassium hydroxide purified by alcohol should not be employed in the preparation of alkaline pyrogallol, and many authors have mentioned this precaution in their description of the reagent. Hempel did not state wherein the unsuitability of this preparation lay, and in an attempt to explain why its use is undesirable, the following experiment was performed:

Five grams[2] of pyrogallol was dissolved in 50 cc. of a solution of potassium hydroxide purified by alcohol of 1.55 specific gravity; 25 cc. of the resulting reagent was introduced into a Hempel pipette for use with mercury and there treated with 100 cc. samples of air in the manner previously described. It was found that, within the limits of accuracy of the apparatus, the absorption of oxygen was complete, and that the only noticeable difference between this reagent and one prepared by using potassium hydroxide not purified by alcohol is in the specific absorption, which is about 18 in the first case and about 21 in the second.

The apparent discrepancy between the results of this experiment and Hempel's statement may perhaps be explained by the assumption either that the method of manufacture of potassium hydroxide purified by alcohol has been changed in such a manner since the publication of Hempel's results that the objection to the use of this substance no longer holds, or that Hempel's objection was made on the ground of incomplete absorption, apparent in his apparatus for exact analysis, but not noticeable in the use of the Hempel apparatus for technical analysis.

[1] *Ber.*, **20** (1887), 1865

[2] This experiment was made before the question of the most desirable reagent for technical use had been settled.

### THE USE OF SODIUM HYDROXIDE IN PLACE OF POTASSIUM HYDROXIDE

From the experiments of Weyl[1] and his co-workers and of Berthelot,[1] it is not clear but what sodium hydroxide might be used to replace potassium hydroxide in the preparation of alkaline pyrogallol, a substitution that would result in a material decrease in the cost of the reagent. Accordingly, a solution was prepared by dissolving 5 g. of pyrogallol in 50 cc. of a solution of sodium hydroxide of 1.475 specific gravity prepared by dissolving 87.5 g. of stick sodium hydroxide in 900 cc. of water: 25 cc. of this reagent was transferred to a Hempel pipette for use with mercury and it was then treated with a 100 cc. sample of air. It was found that the absorption at the end of 3-minute shaking amounted to only 10 per cent, but at the end of 12 minutes absorption was complete. From this experiment it seems that such a reagent would scarcely be satisfactory for general use as an absorbent for oxygen.

### SUMMARY

I—After a consideration of the various factors that determine the desirability of a solution of alkaline pyrogallol for general use, it was decided that the solution prepared by dissolving 15 g. of pyrogallol in 100 cc. of a solution of potassium hydroxide of specific gravity 1.55 is the most desirable. For the preparation of this solution of alkali there is needed from 1.5 to 2 parts of potassium hydroxide in stick form to 1 part of water, the amount depending upon the water content of the preparation. The volume of reagent that is obtained is about 110 cc. and there are thus 13.6 g. of pyrogallol and 71.5 g. of potassium hydroxide to 100 cc. of solution. If any carbon monoxide is formed, the amount is too small to have any bearing upon the use of the reagent for technical purposes.

II—Different values of the specific absorption of this reagent for different conditions are given in round numbers in the following tabulation. It is understood that the temperature of the reagent was between 20–24° C., that the method of shaking previously described was closely followed, that the initial volume of the gas sample was always 100 cc., and that the volume of the reagent was 25 cc. for the first pipette and 185 for the second.

| Specific Absorption in Hempel Pipette for Use with Mercury | | | | |
|---|---|---|---|---|
| No. of Minutes Samples were Shaken | 1 | 2 | 3 | 4 |
| (*a*) For gas samples containing 20.9 per cent oxygen | 27 | 30 | 31 | |
| (*b*) For gas samples containing about 90.0 per cent oxygen | 21 | 24 | 24 | |

| Specific Absorption in Hempel Double Pipette for Liquid Reagents | | | | | |
|---|---|---|---|---|---|
| (*a*) For gas samples containing 20.9 per cent oxygen | 25 | 29 | 31 | | |
| (*b*) For gas samples containing about 90.0 per cent oxygen | 0 | 27 | 30 | 31 | 32 |

In the application of these figures to routine gas analyses, the conditions that have been specified should be followed accurately, otherwise proper allowance should be made for any deviation. Probably the greater portion of the samples that are analyzed for oxygen contain less than 20.9 per cent of it, and the specific absorptions for samples of this composition are applicable to all samples containing less oxygen.

[1] *Loc. cit.*

The specific absorption for samples containing 90.0 per cent oxygen are applicable to all samples containing less than this amount of oxygen and probably are applicable, for all practical purposes, to the analysis of nearly pure oxygen. Due allowance should be made in the use of solutions that are nearly exhausted if they are not used frequently, or if they have previously been employed at temperatures considerably above 24° C.

III—The objection to the use of potassium hydroxide purified by alcohol does not appear to be valid.

IV—The substitution of sodium hydroxide for potassium hydroxide is not practicable.

Determinations of the specific absorption of the proposed reagent in some of the other forms of absorbing apparatus are being made at the present time and it is planned to present the results that are obtained as a subsequent article of this series.

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## THE INDICATOR IN PYROLIGNEOUS ACID

By J. M. JOHLIN

Received April 26, 1915

The fact that pyroligneous acid contains its own indicator has long been a well-known fact employed in the wood distillation industries, and was recently referred to in THIS JOURNAL.[1] There seems to be no theory or explanation offered in the literature regarding the nature of the indicator which, when the neutral point is reached, turns pyroligneous acid "a pronounced wine-red."

The author has observed that when milk of lime prepared from chemically pure lime is added to pyroligneous acid this color reaction does not take place. It seemed evident then that this reaction must be due to impurities in the lime as well as in the pyroligneous acid. Trial experiments showed that milk of lime, to which traces of ferric salts had been added, gave with pyroligneous acid the color reactions noted.

The color thus produced is not unlike that caused by the addition of ferric salts to solutions containing tannins. Tests showed that tannins, gallic acid and pyrogallic acid dissolved in dilute acetic acid produced, with milk of lime containing traces of iron salts, color reactions comparable to those produced between pyroligneous acid and the same sample of milk of lime.

Since tannins are nonvolatile and cannot be distilled it does not seem likely that any of these should be found in pyroligneous acid. Pyrogallic acid boils close to 300° and is not volatile with steam. It is not probable then that this compound should be present in redistilled pyroligneous acid.

Guaiacol and its homologues, methyl-, ethyl-, and propyl-guaiacol have been found[2] present among the products of destructively distilled wood. Tests made with guaiacol and milk of lime containing iron failed to give any color reactions, though the same sample of milk of lime gave decided color reactions with pyroligneous acid. Guaiacol or its homologues should not then be held accountable as the indicator present in pyroligneous acid.

The ethers of pyrogallic acid as well as those of its homologues, methyl-, and propyl-pyrogallic acid have been found[1] by Hofmann to be present in wood tar. As a rule these are compounds which are readily volatile with steam and give color reactions with ferric salts similar to those referred to. Many of these ethers have been synthetically prepared and similar color reactions were noted. The author has synthetically prepared the dimethyl ether of pyrogallic acid and found that even minute traces of this ether dissolved in water gave with milk of lime, known to contain iron, color reactions comparable to those obtained with pyroligneous acid.

It seems not at all improbable then that the indicator present in pyroligneous acid consists of the volatile ethers of pyrogallic acid and its homologues.

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## ON THE KAMBARA EARTH AND ITS BLEACHING ACTION ON OILS

By SEIICHI UENO

Received January 4, 1915

Kambara earth is called "acid earth" or "acid clay" in Japan and is widely used in oil factories as the bleaching and refining agent of mineral and fatty oils. On account of the simplicity of the decolorizing method and the cheapness of the works, this use of the earth has greatly increased. This earth was recently studied by K. Kobayashi[2] but, as far as I know, no reports on the bleaching action of the earth on fatty oils have been published.

### OCCURRENCE, PRODUCTION, MINING AND PREPARATION

The so-called "Kambara" and similar earths are widely distributed in Japan. Although the acidic earths occur in several localities, the most effective material for the bleaching and refining of oils is found at Kawahigashi village, Kitakambara district, Echigo province. Kawahigashi is an inland village situated 7 miles southeast of the town Shibata.

The strata of the earth mine are brownish orange, light yellow and bluish green. The earth is worked much the same as any clay bank: first about 2 to 3 ft. of the surface must be removed with pick and shovel, then the earth is dug in much the same manner.

The massive earth is brought to a small factory by hand-cars and is crushed into fist-sized lumps that are then dried in a flat, iron pan with direct fire and ground to bean-sized grains, causing the loss of about 40 per cent in weight on account of the evaporation of water. The dried earth is brought to a water-mill barn where it is ground to very fine powder and passed through a silk sieve. The powdered and refined earth is put in a paper sack covered with a straw bag. The weight of a bag is 20 Kwan (165.6 lbs.) and the earth factory can produce 130 bags per day. One bag of earth costs about $0.50 net.

### PROPERTIES AND COMPOSITIONS OF THE EARTHS

The factory does not sort the earths according to

[1] THIS JOURNAL, 7 (1915), 47.
[2] Cf. Beilstein, "Organische Chemie."

[1] Cf. Beilstein, "Organische Chemie."
[2] THIS JOURNAL, 4 (1912), 891.

color, so that the commercial Kambara earth is a mixture of the three kinds described above. An acidic earth is also found in the province of Iga. This earth is used to bleach oils in the vicinity, but its bleaching power is not as great as that of the Kambara earth. Analyses of these earths appear in Table I.

TABLE I—ANALYSES OF BLEACHING EARTHS

| | Three Varieties of Kambara Earth | | | Iga Earth |
|---|---|---|---|---|
| Per cent | Bluish green | Brownish orange | Light yellow | |
| $SiO_2$ | 70.99 | 68.42 | 63.76 | 49.90 |
| $Fe_2O_3$ | 2.86 | 4.48 | 2.27 | 4.89 |
| $Al_2O_3$ | 15.76 | 15.36 | 14.33 | 19.83 |
| MnO | .... | 1.07 | | |
| CaO | 1.82 | 1.27 | 1.54 | 0.84 |
| MgO | 2.38 | 2.38 | 2.28 | 3.08 |
| $Na_2O$ | 0.43 | 0.38 | 0.29 | 0.40 |
| $K_2O$ | 0.12 | 0.10 | 0.14 | 0.27 |
| Ignition loss | 5.75 | 6.57 | 15.55 | 20.97 |
| Total | 100.07 | 100.03 | 100.16 | 100.19 |

The Kambara earth is an amorphous and slightly plastic substance and gives an acidic reaction to litmus paper. It is useful not only for oil bleaching and refining purposes, but may also be used instead of kieselguhr as a carrier for nickel catalysts in the oil-hardening industry.

## BLEACHING ACTION OF THE KAMBARA EARTH

### 1—EXPERIMENTS ON THE BLEACHING OF FATTY OILS

The method used in treating oils in the following experiments consisted essentially in heating a mixture of oil and earth. The bleaching actions of the various earths were tested by weighing accurately into porcelain basins, 1, 2.5, and 5 g. of each dried earth: 100 g. of crude rape-seed oil (A) were then run into each basin. Each mixture was heated on the sand bath a few

TABLE II—BLEACHING ACTION OF VARIOUS EARTHS

Color of original rape-seed oil (A), red 2.00, yellow 65.10

| Sample No. | (1) | | (2) | | (3) | |
|---|---|---|---|---|---|---|
| Weight of Earth Used | 1 gram | | 2.5 grams | | 5 grams | |
| | Red | Yellow | Red | Yellow | Red | Yellow |
| Light yellow earth | 1.05 | 26.2 | 0.60 | 5.20 | 0.07 | 1.40 |
| Brownish orange earth | 1.00 | 12.05 | 0.70 | 5.20 | 0.34 | 2.50 |
| Pale bluish green earth | 1.65 | 26.00 | 0.70 | 5.50 | 0.04 | 1.40 |
| Commercial earth | 0.52 | 4.70 | 0.40 | 2.30 | 0.04 | 1.65 |

minutes, keeping the mass well stirred. When the decolorization was thought to be complete, the contents were allowed to cool a little and then the oil was immediately poured onto a filter paper, to remove the spent earth. The bleached oils were then compared by means of a J. W. Lovibond Tintometer through a 5 mm. thickness of oil.

From Table II it was concluded that the three colors of the earth could not be distinguished by their bleaching actions; indeed, the three earths when dried and powdered are similar in color and appearance.

When the earth is mixed with oils and warmed, its color is changed from brownish black to deep black, due to the absorption, or adsorption, of the coloring matters of the oils.

The earth which had been used to bleach the oils, was termed "spent residual earth." The spent residual earth was filtered and washed with ether three times and then dried. The colors of these residual earths were compared, with the results shown in Table III.

TABLE III COLORS OF SPENT RESIDUAL EARTHS

| Kind of Original Earth | Number (1) | | Number (2) | | Number (3) | |
|---|---|---|---|---|---|---|
| | Wet state | Dry state | Wet state | Dry state | Wet state | Dry state |
| Light yellow | Dark brown | Light brown | Dark brown | Dark brown | Dark brown | Reddish brown |
| Brownish orange | Black-brown | Dark brown | Black-brown | Dark brown | Black-brown | Black-brown |
| Pale bluish green | Black-brown | Brownish yellow | Black-brown | Brownish brown | Black-brown | Brown |
| Commercial | Dark brown | Light brown | Dark brown | Dark brown | Dark brown | Reddish brown |

The color of the spent residual earth is related to the degree of oil-bleaching of the originally used earth, and the more deeply colored earth served as a bleaching agent more effectively than the lighter colored earth. The brownish bleached better than the greenish, so that one can easily foretell the bleaching properties of an unknown earth and also distinguish the end point of the bleaching action.

### 2—RELATION BETWEEN TIME AND TEMPERATURE OF TREATMENT

Attempts were made to find the general relation between the temperature and time of treatment. When the earth is mixed with rape-seed oil (A), at ordinary temperature, it soon absorbs or adsorbs the color of the oil and becomes dark brown. As a test 40 g. of rape-seed oil (A), mixed with 5 per cent (by weight) of the earth, were gently heated on the sand bath with continuous stirring, kept at 150°–160° C. for the intervals of time noted and compared with the color of the bleached oils, with the results shown in Table IV.

TABLE IV—EFFECT OF TIME ON BLEACHING OF RAPE-SEED OIL

| | Red | Yellow |
|---|---|---|
| Original rape-seed oil (A) | 2.00 | 65.10 |
| Heated to 160° C. | 0.04 | 1.40 |
| After standing 5 minutes | 0.17 | 1.90 |
| After standing 10 minutes | 0.24 | 2.20 |
| After standing 30 minutes | 0.40 | 3.40 |
| After standing 60 minutes | 0.58 | 4.80 |

Also, soya bean oil was mixed and treated as indicated in Table V, with the results there given

TABLE V—EFFECT OF TIME AND TEMPERATURE ON BLEACHING OF SOYA BEAN OIL

| Temperature ° C. | Time (Min.) | Bleached oil | | Spent residual earth (Dry state) |
|---|---|---|---|---|
| | | Red | Yellow | |
| 22 | 30 | 1.35 | 39.66 | Light bluish yellow |
| 60 | 1 | 1.65 | 48.20 | Brown |
| 85-90 | 1 | 0.76 | 31.50 | Light brownish yellow |
| 92 | 1 | 1.65 | 29.00 | Dark bluish brown |
| 92–94 | 60 | 0.58 | 6.00 | Light brownish yellow |
| 92–94 | 150 | 0.52 | 3.90 | Light brownish yellow |
| 110 | 14 | 0.84 | 20.00 | Light brownish yellow |
| 110 | 30 | 0.70 | 9.60 | Brownish yellow |
| 110 | 60 | 0.50 | 7.00 | Brown |
| 130 | 1 | 0.52 | 5.00 | Brown |
| 130 | 60 | 0.38 | 3.60 | Brown |
| 140 | 1 | 0.09 | 1.65 | Brown |
| 150–160 | 10 | 0.18 | 1.95 | Brown |
| 150–160 | 30 | 0.38 | 2.60 | Brown |
| 170–180 | 10 | 0.38 | 2.45 | Dark brown |
| 190–200 | 10 | 0.40 | 3.05 | Dark brown |
| 200–210 | 10 | 0.70 | 4.70 | Dark brown |

which indicate that the oil-bleaching action of the earth increases, with rise of temperature, to a maximum at about 140° C. and then gradually decreases. The bleaching action increased with the time for temperatures under 130° C. but decreased for temperatures above about 150° C. The optimum temperature varied according to the kind of oils and fats; drying oils, fish oils, etc., were bleached, generally, at lower temperatures than soya bean oil.

### 3—INFLUENCE OF ATMOSPHERIC GASES

In the apparatus shown in Fig. 1, 100 grams of oil in A were mixed with 5 per cent of the earth and violently agitated; the gas, kept at the required temperature, passed through the oil for about 15 minutes. The results obtained appear in Table VI and show that air,

especially oxygen, injures the color of oil; carbon dioxide affects it but little and hydrogen appears to help the bleaching action. It is easily seen at the same

TABLE VI

| Temp °C | Soya Bean Oil—R = 1.95 and Y = 22.59 Air R | Y | Hydrogen R | Y | Carbon dioxide R | Y | Rape Oil R = 1.65 Y = 53.20 Hydrogen R | Y |
|---|---|---|---|---|---|---|---|---|
| 120 | | | | | 0.30 | 3.01 | | |
| 140 | 0.31 | 1.60 | 0.12 | 1.30 | 0.21 | 2.60 | 0.01 | 0.33 |
| 150 | | | | | | | 0.07 | 0.37 |
| 160 | | | 0.13 | 1.56 | 0.15 | 1.65 | 0.03 | 0.36 |
| 170 | | | | | | | 0.02 | 0.34 |
| 180 | | | 0.15 | 1.45 | 0.13 | 1.43 | 0.01 | 0.32 |
| 190 | | | | | | | 0.04 | 0.38 |
| 200 | | | 0.15 | 1.55 | 0.11 | 1.30 | 0.05 | 0.42 |
| 220 | | | 0.10 | 1.10 | 0.13 | 1.40 | | |

time that the bleaching action of the earth is not influenced very much by the factors of time and temperature, in the currents of inactive and reducing gases.

### 4—BLEACHING ACTION ON VARIOUS OILS

Table VII shows some interesting comparisons of the bleaching action of the earth on various oils. It appears that the degree of the bleaching action of the earth depends upon the properties and compositions of the oils and also upon the impurities in the oils; nitrogenous matter, mucilage, etc., hinder the bleaching action of the earth.

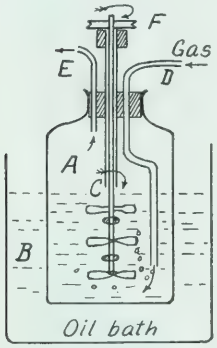

FIG. 1

It has been pointed out by others that the earth bleaching method does not give such good results with chrysalis, rice and soy oils,[1] since these oils contain large quantities of impurities, but they too can be well bleached by the earth method, after the removal of impurities with suitable chemicals.

### 5—PROPERTIES OF BLEACHED OILS

The well bleached oil is nearly colorless. With regard to the chemical characteristics of the bleached oils, according to a number of my experiments, the values are not essentially different from those of the

TABLE VII—ACTION OF 5 PER CENT OF KAMBARA EARTH ON VARIOUS OILS AT 150° C

| Kind of Oil | Tint of original oil R | Y | Tint of bleached oil R | Y | Ratio of original color to bleached color R | Y | Color of residual earth (wet) |
|---|---|---|---|---|---|---|---|
| Perilla | 1.3 | 16.2 | 1.05 | 5.67 | 1.24 | 2.86 | Black-brown |
| Linseed | 1.0 | 6.00 | 0.12 | 2.50 | 8.28 | 2.40 | Brownish black |
| Soya bean | 3.20 | 48.5 | 0.51 | 3.00 | 6.28 | 16.17 | Black-brown |
| Rape seed (A) | 2.00 | 65.10 | 0.04 | 1.40 | 50.0 | 46.6 | Black-brown |
| Rape seed (B) | 2.60 | 68.5 | 0.08 | 1.50 | 32.6 | 45.7 | Black-brown |
| Rape seed (treated at 140° C.) | 2.60 | 68.5 | 0.04 | 1.30 | 65.2 | 52.6 | Black-brown |
| Apricot kernel | 0.38 | 1.68 | 0.10 | 0.07 | 3.8 | 24.0 | Dark brown |
| Tsubaki | 0.00 | 0.40 | 0.00 | 0.08 | | 5.0 | Brown |
| Tsubaki (commercial) | 0.10 | 2.80 | 0.00 | 0.20 | | 14.0 | Brown |
| Sardine | 8.2 | 39.8 | 4.7 | 37.0 | 1.74 | 1.65 | Black-brown |
| Machine (mineral) | 29.0 | 12.0 | 19.0 | 30.8 | 1.52 | More colored | Brownish black |
| Engine (2 samples) | Deep brown | | Almost unbleached | | | | Deep black |
| Crude glycerine | Black | | Almost unbleached | | | | Brownish black |
| Olein | Dark brown | | Almost unbleached | | | | Brownish black |

original oils. On account of their harmless effect on nickel catalyzer, oils bleached by the earth method can be recommended for use as the raw materials in oil-hardening plants.

### 6—INFLUENCE OF WATER

The influence of water on the bleaching action of Kambara earth was determined by mixing water with 5 grams of the earth, adding 100 grams of rape oil (B) and treating at 140° C. for a definite number of minutes.

TABLE VIII EFFECT OF WATER ON BLEACHING ACTION

| Per cent water added | | 5 | 10 | 25 | 50 | 100 | 200 |
|---|---|---|---|---|---|---|---|
| Tint of bleached oil | R | 0.32 | 0.38 | 0.50 | 1.65 | 2.10 | 2.10 |
| | Y | 2.80 | 2.90 | 7.00 | 45.70 | 49.50 | 66.50 |

Table VIII shows that the presence of water affects the bleaching action of the earth. It was also found that the bleaching power decreased with the moisture content of the earth. It is very important, therefore, in oil bleaching, to have the earth completely dry.

### 7—INFLUENCE OF ACIDS AND ALKALIES

ACIDS—The effects of hydrochloric, phosphoric and three organic acids on the bleaching action of Kambara earth were studied by means of the experiments outlined in Table IX. From these and previous results it is evident that the presence of strong inorganic acids

TABLE IX EFFECT OF ACIDS ON BLEACHING OF RAPE OIL (B)

Treatments of 100 grams of Oil at 140° C. as described in Section I

| Earth Used | Acid Used | Bleached oil R | Y | Color of spent Residual earth |
|---|---|---|---|---|
| 50 grams (*a*) | HCl (sp. gr. 1.2) (*a*) | 0.58 | 3.60 | ... |
| 20 grams | 2 cc. HCl (sp. gr. 1.2) | 1.35 | 4.2 | ..... |
| 5 grams | 2 cc $H_3PO_4$ (sp. gr. 1.7) | 0.34 | 3.60 | ... |
| 50 per cent of acid mixed with the earth | Glacial acetic | 0.28 | 1.85 | Black brown |
| | Oxalic | 0.26 | 1.85 | Black brown |
| | Stearic | 0.28 | 1.95 | Brownish black |

(*a*) Fifty grams of the earth and 50 cc of concentrated hydrochloric acid (sp. gr. 1.2) were mixed, evaporated on the sand bath, powdered, and sieved. Then 50 grams of this prepared earth were added to 100 grams of rape oil (B) and treated at 140° C. as above.

decreases the bleaching action of the earth, but that weak acid, such as phosphoric, does not affect it. The presence of 50 per cent of organic acid in the oil does not affect the bleaching power.

ALKALIES—It has been pointed out by other authors that the bleaching action of fuller's earth is affected by a previous treatment with alkalies, but no statement is found with regard to the action of alkalies on the Kambara earth; this was accordingly tested as follows:

(*a*) A 5-gram portion of the earth, 10 cc. of $N/5$ sodium carbonate solution and a suitable quantity of water were mixed into a paste in a porcelain dish. The pasty mass was evaporated on a water bath and the dried earth well sieved.

(*b*) A second portion of earth was mixed with 2 grams of calcium hydroxide and water and after evaporation, the dried mass was powdered.

(*c*) A third portion of earth was mixed with a dilute sodium hydroxide solution, boiled and filtered; then washed with hot water, dried on a sand bath and powdered.

Five-gram portions of each of the above specially treated earths were then added to 100-gram portions

[1] Soy oil is a by product of Soy making in Japan and is called "*Shoyu oil*." It is of almost no value.

of oil and treated at 140° C. The results, given in Table X, show that alkalies decrease the bleaching action of Kambara earth considerably.

TABLE X—ACTION OF ALKALIES ON BLEACHING POWER OF KAMBARA EARTH

| Earth treated with | Oil used | Tint of bleached oil R | Y |
|---|---|---|---|
| $Na_2CO_3$ | Rape oil (B) | 1.00 | 19.50 |
| $Ca(OH)_2$ | Rape oil (B) | 0.64 | 9.00 |
| NaOH solution | Soya oil | 1.55 | 30.80 |
| (Original tint of Soya oil) | | 1.95 | 23.50 |

8—EARTH TREATED AT HIGH TEMPERATURE

Portions of Kambara earth were heated to the temperatures indicated in Table XI: 5-gram samples of this heated earth were mixed with 100 grams of rape oil (B) and the bleaching action tested with the results given.

TABLE XI

| Temperature to which earth had been heated | Bleached oil R | Y |
|---|---|---|
| 300° C. | 0.34 | 2.50 |
| 400° C. | 0.40 | 2.90 |
| About 600° C. | 0.54 | 3.00 |
| Dull red heat | 0.64 | 3.10 |
| Bright red heat | 1.64 | 21.65 |
| Ordinary earth | 0.08 | 1.50 |

The earths which were heated to a high temperature, still turned the blue litmus paper to red. On reference to Table XI it will be seen that the earth which was heated to a very high temperature lost its bleaching power considerably, notwithstanding its acidic behavior to litmus paper. According to this fact, the bleaching action may not be derived from the acidic property of the earth. This statement is further corroborated by facts reported below.

9—THE RELATION BETWEEN THE NUMBER OF TREATMENTS AND THE COLOR OF THE BLEACHED OILS

(*a*) A 100-gram sample of oil was given two treatments with 5-gram portions of earth.

(*b*) A 100-gram sample of oil was given three successive treatments with 2.5-gram portions of earth and a final 5-gram treatment.

TABLE XII—EFFECT OF NUMBER OF TREATMENTS ON RAPE OIL (B)

| Treatment number | Grams of earth used | Bleached oil R | Y |
|---|---|---|---|
| 1*a* | 5.0 | 0.04 | 1.30 |
| 1*b* | 5.0 | 0.02 | 1.30 |
| 2*a* | 2.5 | 0.40 | 2.30 |
| 2*b* | 2.5 | 0.30 | 2.10 |
| 2*c* | 2.5 | 0.28 | 1.70 |
| 2*d* | 5.0 | 0.04 | 1.05 |

The results of these tests, as given in Table XII, show the ineffectiveness of repeated treatments in comparison with the amount of labor required.

10—PROPERTIES OF SPENT RESIDUAL EARTH

The spent residual earth has an acid reaction to litmus paper: it is a brownish black to black muddy substance in the wet state in oil, and in such condition does not decolorize oil appreciably. For example, 10 grams of the spent residual earth (calculated to the oil-free basis) mixed with 100 grams of rape oil (B) and treated gave an oil reading R 2.60, Y 68.50.

After the oil had been extracted from the spent residual earth with solvent, and the earth dried and powdered, rape oil (B) was bleached by the treatment of 5 per cent of this spent earth to R 1.55, Y 30.63.

Next the following experiments were tried:

(*a*) Rape oil (B) was bleached by adding 10 per cent of the earth. Result: R 0.10, Y 2.10.

(*b*) The residual earth of (*a*) washed with solvent, added to 100 grams of rape oil and treated. Result: R 0.38, Y 2.80.

(*c*) The residual earth of (*b*) washed with solvent, added to 100 grams of rape oil and treated. Result: R 0.72, Y 3.90.

It will be seen from the experimental results that the spent residual earth mixed with oil has no bleaching power on oils, but if it is washed with solvent and the absorbed oil removed, the bleaching property is recovered to a considerable extent.

11—FRACTIONAL DIFFUSION OF OILS AND FATTY ACIDS BY TREATING WITH THE EARTH

(*a*) Experiments were made on linseed oil. Although carried out with care, these experiments gave only negative results.

(*b*) Experiments on the fatty acids of linseed oil were made by taking up 100 cc. of the mixed fatty acids obtained from linseed oil, into a tap funnel, as shown in Fig. 2, and filtering in a steam oven in a current of hydrogen.

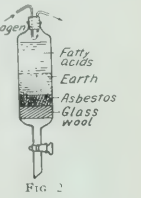

FIG 2

This experiment, however, was probably not an entirely satisfactory one, since it is difficult to prevent the oxidation and polymerization of higher unsaturated fatty acids at the somewhat high temperature. But it appears that the fatty acids have been fractionally diffused by treating with the Kambara earth, in some portion.

TABLE XIII

Each 10 cc. of the fractional filtrate were taken and iodine value and refractive index determined.

| | Iodine No. (Wijs) | $n_D$ 20° (Zeiss butyro-refractometer) |
|---|---|---|
| 1st filtrate | 188.73 | 72 |
| 2nd filtrate | 189.90 | 71 |
| 3rd filtrate | 186.20 | 71 |
| 4th filtrate | 180.27 | 75 |
| Original fatty acids | 191.67 | 70 |

12—ACTION FOR SOME ORGANIC COLORING MATTERS

METHYL VIOLET—2 grams of the earth were mixed with an alcoholic solution of methyl violet (R 49.5, Y 30.6) shaken, allowed to settle and filtered.

TABLE XIV—EFFECT OF VARIOUS EARTHS ON METHYL VIOLET

| Kinds of Earth | Solution of filtrate Cc. | R | Y | Color of adsorbed earth washed with alcohol: Wet | Dried in air | Dried in a steam oven |
|---|---|---|---|---|---|---|
| Kambara | 20 | 20.0 | 10.4 | Beautiful purple | | Beautiful purplish blue |
| Kambara | 10 | 3.3 | 3.3 | | | |
| Sample of Echigo | 10 | 15.0 | 8.4 | | | |
| Iga | 10 | 33.5 | 14.0 | Violet | Green | Deep green |
| Bitchu, red. | 10 | 36.5 | 17.0 | Violet | Grayish violet | Light greenish blue |
| Bitchu, yellow | 10 | 18.5 | 2.7 | | | Light purplish blue |

Methyl violet solution is green with inorganic acids and blue with very weak acids. It is a curious thing that the Bitchu and Iga earths which have the weak bleaching power on oil, turn green, and a sample of Echigo earth, which has no acidic property, is similar to the Kambara earth in respect to coloration.

ALKALI-BLUE—The Kambara earth absorbs alkali-blue and turns to violet-blue. The solution is almost decolorized. When the colored earth is washed with alcohol several times the alcohol dissolves some of

the absorbed color. The color of the dry colored earth is not altered by mixing with linseed oil, but the drying property of the oil is decreased.

METHYL ORANGE—A dilute solution is almost decolorized by an earth and the earths themselves change color as follows:

| | |
|---|---|
| Kambara earth | Pink |
| Iga, Echigo, Bitchu | Brown to reddish brown |

A concentrated solution changes all the earths to orange-red.

CRUDE CHLOROPHYLL—Crude chlorophyll solution is prepared by extracting green leaves with ether and mixing with bleached rape oil (R 0.0, Y 0.42) and the tint of the solution is R 0.74, Y 20.42, B 0.16. Five grams of the earth were mixed with 100 grams of the chlorophyll oil solution, treated at 110° C., filtered, cooled; the result was R 0.70, Y 4.5, B 0.00.

ALCOHOLIC SOLUTION OF CRUDE CHLOROPHYLL (Y 2.3, B 0.86)—100 grams of the chlorophyll solution were mixed with 5 grams of the earth and treated at 22° C., 10 minutes; the result was Y 1.75, B 0.16.

AN OIL DYESTUFF GREEN CORI BASE (Y 1.0, B 3.1) was dissolved in bleached rape oil, treated with 5 per cent of the earth at a temperature of 22° C. for 10 minutes: the result was Y 1.75, B 0.10.

It appears that the bleaching action of the earth is not similar in the cases of the oil dyes and the dyestuff solutions tested. Although the earth has an effective bleaching power on a dyestuff solution, it did not bleach the oil so effectively.

### 13—A COLOR REACTION ON COD LIVER OIL

A few grams of the earth were mixed with cod liver oil in a test tube and then shaken: the earth became a beautiful bluish green color. The coloration seems due to the presence of coloring principles in the oil and is a very characteristic one. According to my experiments most other oils have not such a coloration, so that this coloration would seem applicable to the detection of cod liver oil.

### SUMMARY AND CONCLUSIONS

The foregoing investigations seem to have established the following conclusions:

1—The Kambara earth has a remarkable bleaching action on fatty oils.

2—The bleaching action of the earth is affected by the presence of impurities in oils.

3—The bleaching power of the earth on oils varies with the time and temperature of the treatments. At low temperatures the longer treatment is more effective than the shorter. In the case of high temperatures, shorter treatment is better than longer.

4—The presence of air while the oil is under treatment influences the color of the bleached oil.

5—Contact with hydrogen or carbon dioxide while the oil is undergoing treatment does not lessen the bleaching power of the earth.

6—In the current of hydrogen or carbon dioxide gas, the bleached oil is very little affected by time and temperature.

7—The presence of free water with the earth seriously decreases its bleaching power.

8—The presence of strong inorganic acid with the earth lessens the bleaching power, but phosphoric acid does not affect it.

9—The bleaching power of the earth is greatly decreased by the presence of alkalies.

10—Kambara earth heated to dull redness loses some of its bleaching power. Earth heated to a bright red condition loses its bleaching power entirely.

11—The acid value and other chemical characteristics of the bleached oil are not different from those of the original oil.

12—Oil bleached by the earth method is a desirable raw material for the manufacture of hardened oil.

13—The color of the spent residual earth depends upon the degree of bleaching accomplished.

14—Spent residual earths have no bleaching power, but if well washed with solvent, they bleach oil effectively. Well washed spent residual earth has an acidic reaction to litmus paper.

15—When Kambara earth is mixed with cod liver oil, the earth soon assumes a beautiful bluish green color. This coloration appears to be applicable for the detection of cod liver oil.

The author's best thanks are due to Mr. M. Tsujimoto, for kind advice in connection with the work reported in this article.

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## THE DETERMINATION OF SULFATES IN WATER BY BENZIDINE HYDROCHLORIDE

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Benzidine hydrochloride was first used in the determination of sulfates by Raschig[1] who thoroughly developed the technic of the method for its use in coal analysis. Friedham and Nydegger[2] investigated the errors in the method with some thoroughness and concluded that the method was quite as accurate for determining soluble sulfates as the quick precipitation by means of barium chloride. Jacobson,[3] in a search for a rapid method for sulfates in connection with the control of water softening, was the first to use the method in water analysis. His conclusions were that the method was quite accurate enough for rapid boiler water analysis. His data, however, are meager, the results of only six determinations being given with an error of 8 per cent on an average of 135 parts per million of $SO_4$. With the idea in mind of further investigating the method and obtaining more data on its use in water analysis, this work was undertaken.

The method consists in precipitating the sulfate by means of benzidine hydrochloride, as benzidine sulfate, which, being insoluble in water, is filtered off suspended in water and titrated in the hot with standard alkali, using phenolphthalein as indicator. This titration is rendered possible by the very weak basic properties of benzidine.

[1] *Z. angew. Chem.*, **1903**, pp. 617, 818.
[2] *Ibid.*, **1907**, p. 9
[3] Illinois Water Survey, *Bull.* **8** 1911, p. 11.

The method of procedure at first used was the same as that employed by Jacobson. To 250 cc. of the water to be tested, 150 cc. of the benzidine hydrochloride solution (2 grams benzidine per liter) were added. The solution was stirred, allowed to settle, filtered rapidly by means of suction, and washed with about 25 cc. of water. The precipitate was returned to the beaker and water added; the mixture was heated to boiling and titrated with 0.05 *N* NaOH, using phenolphthalein as the indicator. Rapid filtration was best accomplished by filtering on a disc of filter paper (preferably Schleicher-Schüll No. 589) placed in a Gooch crucible and protected by a Witt plate.

The influence of concentration of benzidine hydrochloride was first determined. For this work a 0.10 *N* solution of sodium sulfate was used, being prepared by exactly neutralizing a given quantity of 0.2 *N* sulfuric acid with 0.2 *N* sodium hydroxide. Suitable portions of this solution were diluted with distilled water to give five solutions containing the specified amounts of $SO_4$. Using a variable excess of benzidine hydrochloride, a series of sulfate determinations were made on each of the above solutions, 250 cc. being taken for each determination. Table I contains the average of three determinations in each series. Judging from these results, an excess of not less than 25 per cent of benzidine hydrochloride appears satisfactory in obtaining a complete precipitation.

TABLE I EXCESS OF BENZIDINE HYDROCHLORIDE REQUIRED

Total volume, 500 cc., benzidine hydrochloride, 2 g. per liter.

| Excess benzidine hydrochloride | Parts per million $SO_4$ | | | | |
|---|---|---|---|---|---|
| Per cent | | | Present | | |
| 0 | 48 | 96 | 192 | 384 | 480 |
| | | | Found | | |
| 10 | 26 | 80 | 180 | 300 | 400 |
| 15 | 38 | 88 | 186 | 375 | 460 |
| 25 | 48 | 96 | 192 | 384 | 480 |
| 35 | 48 | 96 | 192 | 384 | 480 |
| 45 | 48 | 96 | 192 | 384 | 480 |
| 60 | 48 | 96 | 192 | 384 | 480 |

With the idea of reducing the volume of liquid to be filtered, a stronger solution of benzidine hydrochloride (8 g. benzidine per liter) was tried with the results as shown in Table II.

TABLE II SULFATE IN SODIUM SULFATE BY MEANS OF BENZIDINE HYDROCHLORIDE

Benzidine hydrochloride, 8 g. per l. 30 per cent excess used in each determination. Total volume, 300 cc.

| Parts per million $SO_4$ | | | Parts per million $SO_4$ | | | Parts per million $SO_4$ | | |
|---|---|---|---|---|---|---|---|---|
| Present | Found | Error | Present | Found | Error | Present | Found | Error |
| 10 | 10.0 | 0.00 | 100 | 100.2 | +0.20 | 300 | 298.0 | −0.70 |
| 30 | 30.0 | 0.00 | 150 | 150.1 | +0.01 | 350 | 351.0 | +0.30 |
| 50 | 50.0 | 0.00 | 200 | 199.8 | 0.10 | 400 | 401.0 | +0.25 |

The results seem to be quite as accurate as those obtained with the weaker solution, so that in all of the subsequent work the stronger solution of benzidine hydrochloride was used.

For the purpose of investigating the adaptability and accuracy of the method in determining sulfates in natural waters, the method was used in parallel with the quick precipitation of sulfates by barium chloride on about 100 waters of varying composition.

The procedure with benzidine hydrochloride was the same as previously outlined with the exception that the strong benzidine hydrochloride solution (8 g. benzidine per liter) was used, and that 10 cc. of a 1 per cent hydroxylamine hydrochloride solution was added in those waters that contained ferric iron. Ferric iron, as pointed out by Raschig,[1] reacts with the benzidine hydrochloride in such a manner as to give low results. Ferrous iron, however, does not have this disturbing influence. By using hydroxylamine hydrochloride the ferric iron present can be readily reduced to the ferrous condition. The hydroxylamine will not react with the benzidine hydrochloride.[2]

Using barium chloride, the procedure was as follows: 250 cc. of the water to be tested were evaporated to dryness in a casserole. The residue was moistened with 5 cc. of concentrated HCl, diluted with hot water and filtered. The filtrate was made up to 200 cc. and after heating to boiling 10 cc. of barium chloride (50 g. per liter) were added at once with vigorous stirring. After allowing the precipitate to settle over night, the $BaSO_4$ was filtered off on to a Gooch crucible, dried at 180° C., ignited 5 minutes on a Meker burner and weighed.

Table III contains a few typical results. The results obtained by both methods agree closely enough for all practical purposes. The benzidine hydrochloride method, however, has the advantage, since with it results can be had in 30 minutes while with the barium chloride method 6 hours and more, generally 12, are required.

TABLE III—COMPARISON OF RESULTS OBTAINED WITH BARIUM CHLORIDE AND WITH BENZIDINE

| Lab. No. | Parts per million $SO_4$ $BaCl_2$ | Benzidine | Diff. | Lab. No. | Parts per million $SO_4$ $BaCl_2$ | Benzidine | Diff |
|---|---|---|---|---|---|---|---|
| 6678 | 80.6 | 84.5 | +3.9 | 7084 | 343.9 | 341.5 | −2.4 |
| 6682 | 76.5 | 80.6 | +4.1 | 7087 | 101.2 | 107.5 | +6.3 |
| 6723 | 254.2 | 257.3 | +3.1 | 7114 | 51.0 | 46.0 | −5.0 |
| 6729 | 87.6 | 96.0 | +8.4 | 7128 | 19.8 | 15.4 | −4.4 |
| 6742 | 68.7 | 76.8 | +8.1 | 7139 | 38.8 | 38.4 | −0.4 |
| 6804 | 45.4 | 40.3 | −5.1 | 7142 | 24.7 | 19.2 | −5.5 |
| 6887 | 584.7 | 583.7 | −1.0 | 7144 | 48.0 | 46.0 | −2.0 |
| 6942 | 62.2 | 63.4 | +1.2 | 7148 | 16.2 | 21.0 | +4.8 |
| 7081 | 29.6 | 32.6 | +3.0 | 7155 | 26.3 | 25.0 | −1.3 |
| 7082 | 173.2 | 180.5 | +7.3 | 7156 | 51.8 | 63.4 | +1.6 |

Table IV contains a complete analysis of the waters used in Table III, and will give some idea of the character of the waters on which the method was used.

TABLE IV COMPOSITION OF WATER ANALYZED (PARTS PER MILLION)

| Lab. No | City | Total solids | Fe (ic) | Ca | Mg | Na | Cl | $HCO_3$ | $SO_4$ | $NO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 6678 | Atchison | 342 | 4.0 | 47.6 | 19.8 | ... | 10.0 | 119.5 | 80.6 | 0.5 |
| 6682 | Arkansas City | 800 | 0.3 | 116.9 | 20.3 | 207 | 240.0 | 268.0 | 76.5 | 2.0 |
| 6723 | Waldo | 873 | .. | ... | ... | ... | 4.4 | 307.8 | 254.2 | 1.5 |
| 6729 | Pittsburg | 329 | 5.0 | 66.5 | 2.0 | 141 | 88.0 | 330.0 | 87.6 | .. |
| 6742 | Hutchinson | 915 | 9.5 | 107.0 | 31.7 | 243 | 406.0 | 264.0 | 68.7 | 0.5 |
| 6804 | Osborne | 464 | 2.5 | 109.0 | 14.4 | 31 | 19.0 | 393.0 | 45.4 | 4.0 |
| 6887 | Washington | 1297 | 15.2 | 154.7 | 22.7 | ... | 44.0 | 266.0 | 584.7 | 1.0 |
| 6942 | St. Marys | 582 | 0.5 | 58.5 | 26.8 | 71 | 46.0 | 376.0 | 62.2 | 6.0 |
| 7081 | St. Francis | 268 | 1.4 | 56.7 | 9.1 | 28 | 30.0 | 224.5 | 29.5 | 1.2 |
| 7084 | Cimaron | 844 | .. | ... | ... | ... | 52.0 | 244.0 | 343.9 | 0.0 |
| 7087 | Mineral | 1005 | 1.0 | 61.3 | 32.2 | 273 | 344.0 | 391.0 | 101.2 | .. |
| 7114 | Winfield | 241 | 8.4 | 55.0 | 10.8 | ... | 20.0 | 176.0 | 51.0 | 0.5 |
| 7128 | Kanopolis | 301 | 1.0 | ... | .. | .. | 10.0 | 187.8 | 19.8 | 10.0 |
| 7139 | Junction City | 332 | 1.2 | 52.0 | 19.8 | 55 | 34.0 | 295.5 | 38.8 | 0.5 |
| 7142 | Ellis | 373 | 1.2 | 78.0 | 14.6 | 33 | 12.0 | 312.5 | 24.7 | 1.0 |
| 7144 | Turon | 803 | 1.0 | ... | .. | .... | 320.0 | 246.5 | 46.0 | 1.0 |
| 7148 | Neodesha | 184 | 1.2 | 59.0 | 13.0 | ... | 20.0 | 214.7 | 21.0 | 0.7 |
| 7155 | Abilene | 215 | 1.2 | 40.5 | 9.8 | 11 | 14.0 | 156.0 | 25.0 | 1.0 |
| 7156 | Blue Rapids | 394 | 1.2 | 37.0 | 23.0 | 72 | 18.0 | 330.0 | 63.4 | 0.7 |

For ordinary routine water analysis the following procedure is recommended: To 250 cc. of the water (less if the $SO_4$ content is greater than 500 parts per million) add 10 cc. of a 1 per cent solution of hydroxylamine hydrochloride (more if the iron content of the water is very high) and 20 cc. of benzidine hydrochloride. Stir vigorously and allow the silky white precipitate to settle. Filter on a disc of black ribbon

[1] *Loc. cit.*

[2] Raschig, *Loc. cit.*

filter paper in a Gooch crucible with suction. Wash twice with cold distilled water without allowing the precipitate to become dry. Transfer the precipitate to the original beaker, add water and heat to boiling. Titrate with 0.05*N* NaOH, using phenolphthalein as the indicator.

9.6 × cc. 0.05*N* NaOH = parts per million $SO_4$.

The benzidine hydrochloride solution is made up as follows: Place 8 g. of benzidine in an agate mortar and add enough water to make a paste. Wash the paste into a 1 liter flask, add 10 cc. concentrated HCl, and make up to the mark. Filter, if necessary. 1 cc. = 0.0026 g. $SO_4$.

### CONCLUSIONS

I—The benzidine hydrochloride method is applicable for the determination of sulfates in water.

II—The results with the use of benzidine hydrochloride compare favorably with those obtained with the use of barium chloride.

III—The benzidine hydrochloride method is much more rapid than the barium chloride method, for which reason it is very well adapted to routine water analysis.

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## EXAMINATION OF TOMATO PULP

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Tomato pulp is prepared in very large quantities for the manufacture of ketchup and pulp. While a considerable amount of pulp used for this purpose is made by the ketchup manufacturers, the preparation of pulp for sale as such has reached considerable proportions. There is also an increasing amount of this product placed on the market in small containers for household use in the preparation of soup.

While the greater part of the pulp placed on the market is made from whole tomatoes, there are a number of plants that manufacture pulp from trimming stock in connection with the canning of tomatoes. Since the latter product is given a lower grade commercially than whole tomato pulp and has a somewhat different composition, it becomes important to be able to distinguish the two by examination in the laboratory.

It is found that the results of the samples examined in this laboratory during the last season afford a basis for this distinction. They also make it possible to simplify the examination which we have heretofore found necessary.

### COMPOSITION OF WHOLE TOMATO PULP

The results obtained by the examination of 33 samples of whole tomato pulp are given in Table I. The concentration of the samples varies from unconcentrated pulp as it runs from the cyclone, to pulps of very heavy consistency. This table contains the data from which Table III and IV were calculated, although during the season a partial analysis was made of a large number of other samples, and the data secured therefrom were in all respects confirmatory of the relations calculated from Table I.

In addition to the data obtained by the various determinations, Table I gives the relation between the results of the determinations for each individual sample. For instance, the ratio of pulp solids to filtrate solids (pulp solids divided by filtrate solids) varies in the different samples from 1.091 to 1.154, and, with the exception of two samples, it varies from 1.100 to 1.145. The average of the 33 samples was 1.12. The relation of insoluble solids to total solids (expressed as per cent of insoluble solids in total solids) is shown in Table I. Considering the variations in the methods employed by different manufacturers in the preparation of tomato pulp, the per cent of insoluble solids in the total solids as shown by this column is closer than we might expect, varying in most of the samples from 11 to 14 per cent.

The per cent of sugar in the soluble solids, as shown by Table I, varies in most of the samples from 50 to 55 per cent. This figure cannot be expected to be constant in different localities and in different years.

The acid, estimated as citric, constitutes in most of the samples from 9 to 10 per cent of the soluble solids.

Of especial interest is the refractive constant of the filtered liquor, shown in the last column of Table I. The refractive constant of the various samples is much more uniform than might be expected from a product of this nature.

On the whole, Table I is chiefly interesting as affording the data from which Tables III and IV were calculated. The uniformity of the relations shown in Table IV is such that it is usually possible from one determination on the filtrate and the determination of solids in the pulp by drying to distinguish pulp made from whole tomatoes from that made from trimming stock. For instance, if the specific gravity or index of refraction of a filtrate prepared from a pulp of unknown origin, and the per cent of solids in the pulp by drying, do not agree with the relation between these determinations as shown in Table IV, it may be assumed that the sample was not prepared from whole tomatoes, or that some other substance, such as salt, has been added. Moreover, trimming stock pulp rarely conforms to the relations found in whole tomato pulp. For instance, the insoluble solids are usually higher and the acid lower in trimming stock pulp.

### COMPOSITION OF TRIMMING STOCK PULP

In Table II are given the results of the examination of 21 typical samples of trimming stock pulp prepared at different plants and in different localities. This table is of especial interest in showing that the relations between the results of the various analytical determinations differ from those of whole tomato pulps as given in Table IV. For instance, in No. 1470 the immersion refractometer reading is 45.90, and the per cent of solids is 9.54, whereas, according to Table IV, the per cent of solids in the pulp corresponding to an index of refraction of 45.90 should be 8.57. The specific gravity of the pulp is 1.0373, which, according to Table IV, should correspond to 8.98 instead of 9.54. Of course it cannot be said definitely that a pulp

which on examination is found to conform to all the relations shown in Table IV is necessarily whole tomato pulp. It is entirely possible for an occasional sample of trimming stock pulp to conform to all the relations shown in that table; moreover, the extent to which different samples of trimming stock pulp will vary from the relations shown in Table IV differs with the manner of preparation. For instance, if a portion of the juice is discarded in the manufacture of trimming stock pulp, as is still the practice of some manufacturers, the variation from whole tomato pulp will be greater than otherwise and the variation will increase with the amount of juice discarded.

## METHODS OF ANALYSIS

The methods given may also be applied to the examination of raw tomatoes and canned tomatoes. In applying the relations given below to the results obtained by the examination of tomato pulp or cup for the determination of specific gravity, air bubbles are introduced which it is found impossible to remove without the aid of a centrifuge. These can be completely removed by whirling the specific gravity flask in a centrifuge for about one minute at a speed of about 1000 r. p. m. A hand Babcock milk tester is satisfactory for this purpose. This causes the pulp to settle into the flask, because of the elimination of the air bubbles. The flask is again filled and centrifuged; this is continued until the surface of the pulp remains at the top of the flask. A few drops of pulp are added to bring the contents above the top of the flask and the pulp is then "struck off" with a straight edge, the outside of the flask washed and dried and the flask and contents weighed.

A table can be constructed readily giving in parallel columns the weight of flask and contents and the specific gravity of the pulp. For the use of Table IV, the

TABLE I—COMPOSITION OF WHOLE TOMATO PULPS

| | Composition of Pulps | | | Filtrate from Pulps | | | | | Ratio of pulp solids to filtrate solids | Per cent insoluble solids in total solids | Solids of Filtrate | | | Refractive constant of filtered liquor(*f*) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Immersion refractometer 17.5° C. | | | Percentages | | | |
| Sample No. | Sp. gr. at 20° C. | Per cent total solids(*a*) | Per cent insoluble solids | Sp. gr. at 20° C. | Per cent solids(*a*) | Per cent sugar(*d*) | Per cent acid as citric | | | | Sugar | Acid | Ratio sugar to acid | |
| 1290 | 1.0252 | 5.94 | 0.66 | 1.0233 | 5.24 | 2.41 | 0.58 | 36.24 | 1.133 | 11.1 | 46.0 | 11.1 | 4.1 | 0.20556 |
| 1291 | 1.0273 | 6.54 | 0.78 | 1.0252 | 5.71 | 3.10 | 0.53 | 37.80 | 1.145 | 11.9 | 54.3 | 9.4 | 5.8 | 0.20550 |
| 1292 | 1.0334 | 5.30 | 0.80 | 1.0211 | 4.88 | 2.48 | 0.49 | 34.51 | 1.127 | 14.6 | 50.8 | 10.1 | 5.0 | 0.20564 |
| 1293 | 1.0293 | 7.02 | 0.74 | 1.0276 | 6.28 | 3.35 | 0.61 | 40.04 | 1.118 | 10.5 | 53.4 | 9.7 | 5.5 | 0.20548 |
| 1294 | 1.0272 | 6.48 | 0.69 | 1.0256 | 5.82 | 3.20 | 0.55 | 38.27 | 1.113 | 10.6 | 55.0 | 9.5 | 5.8 | 0.20525 |
| 1295 | 1.0361 | 8.67 | 0.95 | 1.0340 | 7.69 | 4.36 | 0.67 | 46.03 | 1.127 | 11.0 | 56.8 | 8.7 | 6.5 | 0.20534 |
| 1296 | 1.0380 | 9.00 | 1.06 | .... | 8.05 | 4.47 | 0.66 | 46.86 | 1.117 | 11.8 | 55.5 | 8.2 | 6.8 | .... |
| 1297 | 1.0465 | 11.20 | 1.19 | 1.0446 | 10.27 | 5.61 | 0.89 | 56.70 | 1.091 | 10.6 | 54.6 | 8.9 | 6.3 | 0.20544 |
| 1299 | 1.0417 | 10.07 | 1.23 | 1.0394 | 9.09 | 4.96 | 0.81 | 51.75 | 1.108 | 12.2 | 54.6 | 8.9 | 6.1 | 0.20550 |
| 1300 | 1.0322 | 7.70 | 0.93 | 1.0304 | 6.88 | 3.55 | 0.67 | 42.84 | 1.119 | 12.1 | 51.6 | 9.7 | 5.3 | 0.20546 |
| 1301 | 1.0312 | 7.36 | 0.91 | .... | 6.68 | 3.27 | 0.69 | 41.56 | 1.102 | 12.4 | 48.9 | 10.3 | 4.8 | .... |
| 1302 | 1.0310 | 7.45 | 0.91 | 1.0293 | 6.61 | 3.43 | 0.64 | 41.76 | 1.127 | 12.2 | 51.9 | 9.7 | 5.4 | 0.20551 |
| 1303 | 1.0340 | 8.17 | 0.91 | 1.0323 | 7.29 | 3.77 | 0.71 | 44.65 | 1.120 | 11.1 | 51.7 | 9.7 | 5.3 | 0.20549 |
| 1304 | 1.0292 | 6.88 | 0.88 | 1.0274 | 6.20 | 3.03 | 0.64 | 39.74 | 1.110 | 12.8 | 48.9 | 10.4 | 4.7 | 0.20546 |
| 1305 | 1.0371 | 9.03 | 1.19 | .... | 7.98 | 4.14 | 0.82 | 47.30 | 1.132 | 13.2 | 51.9 | 10.3 | 5.0 | .... |
| 1306 | 1.0370 | 8.95 | 0.98 | .... | 8.01 | 4.71 | 0.69 | 47.60 | 1.117 | 11.0 | 58.8 | 8.7 | 6.8 | .... |
| 1307(*b*) | 1.0328 | 7.86 | 1.01 | 1.0308 | 6.97 | 3.79 | 0.66 | 43.15 | 1.126 | 12.9 | 54.4 | 9.5 | 5.7 | 0.20544 |
| 1481 | 1.0449 | 10.82 | .... | 1.0421 | 9.64 | 5.15 | 0.99 | 54.20 | 1.123 | .... | 53.4 | 10.3 | 5.2 | 0.20545 |
| 1482 | 1.0444 | 10.83 | .... | 1.0422 | 9.86 | 5.62 | 0.94 | 54.75 | 1.100 | .... | 57.0 | 9.6 | 6.0 | 0.20554 |
| 1483 | 1.0464 | 11.21 | .... | 1.0441 | 10.19 | 5.67 | 0.98 | 56.45 | 1.100 | .... | 55.6 | 9.6 | 5.8 | 0.20550 |
| 1484 | 1.0423 | 10.27 | .... | 1.0396 | 9.23 | 5.42 | 0.81 | 52.10 | 1.114 | .... | 58.7 | 8.8 | 6.7 | 0.20544 |
| 1485 | 1.0347 | 8.55 | .... | 1.0332 | 7.73 | 4.35 | 0.72 | 45.85 | 1.106 | .... | 56.3 | 9.3 | 6.0 | 0.20529 |
| 1477(*c*) | 1.0610 | 13.86 | .... | 1.0579 | 12.75 | 6.55 | 0.97 | 67.15 | 1.111(*e*) | .... | 51.4 | 7.7 | 6.7 | .... |
| 1479 | 1.0411 | 10.00 | 1.21 | 1.0386 | 8.96 | .... | .... | 51.57 | 1.116 | 9.8 | .... | .... | .... | 0.20554 |
| 1486 | 1.0169 | 4.34 | 0.62 | 1.0158 | 3.76 | .... | .... | .... | 1.154 | 14.3 | .... | .... | .... | .... |
| 1491 | 1.0198 | 4.97 | 0.63 | 1.0188 | 4.40 | .... | .... | 32.67 | 1.128 | 12.7 | .... | .... | .... | 0.20565 |
| 1496 | 1.0341 | 8.27 | 1.15 | 1.0318 | 7.31 | .... | .... | 44.86 | 1.131 | 13.9 | .... | .... | .... | 0.20554 |
| 1515 | 1.0352 | 8.56 | 1.15 | 1.0331 | 7.61 | .... | .... | 46.20 | 1.125 | 13.5 | .... | .... | .... | 0.20556 |
| 1529 | 1.0209 | 5.11 | 0.89 | 1.0195 | 4.54 | .... | .... | 32.96 | 1.125 | 17.4 | .... | .... | .... | 0.20556 |
| 1530 | 1.0252 | 6.21 | 0.98 | 1.0231 | 5.42 | .... | .... | 36.31 | 1.145 | 15.8 | .... | .... | .... | 0.20553 |
| 1531 | 1.0291 | 7.17 | 1.08 | 1.0273 | 6.27 | .... | .... | 40.09 | 1.143 | 15.1 | .... | .... | .... | 0.20547 |
| 1224(*c*) | 1.0486 | 11.22 | 0.91 | 1.0468 | 10.33 | .... | .... | 57.62 | 1.124(*e*) | 11.8 | .... | .... | .... | .... |
| 1325 | 1.0327 | 7.86 | 0.93 | .... | 6.99 | .... | .... | 43.80 | 1.123 | .... | .... | .... | .... | .... |

(*a*) Determined by drying *in vacuo* at 70° C.
(*b*) Composite of 1290 to 1306 inclusive.
(*c*) This sample contained salt.
(*d*) Expressed as invert.
(*e*) Salt-free ratio.
(*f*) Calculated by formula of Lorentz-Lorenz, $\frac{n^2 - 1}{(n^2 + 2)2}$

or canned tomatoes, it is assumed that no substance such as sugar or salt has been added. If sodium chloride is found to be present in excess of the amount normal to tomatoes (from 0.05 to 0.1 per cent), it is necessary to determine the amount of salt and make correction therefor before applying the relations given below.

In examining raw tomatoes, care must be taken to secure a representative sample of the juice. This cannot be done by applying pressure directly, as the juice of the seed receptacles is of different composition from that of the fleshy part of the tomato. It is necessary, therefore, to crush the sample and thoroughly cook it in a flask surrounded by boiling water and connected with a reflux condenser.

## DETERMINATION OF SPECIFIC GRAVITY

In pouring the sample of tomato pulp into a flask specific gravity should be determined at 20° C. If the temperature varies from this, the specific gravity may be corrected by the correction table for Brix hydrometers, changing the Brix degrees in that table to the corresponding specific gravity, and also allowing for the fact that the correction table mentioned is based on $17^1/_2$° instead of 20° C.

## DETERMINATION OF SOLIDS

1. BY THE EXAMINATION OF THE PULP—The total solids in tomato pulp may be determined by drying *in vacuo* at 70° C.; by drying at atmospheric pressure at the temperature of boiling water; by calculation from the specific gravity of the pulp; or from the percent of solids, specific gravity or index of refraction of the filtrate. The solids obtained by different methods on 31 samples of pulp are given in Table III.

(*a*). BY DRYING—By drying either *in vacuo* or at

atmospheric pressure, it is our experience that after the sample has reached apparent dryness, four hours' drying gives complete results. From 2 to 4 grams should be taken for the determination, and enough water added to distribute the sample uniformly over the bottom of the flat-bottomed dish.

The solids as determined by drying *in vacuo* at 70° C. are about 108.5 per cent of the result obtained by drying at the temperature of boiling water at atmospheric pressure. This figure is the average of the results obtained by the examination of 20 samples of pulp, in all of which the per cent of solids obtained by drying *in vacuo* agree quite closely with the per cent obtained by drying at atmospheric pressure multiplied by 1.085. In 15 of the 20 samples examined, the difference did not exceed 0.10 per cent, and in only one case did it exceed 0.20 per cent. The results obtained by the subsequent examination of a considerable number of other samples confirm this relation.

(*b*). BY CALCULATION FROM THE SPECIFIC GRAVITY OF THE PULP—There is a very exact relation between the specific gravity of pulp (determined by the method given above) and the per cent of total solids as determined by drying. The solids corresponding to pulps of various specific gravities are given in Table IV, or may be obtained from the following formula which is derived from the same table:

Per cent SOLIDS
= 228 (sp. gr. of pulp —1.000) + 19.1 (sp. gr. of pulp —1.015).

2. BY THE EXAMINATION OF THE FILTRATE—If a sample of pulp of considerable size be thrown on a folded filter, a filtrate is obtained whose composition has a definite relation to that of the whole pulp.

(*a*). BY DRYING—The per cent of solids in the filtrate may be determined by drying *in vacuo* at 70° C., or under atmospheric pressure at the temperature of boiling water.

As in the case of the drying of pulp, a constant relation is found to exist between the per cent of solids as determined by drying *in vacuo* at 70° C., and the per cent of solids as determined by drying at atmospheric pressure at the temperature of boiling water. The per cent of solids in the filtrate obtained by drying at atmospheric pressure, multiplied by 1.125, gives the per cent of solids obtained by drying *in vacuo*. This relation is shown in detail in Table IV.

The per cent of solids in the filtered liquor obtained by drying *in vacuo*, multiplied by 1.12, gives the per cent of solids in the original pulp obtained by drying *in vacuo*. This relationship is shown in Table I, in the column headed "Ratio of pulp solids to filtrate solids," and also in Table IV.

Of the 33 samples shown in Table I. the result obtained by multiplying the per cent of solids in the filtrate (obtained by drying *in vacuo*) by the factor 1.12 is very nearly identical with the per cent of solids in the pulp (obtained by drying *in vacuo*). In 22 of the 33 samples the difference between these two figures is less than 0.1 per cent. In 17 samples it

TABLE II. COMPOSITION OF TRIMMING STOCK PULPS

| | Composition of Pulps | | | Composition of Liquor Obtained by Filtering Pulps | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Specific gravity at 20° C. | Per cent total solids | Per cent insoluble solids | Specific gravity at 20° C. | Per cent solids(*a*) | Per cent sugar(*e*) | Per cent acid as citric | Immersion refractometer at 17.5° C. | Ratio of pulp solids to filtrate solids | Per cent insoluble solids in total solids | Per cent sugar in solids of liquor | Per cent acid in solids of liquor | Ratio of acid to sugar |
| 1470 | 1.0373 | 9.54 | | 1.0337 | 7.68 | 4.11 | 0.58 | 45.70 | 1.241 | | 53.5 | 7.6 | 7.0 |
| 1471 | 1.0385 | 9.40 | | 1.0334 | 7.62 | 4.05 | 0.59 | 45.75 | 1.233 | | 53.2 | 7.7 | 6.9 |
| 1470-1 | 1.0349 | 8.56 | | 1.0302 | 7.11 | | .... | 42.87 | 1.203 | | | | |
| 1470-2 | 1.0316 | 7.88 | | 1.0279 | 6.55 | | .... | 40.75 | 1.203 | | | | |
| 1470-3 | 1.0284 | 7.00 | | | 5.83 | | .... | 37.80 | 1.201 | | | | |
| 1470-4 | 1.0258 | 6.62 | | 1.0232 | 5.53 | | .... | 36.40 | 1.197 | | | | |
| 1471-1 | 1.0334 | 8.12 | | 1.0288 | 6.86 | | .... | 41.60 | 1.184 | | | | |
| 1471-2 | 1.0258 | 6.41 | | 1.0227 | 5.41 | | .... | 36.10 | 1.184 | | | | |
| 1471-3 | 1.0299 | 7.48 | | 1.0275 | 6.14 | | .... | 39.25 | 1.218 | | | | |
| 1471-4 | 1.0191 | 4.74 | | 1.0168 | 3.94 | | .... | 30.55 | 1.203 | | | | |
| 1572 | 1.0443 | 10.28 | | 1.0400 | 9.28 | | .... | 52.47 | 1.109 | | | | |
| 1573 | 1.0392 | 9.53 | 1.22 | 1.0369 | 8.53 | | .... | 49.33 | 1.117 | 12.8 | | | |
| 1574 | 1.0427 | 10.29 | 1.17 | 1.0401 | 9.29 | | .... | 52.40 | 1.109 | 11.4 | | | |
| 1575 | 1.0386 | 9.73 | 1.29 | 1.0369 | 8.28 | | .... | 49.37 | 1.175 | 13.3 | | | |
| 1662(*b*) | 1.0204 | 4.85 | 0.18 | 1.0201 | 4.65 | | | 33.27 | 1.042 | 3.7 | | | |
| 1664(*c*) | 1.0577 | 13.2 | 0.62 | 1.0566 | 12.70 | | .... | 66.92 | 1.040 | 4.7 | | | |
| 1665 | 1.0331 | 7.74 | 1.10 | 1.0304 | 6.89 | | .... | 42.65 | 1.123 | 14.3 | | | |
| 701 | 1.0200 | 4.89 | 0.72 | 1.0184 | 4.36 | 2.35 | 0.30 | 32.09 | 1.140 | 14.7 | 54.8 | 7.0 | 7.8 |
| 703(*d*) | 1.0180 | 4.24 | 0.10 | 1.0178 | 4.15 | 2.32 | 0.29 | 32.09 | 1.022 | 2.4 | 55.9 | 7.0 | 8.0 |
| 705 | 1.0388 | 9.85 | 1.83 | 1.0359 | 8.08 | 4.07 | 0.51 | 47.85 | 1.220 | 18.6 | 50.4 | 6.2 | 8.0 |
| 706 | 1.0333 | 8.35 | 0.98 | | 7.20 | 3.51 | 0.46 | 44.69 | 1.145 | 11.7 | 48.3 | 6.3 | 7.6 |

(*a*) Determined by drying *in vacuo* at 70° C.
(*b*) Unconcentrated tomato juice from peeling table.
(*c*) No. 1662 concentrated.
(*d*) Clear liquor separated from unconcentrated pulp on standing
(*e*) Expressed as invert.

TABLE III. COMPARISON OF METHODS FOR THE DETERMINATION AND CALCULATION OF SOLIDS IN WHOLE TOMATO PULP

| | Per Cent Solids in Liquor from Filtered Pulp | | | | Per Cent Solids in Pulp | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Drying | Calculated from | | | By drying | Calculated from | | | |
| Sample No. | *in vacuo* at 70° C. | Refr. ind. Table 4 | Sp. gr. Table 4 | Sp. gr. See (*a*) | *in vacuo* at 70° C | Refr. ind. Table 4 | Specific gravity of Filtered Pulp in liquor Table 4 | Filtered liquor Table 4 | Filtered liquor See (*b*) |
| 1290 | 5.24 | 5.31 | 5.35 | 5.35 | 5.94 | 5.95 | 6.00 | 5.97 | 5.99 |
| 1291 | 5.71 | 5.67 | 5.78 | 5.80 | 6.54 | 6.36 | 6.48 | 6.47 | 6.50 |
| 1292 | 4.88 | 4.87 | 4.85 | 4.85 | 5.50 | 5.47 | 5.44 | 5.52 | 5.43 |
| 1293 | 6.28 | 6.21 | 6.33 | 6.35 | 7.02 | 6.96 | 7.10 | 6.98 | 7.11 |
| 1294 | 5.82 | 5.79 | 5.87 | 5.89 | 6.48 | 6.49 | 6.58 | 6.45 | 6.60 |
| 1295 | 7.69 | 7.67 | 7.82 | 7.82 | 8.67 | 8.59 | 8.77 | 8.63 | 8.76 |
| 1296 | 8.05 | 7.88 | .... | .... | 9.00 | 8.83 | .... | 9.11 | .... |
| 1297 | 10.27 | 10.27 | 10.25 | 10.26 | 11.20 | 11.50 | 11.47 | 11.20 | 11.49 |
| 1299 | 9.09 | 9.06 | 9.05 | 9.06 | 10.07 | 10.15 | 10.14 | 10.02 | 10.15 |
| 1300 | 6.88 | 6.91 | 6.98 | 6.99 | 7.70 | 7.75 | 7.82 | 7.68 | 7.83 |
| 1301 | 6.68 | 6.59 | .. | .. | 7.36 | 7.38 | .. | 7.43 | .. |
| 1302 | 6.61 | 6.64 | 6.73 | 6.74 | 7.45 | 7.44 | 7.54 | 7.40 | 7.55 |
| 1303 | 7.29 | 7.34 | 7.42 | 7.43 | 8.17 | 8.23 | 8.33 | 8.12 | 8.32 |
| 1304 | 6.20 | 6.16 | 6.30 | 6.30 | 6.88 | 6.90 | 7.06 | 6.95 | 7.06 |
| 1305 | 7.98 | 7.98 | .. | .. | 9.03 | 8.94 | .. | 8.88 | .. |
| 1306 | 8.01 | 8.05 | .. | .. | 8.95 | 9.02 | .. | 8.86 | .. |
| 1307 | 6.97 | 6.96 | 7.08 | 7.08 | 7.86 | 7.81 | 7.93 | 7.83 | 7.93 |
| 1481 | 9.64 | 9.67 | 9.68 | 9.68 | 10.82 | 10.83 | 10.84 | 10.80 | 10.84 |
| 1482 | 9.86 | 9.81 | 9.70 | 9.71 | 10.83 | 10.98 | 10.86 | 10.70 | 10.88 |
| 1483 | 10.19 | 10.21 | 10.15 | 10.14 | 11.21 | 11.43 | 11.36 | 11.17 | 11.36 |
| 1484 | 9.23 | 9.15 | 9.10 | 9.11 | 10.27 | 10.25 | 10.19 | 10.17 | 10.20 |
| 1485 | 7.73 | 7.64 | 7.63 | 7.64 | 8.55 | 8.56 | 8.55 | 8.30 | 8.56 |
| 1479 | 8.96 | 9.03 | 8.87 | 8.88 | 10.00 | 10.10 | 9.94 | 9.88 | 9.85 |
| 1486 | 3.76 | .. | 3.62 | 3.63 | 4.34 | .. | 4.05 | 3.90 | 4.07 |
| 1491 | 4.40 | 4.44 | 4.30 | 4.32 | 4.97 | 4.97 | 4.82 | 4.62 | 4.84 |
| 1496 | 7.31 | 7.39 | 7.30 | 7.31 | 8.27 | 8.28 | 8.18 | 8.15 | 8.29 |
| 1515 | 7.61 | 7.70 | 7.60 | 7.61 | 8.56 | 8.63 | 8.52 | 8.40 | 8.52 |
| 1529 | 4.54 | 4.52 | 4.47 | 4.49 | 5.11 | 5.06 | 5.01 | 4.90 | 5.03 |
| 1530 | 5.42 | 5.32 | 5.30 | 5.31 | 6.21 | 5.97 | 5.94 | 5.97 | 5.95 |
| 1531 | 6.27 | 6.25 | 6.27 | 6.28 | 7.17 | 7.01 | 7.04 | 6.92 | 7.03 |
| 1325 | 6.99 | 7.13 | .. | .. | 7.86 | 7.99 | .. | 7.81 | .. |

(*a*) The solution factor of O'Sullivan (*J. Chem. Soc.*, **1876**, p. 129) was employed with slight modification. The formula employed was $\frac{1000\,d - 1000}{4.35} =$ per cent solids. In this formula $d$ = specific gravity of solution at 20° C.
(*b*) For the figures in this column the formula given in footnote *a* was employed and the results multiplied by 1.12.

is less than 0.06 per cent, and in 13 samples it is less than 0.05 per cent. In only two samples does it exceed 0.17 per cent.

(*b*). BY CALCULATION FROM THE SPECIFIC GRAVITY OF THE FILTRATE—The specific gravity of the filtered liquor may be determined by means of an ordinary pycnometer. From the specific gravity at 20° C., the per cent of solids in the filtrate as determined by drying *in vacuo* at 70° C., may be obtained from Table IV. It may also be calculated by the following formula, which was derived from the same table:

Per cent SOLIDS IN FILTRATE = 230 (sp. gr. of filtrate − 1.000).

The per cent of solids in the pulp may also be ascertained from the specific gravity of the filtrate at 20° C., from Table IV. The same results may be obtained from the following formula, which was derived from Table III:

Per cent SOLIDS IN PULP = 257.5 (sp. gr. of filtrate at 20° C. —1.000).

It is of interest to note that the table suggested by Windisch for the determination of extract in wine (Bureau of Chemistry, U. S. Dept. Agr., *Bull.* **107,** revised, Table V) may be employed to determine solids in tomato pulp from the specific gravity of the filtered liquor from the same. If the specific gravity of the liquor be determined at 20° C., the figures in the adjoining column, under "Extract," correspond very closely to the per cent of total solids in the original pulp. A still closer agreement is obtained if the figure 0.05 be deducted from the percentage of extract given in the table.

(*c*). BY CALCULATION FROM THE INDEX OF REFRACTION OF THE FILTRATES—The index of refraction of the liquor obtained by filtering tomato pulp may be determined by means of either the Zeiss-Abbé refractometer, or the immersion refractometer at the temperature of 17.5° C. The latter is preferable as

TABLE IV TOMATO PULP AND FILTERED LIQUOR

| FILTRATE FROM PULP | | | | TOMATO PULP | | | | FILTRATE FROM PULP | | | | TOMATO PULP | | | | FILTRATE FROM PULP | | | | TOMATO PULP | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| % solids, 70° C. *in vacuo* | % solids, 100° C. atmos. pr. | Immersion refractometer at 17.5° C. | Sp. gr. at 20° C. | % solids, 70° C. *in vacuo* | % solids, 100° C. atmos. pr. | Specific gravity at 20° C. | | % solids, 70° C. *in vacuo* | % solids, 100° C. atmos. pr. | Immersion refractometer at 17.5° C. | Sp. gr. at 20° C. | % solids, 70° C. *in vacuo* | % solids, 100° C. atmos. pr. | Specific gravity at 20° C. | | % solids, 70° C. *in vacuo* | % solids, 100° C. atmos. pr. | Immersion refractometer at 17.5° C. | Sp. gr. at 20° C. | % solids, 70° C. *in vacuo* | % solids, 100° C. atmos. pr. | Specific gravity at 20° C. | |
| 3.05 | 2.71 | 26.9 | 1.0133 | 3.42 | 3.15 | 1.0150 | | 6.30 | 5.60 | 40.3 | 1.0274 | 7.06 | 6.51 | 1.0297 | | 9.30 | 8.27 | 52.7 | 1.0404 | 10.41 | 9.60 | 1.0433 | |
| 3.10 | 2.75 | 27.1 | 1.0136 | 3.47 | 3.20 | 1.0152 | | 6.35 | 5.64 | 40.6 | 1.0277 | 7.12 | 6.56 | 1.0299 | | 9.35 | 8.31 | 52.9 | 1.0406 | 10.47 | 9.65 | 1.0435 | |
| 3.15 | 2.80 | 27.3 | 1.0138 | 3.53 | 3.25 | 1.0155 | | 6.40 | 5.69 | 40.8 | 1.0279 | 7.17 | 6.61 | 1.0301 | | 9.40 | 8.35 | 53.1 | 1.0409 | 10.52 | 9.70 | 1.0437 | |
| 3.20 | 2.85 | 27.5 | 1.0140 | 3.58 | 3.30 | 1.0157 | | 6.45 | 5.73 | 41.0 | 1.0281 | 7.23 | 6.66 | 1.0304 | | 9.45 | 8.40 | 53.3 | 1.0411 | 10.58 | 9.75 | 1.0440 | |
| 3.25 | 2.89 | 27.7 | 1.0142 | 3.64 | 3.35 | 1.0159 | | 6.50 | 5.78 | 41.2 | 1.0283 | 7.28 | 6.71 | 1.0306 | | 9.50 | 8.45 | 53.5 | 1.0413 | 10.64 | 9.80 | 1.0442 | |
| 3.30 | 2.93 | 27.9 | 1.0144 | 3.70 | 3.41 | 1.0161 | | | | | | | | | | 9.55 | 8.49 | 53.7 | 1.0415 | 10.70 | 9.86 | 1.0444 | |
| 3.35 | 2.97 | 28.1 | 1.0146 | 3.76 | 3.46 | 1.0163 | | 6.55 | 5.82 | 41.4 | 1.0285 | 7.34 | 6.76 | 1.0308 | | 9.60 | 8.53 | 53.9 | 1.0417 | 10.75 | 9.91 | 1.0447 | |
| 3.40 | 3.02 | 28.3 | 1.0149 | 3.81 | 3.51 | 1.0166 | | 6.60 | 5.86 | 41.6 | 1.0287 | 7.40 | 6.82 | 1.0310 | | 9.65 | 8.58 | 54.1 | 1.0419 | 10.80 | 9.96 | 1.0449 | |
| 3.45 | 3.07 | 28.6 | 1.0151 | 3.87 | 3.56 | 1.0168 | | 6.65 | 5.91 | 41.8 | 1.0290 | 7.45 | 6.87 | 1.0313 | | 9.70 | 8.62 | 54.3 | 1.0422 | 10.86 | 10.01 | 1.0451 | |
| 3.50 | 3.11 | 28.8 | 1.0153 | 3.92 | 3.61 | 1.0170 | | 6.70 | 5.95 | 42.0 | 1.0292 | 7.51 | 6.92 | 1.0315 | | 9.75 | 8.67 | 54.5 | 1.0424 | 10.91 | 10.06 | 1.0453 | |
| | | | | | | | | 6.75 | 6.00 | 42.2 | 1.0294 | 7.56 | 6.97 | 1.0317 | | | | | | | | | |
| 3.55 | 3.15 | 29.0 | 1.0155 | 3.98 | 3.67 | 1.0172 | | | | | | | | | | 9.80 | 8.71 | 54.7 | 1.0426 | 10.97 | 10.11 | 1.0456 | |
| 3.60 | 3.20 | 29.2 | 1.0157 | 4.03 | 3.72 | 1.0174 | | 6.80 | 6.04 | 42.4 | 1.0296 | 7.62 | 7.02 | 1.0320 | | 9.85 | 8.75 | 55.0 | 1.0428 | 11.02 | 10.16 | 1.0458 | |
| 3.65 | 3.24 | 29.4 | 1.0160 | 4.09 | 3.77 | 1.0177 | | 6.85 | 6.09 | 42.6 | 1.0298 | 7.68 | 7.08 | 1.0322 | | 9.90 | 8.80 | 55.2 | 1.0430 | 11.08 | 10.21 | 1.0461 | |
| 3.70 | 3.28 | 29.6 | 1.0162 | 4.15 | 3.82 | 1.0179 | | 6.90 | 6.13 | 42.8 | 1.0300 | 7.74 | 7.13 | 1.0324 | | 9.95 | 8.85 | 55.4 | 1.0433 | 11.14 | 10.26 | 1.0463 | |
| 3.75 | 3.33 | 29.8 | 1.0164 | 4.20 | 3.87 | 1.0181 | | 6.95 | 6.18 | 43.1 | 1.0303 | 7.79 | 7.18 | 1.0326 | | 10.00 | 8.89 | 55.6 | 1.0435 | 11.20 | 10.31 | 1.0465 | |
| | | | | | | | | 7.00 | 6.22 | 43.3 | 1.0305 | 7.85 | 7.23 | 1.0329 | | | | | | | | | |
| 3.80 | 3.38 | 30.0 | 1.0166 | 4.26 | 3.93 | 1.0183 | | | | | | | | | | 10.05 | 8.93 | 55.8 | 1.0437 | 11.25 | 10.37 | 1.0467 | |
| 3.85 | 3.42 | 30.3 | 1.0168 | 4.31 | 3.98 | 1.0185 | | | | | | | | | | 10.10 | 8.98 | 56.0 | 1.0439 | 11.30 | 10.42 | 1.0469 | |
| 3.90 | 3.46 | 30.5 | 1.0170 | 4.37 | 4.03 | 1.0188 | | 7.05 | 6.26 | 43.5 | 1.0307 | 7.90 | 7.28 | 1.0331 | | 10.15 | 9.02 | 56.2 | 1.0441 | 11.36 | 10.47 | 1.0472 | |
| 3.95 | 3.51 | 30.7 | 1.0173 | 4.43 | 4.08 | 1.0190 | | 7.10 | 6.31 | 43.7 | 1.0309 | 7.96 | 7.33 | 1.0333 | | 10.20 | 9.07 | 56.4 | 1.0444 | 11.41 | 10.52 | 1.0474 | |
| 4.00 | 3.55 | 30.9 | 1.0175 | 4.48 | 4.13 | 1.0192 | | 7.15 | 6.36 | 43.9 | 1.0311 | 8.02 | 7.38 | 1.0336 | | 10.25 | 9.11 | 56.6 | 1.0446 | 11.47 | 10.57 | 1.0476 | |
| | | | | | | | | 7.20 | 6.40 | 44.1 | 1.0313 | 8.07 | 7.43 | 1.0338 | | | | | | | | | |
| 4.05 | 3.60 | 31.1 | 1.0177 | 4.54 | 4.18 | 1.0194 | | 7.25 | 6.44 | 44.3 | 1.0315 | 8.12 | 7.48 | 1.0340 | | 10.30 | 9.15 | 56.8 | 1.0448 | 11.53 | 10.63 | 1.0478 | |
| 4.10 | 3.64 | 31.3 | 1.0179 | 4.59 | 4.23 | 1.0197 | | | | | | | | | | 10.35 | 9.20 | 57.0 | 1.0450 | 11.59 | 10.68 | 1.0481 | |
| 4.15 | 3.69 | 31.5 | 1.0181 | 4.65 | 4.28 | 1.0199 | | 7.30 | 6.48 | 44.5 | 1.0318 | 8.18 | 7.54 | 1.0342 | | 10.40 | 9.25 | 57.2 | 1.0452 | 11.64 | 10.73 | 1.0483 | |
| 4.20 | 3.73 | 31.7 | 1.0183 | 4.71 | 4.33 | 1.0201 | | 7.35 | 6.53 | 44.7 | 1.0320 | 8.24 | 7.59 | 1.0345 | | 10.45 | 9.29 | 57.4 | 1.0454 | 11.70 | 10.78 | 1.0485 | |
| 4.25 | 3.78 | 31.9 | 1.0185 | 4.76 | 4.38 | 1.0203 | | 7.40 | 6.58 | 44.9 | 1.0322 | 8.30 | 7.64 | 1.0347 | | 10.50 | 9.33 | 57.6 | 1.0457 | 11.76 | 10.83 | 1.0487 | |
| | | | | | | | | 7.45 | 6.62 | 45.1 | 1.0324 | 8.35 | 7.69 | 1.0349 | | | | | | | | | |
| 4.30 | 3.82 | 32.1 | 1.0188 | 4.82 | 4.44 | 1.0205 | | 7.50 | 6.66 | 45.3 | 1.0326 | 8.40 | 7.74 | 1.0352 | | 10.55 | 9.38 | 57.8 | 1.0459 | 11.81 | 10.89 | 1.0490 | |
| 4.35 | 3.86 | 32.3 | 1.0190 | 4.87 | 4.49 | 1.0208 | | | | | | | | | | 10.60 | 9.42 | 58.0 | 1.0461 | 11.87 | 10.94 | 1.0492 | |
| 4.40 | 3.91 | 32.5 | 1.0192 | 4.93 | 4.54 | 1.0210 | | | | | | | | | | 10.65 | 9.47 | 58.2 | 1.0463 | 11.93 | 10.99 | 1.0494 | |
| 4.45 | 3.95 | 32.7 | 1.0194 | 4.99 | 4.59 | 1.0212 | | 7.55 | 6.71 | 45.5 | 1.0328 | 8.46 | 7.79 | 1.0354 | | 10.70 | 9.51 | 58.4 | 1.0465 | 11.99 | 11.04 | 1.0496 | |
| 4.50 | 4.00 | 32.9 | 1.0196 | 5.04 | 4.64 | 1.0215 | | 7.60 | 6.76 | 45.7 | 1.0331 | 8.52 | 7.84 | 1.0356 | | 10.75 | 9.55 | 58.6 | 1.0467 | 12.05 | 11.09 | 1.0499 | |
| | | | | | | | | 7.65 | 6.80 | 45.9 | 1.0333 | 8.57 | 7.89 | 1.0358 | | | | | | | | | |
| 4.55 | 4.04 | 33.1 | 1.0198 | 5.10 | 4.70 | 1.0217 | | 7.70 | 6.84 | 46.2 | 1.0335 | 8.63 | 7.95 | 1.0361 | | 10.80 | 9.60 | 58.8 | 1.0469 | 12.10 | 11.15 | 1.0501 | |
| 4.60 | 4.09 | 33.3 | 1.0200 | 5.16 | 4.75 | 1.0219 | | 7.75 | 6.89 | 46.4 | 1.0337 | 8.68 | 8.00 | 1.0363 | | 10.85 | 9.65 | 59.0 | 1.0471 | 12.15 | 11.20 | 1.0503 | |
| 4.65 | 4.13 | 33.6 | 1.0203 | 5.21 | 4.80 | 1.0222 | | | | | | | | | | 10.90 | 9.70 | 59.2 | 1.0474 | 12.21 | 11.25 | 1.0505 | |
| 4.70 | 4.18 | 33.8 | 1.0205 | 5.27 | 4.85 | 1.0224 | | 7.80 | 6.93 | 46.6 | 1.0339 | 8.74 | 8.05 | 1.0365 | | 10.95 | 9.74 | 59.4 | 1.0476 | 12.26 | 11.30 | 1.0508 | |
| 4.75 | 4.22 | 34.0 | 1.0207 | 5.33 | 4.90 | 1.0226 | | 7.85 | 6.98 | 46.8 | 1.0341 | 8.80 | 8.11 | 1.0367 | | 11.00 | 9.78 | 59.6 | 1.0478 | 12.32 | 11.35 | 1.0510 | |
| | | | | | | | | 7.90 | 7.02 | 47.0 | 1.0344 | 8.85 | 8.16 | 1.0370 | | 11.05 | 9.82 | 59.9 | 1.0480 | 12.37 | 11.40 | 1.0512 | |
| 4.80 | 4.26 | 34.2 | 1.0209 | 5.38 | 4.96 | 1.0228 | | 7.95 | 7.07 | 47.2 | 1.0346 | 8.91 | 8.21 | 1.0372 | | 11.10 | 9.87 | 60.1 | 1.0482 | 12.43 | 11.45 | 1.0515 | |
| 4.85 | 4.31 | 34.4 | 1.0211 | 5.44 | 5.01 | 1.0230 | | 8.00 | 7.11 | 47.4 | 1.0348 | 8.96 | 8.26 | 1.0374 | | 11.15 | 9.92 | 60.3 | 1.0484 | 12.49 | 11.50 | 1.0517 | |
| 4.90 | 4.36 | 34.6 | 1.0213 | 5.49 | 5.06 | 1.0233 | | | | | | | | | | 11.20 | 9.96 | 60.5 | 1.0487 | 12.55 | 11.55 | 1.0519 | |
| 4.95 | 4.40 | 34.8 | 1.0216 | 5.55 | 5.11 | 1.0235 | | | | | | | | | | 11.25 | 10.00 | 60.7 | 1.0489 | 12.60 | 11.60 | 1.0522 | |
| 5.00 | 4.44 | 35.0 | 1.0218 | 5.60 | 5.16 | 1.0237 | | 8.05 | 7.16 | 47.6 | 1.0350 | 9.02 | 8.31 | 1.0377 | | | | | | | | | |
| | | | | | | | | 8.10 | 7.20 | 47.8 | 1.0352 | 9.08 | 8.36 | 1.0379 | | | | | | | | | |
| 5.05 | 4.49 | 35.2 | 1.0220 | 5.66 | 5.21 | 1.0240 | | 8.15 | 7.24 | 48.0 | 1.0354 | 9.14 | 8.41 | 1.0381 | | 11.30 | 10.04 | 60.9 | 1.0491 | 12.65 | 11.66 | 1.0524 | |
| 5.10 | 4.53 | 35.4 | 1.0223 | 5.72 | 5.26 | 1.0242 | | 8.20 | 7.28 | 48.2 | 1.0357 | 9.19 | 8.46 | 1.0383 | | 11.35 | 10.09 | 61.1 | 1.0493 | 12.71 | 11.71 | 1.0526 | |
| 5.15 | 4.58 | 35.6 | 1.0225 | 5.77 | 5.31 | 1.0244 | | 8.25 | 7.33 | 48.4 | 1.0359 | 9.25 | 8.51 | 1.0386 | | 11.40 | 10.13 | 61.3 | 1.0495 | 12.77 | 11.76 | 1.0528 | |
| 5.20 | 4.62 | 35.8 | 1.0227 | 5.83 | 5.36 | 1.0247 | | | | | | | | | | 11.45 | 10.18 | 61.5 | 1.0498 | 12.83 | 11.81 | 1.0531 | |
| 5.25 | 4.66 | 36.0 | 1.0229 | 5.88 | 5.41 | 1.0249 | | 8.30 | 7.38 | 48.6 | 1.0361 | 9.30 | 8.57 | 1.0388 | | 11.50 | 10.22 | 61.7 | 1.0500 | 12.88 | 11.86 | 1.0533 | |
| | | | | | | | | 8.35 | 7.42 | 48.8 | 1.0363 | 9.36 | 8.62 | 1.0390 | | | | | | | | | |
| 5.30 | 4.71 | 36.2 | 1.0231 | 5.94 | 5.47 | 1.0251 | | 8.40 | 7.46 | 49.0 | 1.0366 | 9.42 | 8.67 | 1.0393 | | 11.55 | 10.27 | 61.9 | 1.0502 | 12.94 | 11.92 | 1.0535 | |
| 5.35 | 4.75 | 36.4 | 1.0233 | 6.00 | 5.52 | 1.0253 | | 8.45 | 7.51 | 49.2 | 1.0368 | 9.47 | 8.72 | 1.0395 | | 11.60 | 10.31 | 62.1 | 1.0504 | 12.99 | 11.97 | 1.0538 | |
| 5.40 | 4.80 | 36.6 | 1.0235 | 6.05 | 5.57 | 1.0256 | | 8.50 | 7.55 | 49.4 | 1.0370 | 9.53 | 8.77 | 1.0397 | | 11.65 | 10.35 | 62.3 | 1.0506 | 13.05 | 12.02 | 1.0540 | |
| 5.45 | 4.84 | 36.8 | 1.0238 | 6.11 | 5.62 | 1.0258 | | | | | | | | | | 11.70 | 10.40 | 62.5 | 1.0508 | 13.10 | 12.07 | 1.0542 | |
| 5.50 | 4.89 | 37.1 | 1.0240 | 6.16 | 5.67 | 1.0260 | | | | | | | | | | 11.75 | 10.45 | 62.7 | 1.0511 | 13.16 | 12.12 | 1.0544 | |
| | | | | | | | | 8.55 | 7.60 | 49.6 | 1.0372 | 9.58 | 8.83 | 1.0400 | | | | | | | | | |
| 5.55 | 4.93 | 37.3 | 1.0242 | 6.22 | 5.73 | 1.0263 | | 8.60 | 7.64 | 49.8 | 1.0374 | 9.64 | 8.88 | 1.0402 | | 11.80 | 10.49 | 62.9 | 1.0513 | 13.22 | 12.18 | 1.0547 | |
| 5.60 | 4.98 | 37.5 | 1.0244 | 6.28 | 5.78 | 1.0265 | | 8.65 | 7.68 | 50.0 | 1.0376 | 9.70 | 8.93 | 1.0404 | | 11.85 | 10.53 | 63.1 | 1.0515 | 13.27 | 12.23 | 1.0549 | |
| 5.65 | 5.02 | 37.7 | 1.0246 | 6.33 | 5.83 | 1.0267 | | 8.70 | 7.73 | 50.2 | 1.0379 | 9.75 | 8.98 | 1.0406 | | 11.90 | 10.58 | 63.3 | 1.0517 | 13.32 | 12.28 | 1.0551 | |
| 5.70 | 5.06 | 37.9 | 1.0249 | 6.39 | 5.88 | 1.0270 | | 8.75 | 7.78 | 50.4 | 1.0381 | 9.80 | 9.03 | 1.0408 | | 11.95 | 10.63 | 63.5 | 1.0519 | 13.38 | 12.33 | 1.0554 | |
| 5.75 | 5.11 | 38.1 | 1.0251 | 6.45 | 5.93 | 1.0272 | | | | | | | | | | 12.00 | 10.67 | 63.7 | 1.0521 | 13.44 | 12.38 | 1.0556 | |
| | | | | | | | | 8.80 | 7.82 | 50.7 | 1.0383 | 9.86 | 9.09 | 1.0410 | | | | | | | | | |
| 5.80 | 5.15 | 38.3 | 1.0253 | 6.50 | 5.99 | 1.0274 | | 8.85 | 7.86 | 50.9 | 1.0385 | 9.92 | 9.14 | 1.0413 | | 12.05 | 10.71 | 64.0 | 1.0523 | 13.50 | 12.44 | 1.0558 | |
| 5.85 | 5.20 | 38.5 | 1.0255 | 6.56 | 6.04 | 1.0276 | | 8.90 | 7.91 | 51.1 | 1.0387 | 9.97 | 9.19 | 1.0415 | | 12.10 | 10.75 | 64.2 | 1.0525 | 13.55 | 12.49 | 1.0560 | |
| 5.90 | 5.24 | 38.7 | 1.0257 | 6.61 | 6.09 | 1.0279 | | 8.95 | 7.95 | 51.3 | 1.0389 | 10.02 | 9.24 | 1.0417 | | 12.15 | 10.80 | 64.4 | 1.0527 | 13.60 | 12.54 | 1.0562 | |
| 5.95 | 5.29 | 38.9 | 1.0259 | 6.67 | 6.14 | 1.0281 | | 9.00 | 8.00 | 51.5 | 1.0392 | 10.08 | 9.29 | 1.0419 | | 12.20 | 10.84 | 64.6 | 1.0529 | 13.66 | 12.59 | 1.0565 | |
| 6.00 | 5.33 | 39.1 | 1.0261 | 6.72 | 6.19 | 1.0283 | | | | | | | | | | 12.25 | 10.89 | 64.8 | 1.0531 | 13.72 | 12.64 | 1.0567 | |
| 6.05 | 5.38 | 39.3 | 1.0263 | 6.78 | 6.24 | 1.0285 | | 9.05 | 8.05 | 51.7 | 1.0394 | 10.14 | 9.35 | 1.0421 | | 12.30 | 10.94 | 65.0 | 1.0533 | 13.78 | 12.70 | 1.0569 | |
| 6.10 | 5.42 | 39.5 | 1.0266 | 6.84 | 6.29 | 1.0288 | | 9.10 | 8.09 | 51.9 | 1.0396 | 10.19 | 9.40 | 1.0424 | | 12.35 | 10.98 | 65.2 | 1.0535 | 13.83 | 12.75 | 1.0572 | |
| 6.15 | 5.46 | 39.7 | 1.0268 | 6.89 | 6.35 | 1.0290 | | 9.15 | 8.13 | 52.1 | 1.0398 | 10.25 | 9.45 | 1.0426 | | 12.40 | 11.02 | 65.4 | 1.0537 | 13.89 | 12.80 | 1.0574 | |
| 6.20 | 5.51 | 39.9 | 1.0270 | 6.95 | 6.41 | 1.0292 | | 9.20 | 8.18 | 52.3 | 1.0400 | 10.30 | 9.50 | 1.0428 | | 12.45 | 11.07 | 65.6 | 1.0539 | 13.95 | 12.85 | 1.0576 | |
| 6.25 | 5.56 | 40.1 | 1.0272 | 7.01 | 6.46 | 1.0294 | | 9.25 | 8.22 | 52.5 | 1.0402 | 10.35 | 9.55 | 1.0430 | | 12.50 | 11.11 | 65.8 | 1.0241 | 14.01 | 12.90 | 1.0579 | |

it permits of much greater accuracy. The corresponding percentage of solids in the filtrate and the percentage of solids in the pulp from which it is prepared may be ascertained from the index of refraction by Table IV. The per cent of solids in the filtrate may also be calculated from the scale reading of the immersion refractometer at 17.5° C., by the following formula, which is derived from Table IV:

Per cent SOLIDS IN FILTRATE
= 0.258 (scale reading — 15) — 0.0165 (scale reading — 64).

If the index of refraction has been determined by means of an Abbé refractometer, the per cent of solids in the filtrate may be calculated by the following formula:

Per cent SOLIDS IN FILTRATE = 666 $(n_D - 1.3332) - 207 (n_D - 1.3376)$

The per cent of total solids in tomato pulp may also be ascertained from the index of refraction of the liquor prepared by filtering the pulp as shown in Table IV; or, it may be calculated from the immersion refractometer reading by the following formula, which is derived from Table IV:

Per cent SOLIDS IN PULP
= 0.289 (scale reading of filtrate —15) — 0.0185 (scale reading —26.4).

If the index of refraction of the filtrate has been determined by means of an Abbé refractometer, the per cent of solids in the pulp may be calculated by the following formula:

Per cent SOLIDS IN PULP = 748 $(n_D - 1.3332) - 25.5 (n_D - 1.3376)$

It is of interest to note that the relation between the index of refraction of the liquor obtained by filtering tomato pulp and the per cent of solids in that liquid is very similar to the relation between the index of refraction and dissolved solids in beer and wine extract, as shown in the table prepared by Wagner.[1]

In the formula given above, as well as in Table IV, it is assumed that salt is absent. If it be desired to calculate the percentage of solids in a sample containing salt from the index of refraction of the filtrate, it is necessary first to determine the amount of salt present and make correction therefor. For this purpose the table of Wagner[2] may be employed.

This correction is necessary, however, if the percentage of solids be determined by drying, or calculated from specific gravity.

### DETERMINATION OF INSOLUBLE SOLIDS

Transfer 20 grams of the pulp to an eight-ounce nursing bottle, nearly filled with hot water, mix by shaking, and centrifuge until the insoluble matter is collected in a cake in the bottom of the bottle. Transfer the supernatant liquor onto a double, tared filter paper covering the bottom of a Büchner funnel, using suction to facilitate filtration.

Again fill the nursing bottle with hot water, stir the cake of insoluble solids so that it is thoroughly mixed with the water, centrifuge, and decant the supernatant liquor on the filter. Repeat the centrifuging and the filtration of the supernatant liquor once more, and then finally transfer the insoluble solids to the filter paper and thoroughly wash with hot water. Dry the paper and insoluble solids, and weigh. The insoluble solids are quite hydroscopic and the weight must be taken quickly.

[1] "Ueber quantitative Bestimmungen wasseriger Lösungen mit dem Zeiss-schen Eintauchrefraktometer," Table XVII.

[2] *Ibid.*, Table I.

### DETERMINATION OF SUGAR

The sugar of tomatoes is probably always present as invert sugar. If cane sugar is ever present in the raw product it is doubtless inverted during the concentration of pulp. The per cent of sugar given in Tables I and II was determined by the method of Munson and Walker.[1]

### DETERMINATION OF ACIDITY

Accurate results cannot be obtained by the titration of tomato products in the presence of the insoluble solids. If it be desired to determine the acidity in the entire sample of tomatoes or tomato pulp rather than in the expressed juice, the insoluble solids should first be removed by the method given in the determination of insoluble solids. The per cent of acid given in Tables I and II was obtained by titrating the liquor obtained by filtering the pulp. In products of this nature, the addition of an alkali causes a brownish color which has a tendency to obscure the end point shown by the indicator. To obviate this, the sample should be diluted to at least 200 cc. and a larger amount of indicator employed than is necessary with a clear solution. The following details are suggested:

Dilute 20 grams of the filtrate under examination with over 200 cc. of water. Add at least $^1/_2$ cc. of phenolphthalein solution (prepared by dissolving 1 gram of phenolphthalein in 100 cc. of 95 per cent alcohol) and titrate with sodium hydroxide until the end point is obtained. Add 1 cc. of tenth-normal hydrochloric acid, heat the solution quickly to boiling and boil one minute to expel carbon dioxide. Cool the solution quickly to about room temperature, and then add tenth-normal sodium hydroxide until the end point is obtained. The volume of hydrochloric acid added must, of course, be taken into consideration in the final result.

NATIONAL CANNERS' ASSOCIATION, WASHINGTON, D. C.

## A CONCISE GROUP METHOD FOR THE DETECTION OF GELATINIZING AGENTS, PASTY MATERIAL AND THICKENERS, USED IN FOOD PRODUCTS

By LEON A. CONGDON

Received January 12, 1915

The extreme difficulty of detecting various gelatinizing agents, pasty material and thickeners used in food products, has led the writer to work out a group method, by which these substances can be identified even if the unknown contains one or all of the common substances used for gelatinizing agents, etc., such as starch, dextrin, gelatine, acacia, agar-agar, tragacanth, albumen and pectin bodies of the fruit juices. The use of these substances has been quite general in recent years. Hence a study of these materials and their detection in food products is important to the chemist. Thickeners, pasty materials, and gelatinizing agents frequently are used to cheapen the genuine articles of food. In this class may be mentioned agar-agar, which has been found in imitation lemon slices; starch, agar-agar, and gelatine in imitation jelly; dextrin in imitation cocoa cubes. These materials are also used to cover up inferiority. In this class might be mentioned albumen, or white

Bureau of Chemistry, U. S. Dept. Agr. Bull. 107, revised

TABLE I

REACTIONS WITH WATER-SOLUBLE SOLUTIONS OF THE GELATINIZING AGENTS PASTY MATERIALS AND THICKENERS

| GROUPS | GROUP REAGENTS | |
|---|---|---|
| Group I..... | Iodine solution | Blue coloration indicates *starch*. (Sometimes green apples made into jelly will give traces of starch.)<br>Purple coloration indicates *Amylo-dextrin*.<br>Red coloration indicates *Erythro-dextrin*.<br>No coloration may indicate neither starch nor dextrin, but may be *Achro-dextrin*. |
| Group II..... | Millon's or Stokes' reagent (acid nitrate of mercury) | Mixture, after shaking substance in solution with reagent is cloudy. Yellow precipitate with picric acid solution indicates *Gelatine*.<br>Drop of this reagent. Gelatinous precipitate, soluble in excess of this reagent, indicates *Acacia*.<br>A slight white cloudy precipitate may indicate either *Agar-agar or Tragacanth* or both (test for tragacanth as in Group IV). |
| Group III..... | Concentrated solution of sodium borate | A white gelatinous precipitate indicates either *Agar-agar or Acacia* or *both*.<br>C. T. *Acacia* will give a gelatinous, opaque white precipitate with solution basic lead acetate.<br>*Acacia* may be further tested for as in Group II or Group IV or by adding a solution of tannin which gives a bluish black coloration. |
| Group IV..... | Solution of sodium hydrate | A brownish yellow color on heating indicates *Tragacanth*.<br>A white cloudy precipitate indicates *Acacia*. |
| Group V..... | Solution of mercuric chloride | A slight turbidity may indicate *Dextrin*.<br>A white precipitate may indicate *Albumen* and *Gelatine*. |
| Group VI..... | Schweitzer's reagent (solution of cupra-ammonia) | If a concentrated water solution of the unknown is treated with this reagent and placed on glass slide under microscope, a delicate framework of cupric pectate is evident, showing a *Pectin* of fruit or vegetable origin present. |

of egg, which is sometimes used to glaze coffee beans to make them appear better than they really are. Again the thickeners, etc., are used in such products as ice cream and custards, primarily to add bulk to the product, and to give the material in which they are used a frothy appearance. They are also used in this connection to make the ice cream and custards "stand up." A great many ice cream manufacturers use a so-called "ice cream powder." These "ice cream powders" vary in composition, but generally contain one or more of the following: dextrin, acacia, tragacanth, gelatine, albumen, and starch.

This paper deals more specifically with the detection of these gelatinizing agents, pasty materials, and thickeners in food products by a group method.

The above table, prepared and worked out by the writer on actual experiments in the laboratory, places the above-mentioned materials in six groups: I—the iodine solution group; II—the acid nitrate of mercury group; III—the concentrated solution of sodium borate group; IV—the solution of sodium hydrate group; V—the solution of mercuric chloride group; VI—the solution of cupra-ammonia group. A careful study of this group method shows that a new means for testing agar-agar has been discovered. This test is based on Groups II, III and IV. The characteristic reactions for agar-agar depend on a new test for acacia in Group II, that is, one drop of acid nitrate of mercury plus the unknown water solution, which test yields a stringy gelatinous precipitate, *soluble in excess of the reagent*. Since the reagent in Group III precipitates only agar-agar and acacia, it is simply a test to prove whether one or both are present in the unknown water-soluble mixture. The reagent in Group IV does not precipitate agar-agar, and hence if no precipitate is obtained here, agar-agar is present in Group III; if a white, cloudy precipitate occurs, the unknown is acacia, and if a brownish yellow color occurs on heating, the unknown is tragacanth. Acacia may be further tested for with a solution of soluble basic lead acetate, which gives a whitish gelatinous precipitate and again tested for by the acid nitrate of mercury test in Group II as already indicated. The remaining tests in the other groups given in the table are rather well known, but the writer thinks that this group method will be helpful to those interested in food chemistry.

DIVISION OF FOOD AND DRUGS
KANSAS STATE BOARD OF HEALTH, TOPEKA

## TAMARIND SYRUP

By W. C. Taber[1]

Received March 25, 1915

A syrup prepared from the pulp of tamarinds with added sugar has come into use in the United States as a summer beverage that is highly esteemed by Italians. After dilution with water this syrup forms a refreshing drink. The making of this syrup apparently originated in Italy some years ago. The districts of Lombardy and Piedmont are the Italian sections most prominently identified with the making of this product.

The tamarinds used in this country are practically all imported. They are the fruit of a leguminous tree, *Tamarindus indica*, which grows in tropical and semi-tropical countries. A native probably of Africa, it was early introduced into the East Indies, West Indies, Brazil, Mexico and most of the tropical countries. The fruit is a large, flat pod from 4 to 8 in. long, filled with an acid pulp, seeds and a stringy, fibrous matter. In the samples examined in this laboratory the pulp constituted about sixty per cent of the whole fresh fruit as removed from the pod.

The reported analyses of tamarinds are not uniform. The statements in regard to the presence of citric and malic acids are quite conflicting.

Vauquelin,[2] who published one of the earliest analyses of tamarind, reported a large amount of citric acid as one of the constituents. This report can have little weight as the method of identification was faulty. After concentration, the addition of calcium carbonate produced a precipitate, which, on decomposition, gave an acid precipitate with lime water. This would not be sufficient to distinguish between tartaric acid and citric acid.

[1] Assistant Chemist, Bureau of Chemistry.

[2] *Ann. de Chim.*, [1] **6** (1790), 92

Schmey[1] quotes Nevinney, who found 1.5 to 6 per cent of tartaric acid and up to 9.4 per cent of citric. The methods of analyses used, however, are not given.

Mueller[2] reports the examination of nine samples of tamarind pulp freed from seeds. He found an average of 2.2 per cent of citric acid, which figure included the malic acid which may have been present.

Neumann[3] found on the average from ten East Indian, mostly Calcutta, and one West Indian variety 7.062 per cent of free tartaric acid, 3.05 per cent of citric acid, and 0.969 per cent of malic acid.

Adams[4] reports no citric acid in the pulp.

Octave Remeaud,[5] one of the more recent analysts, reports the results from the pulp of a known sample of the fruit and from two commercial samples. His analyses show a total acidity as tartaric of 11.7 per cent on the known sample, largely due to tartaric acid, with a small amount of undetermined acid. His result on invert sugar is high, 42.30 per cent.

Brunner[6] analyzed twenty-one samples of whole tamarinds from Calcutta, and one from the West Indies, and found on the average 1.76 per cent of citric acid, with possible traces of malic in two cases.

From analyses made by Chace, Tolman and Munson[7] some years ago, it was seen again that the fruit in its natural state is remarkable for its large amount of sugar, over 30 per cent, which is mainly reducing sugar, and for its high degree of acidity which they found to be approximately 10 per cent. It has been stated by Pratt and del Rosario[8] that the tamarind contains more acid and more sugar than any other naturally occurring food. These authors[9] recently report the analysis of Philippine tamarinds in which the total sugar as invert is 41.20 per cent, with less than 1 per cent of sucrose, and with an acidity of 15.33 per cent as tartaric.

Other references to the literature on tamarinds may be found in the article by Brunner,[10] but they are of little importance.

The published analyses agree fairly well as to the amount of tartaric acid present, which is the characteristic acid of the fruit. The sum of the potassium tartrate and tartaric acid was found by Brunner and Neumann to be on the average 11.5 per cent. Mueller obtained a slightly higher figure on the pulp freed from seeds.

The fruit examined in this laboratory, which was purchased in the New York market, had an acidity of about 10 per cent, calculated as tartaric. A large part of the acidity was due to tartaric acid, as found by the quantitative precipitation, and the rest to undetermined acids. No citric acid was found in the syrups made from this fruit, and volatile acids only in very small amounts. In view of the method used in making the syrups as outlined below, it may be doubted whether a sufficient amount of citric acid would be extracted from the tamarinds to give a test, taking it for granted that it was present in the original fruit to the extent of 2 or 3 per cent.

The fact that the acidity was lower than that found by some analysts mentioned above may have been due to incomplete ripeness. Geerligs[1] has shown that the composition of the pulp varies with the different stages of ripening. In a typical case the tartaric acid content increased from 3.25 to 15.8 per cent during sixteen days of ripening, and the sugars from 0.73 to 15.2 per cent.

The manufacturing process employed in making commercial tamarind syrups consists simply in making a water extract of the tamarinds by adding water to the fruit, heating the mixture for a few hours, filtering it, and adding sugar until a solid content of approximately 60 per cent is obtained. There are, however, on the market artificial or imitation tamarind syrups which are prepared from citric or tartaric acids and colored with caramel to give the product the appearance of a syrup containing a large amount of tamarind, and sometimes a small amount of the tamarind may be added, varying from 1 to 5 per cent. Glucose is also added in some cases and other fruit juices such as prune or raspberry.

The formulae used for making the true tamarind syrup vary somewhat in the amount of fruit used, some manufacturers using as much as 30 to 35 per cent. In the opinion of makers of high-class goods, tamarind syrup should be a preparation containing a sufficient amount of the extract of tamarind to impart to it the desired acidity and flavor. They apparently agree that at least 2 pounds of the whole tamarind to the gallon of the finished product, or approximately 20 per cent, is necessary to impart the distinctive flavor and the degree of acidity desired.

Six syrups of tamarinds were prepared in the laboratory in the following manner:

The pulp, separated from the seeds and other extraneous matter, was used in making the extract. The amount of whole fruit was calculated from the pulp, which in this sample was 60 per cent of the whole fruit. The pulp was covered with water, placed on the steam bath for several hours, allowed to stand over night, filtered through a linen filter, and washed with hot water. Sugar was added until the percentage of solids was between 50 and 60, and the solution finally filtered for analysis. The large amounts of invert sugar present in Samples 5 and 6 may be accounted for by the fact that they were evaporated on the steam bath after the addition of sugar.

The table shows plainly the gradual increase with increasing amounts of fruit of the non-sugar solids, solids other than sugar and acids, acidity, total acid as tartaric, ash, alkalinity of ash, phosphoric acid, and color. The color in Samples 5 and 6 was increased by the evaporation of the syrup on the steam bath, which resulted in caramelization. A subsequent sample of the same concentration as Sample 6 showed a

[1] *Allg. Med. Centr. Ztg.*, **65** (1896), 633.
*Pharm. Centralhalle*, **23** (1882), 593.
[2] *Pharmacent.*, (1891), p. 15.
[3] *Ztschr. allg. Oesterreich. apoth. Verein*, Aug., **1905**.
[4] *J. pharm. chim.*, **23** (1906), 424.
[5] *Apoth. Ztg.*, **6** (1891), 53.
[6] U. S. Dept. Agr., Bur. of Chem., *Bull.* **87** (1904), 15.
[7] *Phil. J. Sci.*, **8** (1913), Sec. A, No. 1.
[8] *Ibid.*
[9] *Loc. cit.*
[10] *Intern. Sugar J.*, **10** (1908), 572.

color value less than one-half as much. The test of Denigès[1] reagent in the above samples did not indicate citric acid. While it may be questionable whether

Analysis of Tamarind Syrups Prepared in the Laboratory

| Determination | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|---|---|---|---|---|---|---|
| Amount of whole fruit (per cent) | 2.0 | 4.1 | 8.0 | 12.1 | 16.0 | 24.0 |
| Total solids by refractometer (per cent) | 50.9 | 50.6 | 53.3 | 52.0 | 56.8 | 56.7 |
| Reducing sugar before inversion (per cent) | 4.1 | 9.6 | 9.7 | 14.4 | 42.3 | 43.8 |
| Sucrose, by copper (per cent) | 45.6 | 38.8 | 41.3 | 35.4 | 11.5 | 8.8 |
| Total sugar (per cent) | 49.7 | 48.4 | 51.0 | 49.8 | 53.8 | 56.5 |
| Non-sugar solids (per cent) | 1.2 | 2.2 | 2.3 | 2.2 | 3.0 | 4.1 |
| Solids other than sugar and acid (per cent) | 1.08 | 1.79 | 1.86 | 1.60 | 2.18 | 2.99 |
| Total acidity calculated as tartaric (per cent) | 0.12 | 0.21 | 0.44 | 0.60 | 0.82 | 1.11 |
| Acidity (cc. $N/10$ per 100 g.) | 16.3 | 28.2 | 59.3 | 80.5 | 109.2 | 147.9 |
| Tartaric acid, by wine method (per cent) | ... | ... | 0.31 | 0.34 | 0.51 | 0.58 |
| Ash (per cent) | 0.04 | 0.10 | 0.15 | 0.19 | 0.23 | 0.33 |
| Alkalinity of ash (cc. $N/10$ per 100 g.) | 6.8 | 10.4 | 17.6 | 23.5 | 30.3 | 43.0 |
| Phosphoric acid (per cent) | Trace | 0.004 | 0.008 | 0.01 | 0.016 | 0.018 |
| Color in 1/8 in. cell (degrees Brewer's scale) | 1.5 | 3.0 | 6.0 | 8.0 | 28.0 | 54.0 |
| Citric acid | None | None | None | None | None | None |

there is citric acid present in tamarinds either ripe or unripe, there is at least apparently not a large amount.

Organoleptic tests on the samples gave the following results:

The sample containing 2 per cent of fruit has no perceptible taste other than that due to sugar. The sample containing 4 per cent of the fruit did not differ perceptibly from the first syrup. In the syrup with 8 per cent of fruit some acidity was noticeable, while in the 12 per cent product there was a marked acidity, as well as a slight trace of the characteristic flavor, although not enough for a good product. In the syrup containing 16 per cent of fruit the liquor more nearly approached in general qualities the standard of a good tamarind syrup. The last syrup, having a concentration of 24 per cent, formed the most satisfactory product of the series. These tests agree closely with the opinions of the best manufacturers, that 2 pounds of whole tamarinds to the gallon, or nearly 20 per cent of fruit, are necessary to produce the distinctive flavor and desirable degree of acidity.

The interpretation of analytical results on commercial samples, when added substances are present, is not so simple a matter. The results given above may, however, be of value in some cases, in forming an opinion as to the amount of tamarind fruit used in a syrup, and possibly in regard to its adulteration.

Bureau of Chemistry
Department of Agriculture
Washington, D. C.

## THE HYDROLYSIS OF SUGAR SOLUTIONS UNDER PRESSURE[2]

By W. S. Hubbard and W. L. Mitchel
Received March 22, 1915

In the past few years there have come on the market several syrups under various trade names for the use of the manufacturer of fountain supplies, canned fruit and similar lines requiring a heavy syrup. It is claimed for these syrups that they are better than ordinary sugar syrup in that they will not crystallize out and some even claim that they are sweeter. It is quite well known, however, that these syrups are invert sugar and when they have been correctly prepared will not crystallize out and do make a superior article to use in many food products.

Tartaric acid is used in the preparation of at least one of these syrups on the market, and there is no reason why acetic acid should not be used, for it could be gotten rid of easily. The syrup in which tartaric acid had been used, however, crystallized out into a solid mass after standing two or three months. One in which we were unable to detect any catalytic agent was at the end of six months in as good condition as at the beginning. The latter contained about 46 per cent invert sugar while the former had about 75 per cent.

That bacteria, enzymes, acids, salts, elevated temperatures[1] and carbon dioxide[2] bring about hydrolysis of sugar solutions is known. Ordinary heating brings about hydrolysis, but according to Lund[3] if the air is excluded or the carbon dioxide in the air eliminated, no inversion occurs even on heating 24 hours at 100° C. Lippman[4] and Sheibler[5] found that it was necessary to have moisture present with the carbon dioxide. They report that by raising the temperature and increasing the pressure a complete inversion could be brought about. Follenenius[6] claims to have obtained a very pure invert sugar by injecting a boiling sugar solution into a vessel of carbon dioxide at a pressure of 1.25 to 1.5 atmospheres; others,[5] however, were not able to achieve such good results. When sugar solutions are hydrolyzed by heat alone or by superheated steam[6] a certain amount of color[7] develops which, of course, is objectionable in a commercial article. This investigation was taken up with the idea of finding under what conditions hydrolysis can be successfully carried on without caramelization. Unfortunately, however, we have not been able to carry the work to the point we should desire before publishing, but due to the fact that both of us have since engaged in other fields and see no very immediate prospects of completing the work, we have decided to publish our results. We consider our data of sufficient importance and value to many manufacturers who have been paying a high price for a trade name, to warrant publication.

An autoclave in the bacteriological laboratory was used for obtaining the elevated temperatures and pressure: 250 cc. Erlenmeyer flasks of Jena glass of as near the same shape and age as possible, were employed. They were stoppered with cotton. It was desired to have a glass as insoluble as possible and free from imperfections to avoid introducing outside factors: our final results may have justified this. In the first

[1] *Ann. chim. phys.*, **18** (1899), 415.

[2] This title might better be "The Hydrolysis of Sugar Solutions at Elevated Temperatures," but to the manufacturer the present title better conveys the idea of the process used.—Authors.

[1] Lippman, "Chemie der Zuckerarten," **2**, 1225–1226

[2] Lippman, *Ibid.*, **2**, 1240.

[3] Lund, *Ber.*, **9**, 277.

[4] Lippman, *Ibid.*, **13**, 1823.

[5] Lippman, *Ibid*, **2**, 1240

[6] O. Loew, *Ztschr. Chem.*, **1867**, p. 510

[7] Eckleben, Lippman, "Chemie der Zuckerarten," **2**, 1225.

set of experiments ordinary distilled water was used having a conductivity of about $6 \times 10^{-6}$. The invert sugar was determined by titration with Fehling's solution which had been standardized against chemically pure dextrose. The results of the experiments are given in Table I.

The pressures are expressed in kilograms per square centimeter above atmospheric pressure.

TABLE I—EXPERIMENTAL RESULTS

| Pressure Above atmospheric Kg. per sq. cm. | Temp. ° C. | Time Hrs. | Concentration G. Sugar | Concentration G. Water | Per Cent Inversion Beet Sugar | Per Cent Inversion Cane Sugar |
|---|---|---|---|---|---|---|
| 1 | 120 | 1 | 50 | 50 | 0.78 | 1.85 |
| 1 | 120 | 2 | 50 | 50 | 3.40 | 10.25 |
| 1 | 120 | 3 | 50 | 50 | 12.38 | 31.98 |
| 1.25 | 123.5 | 1 | 150 | 150 | 5.95 | .... |
| 1.25 | 123.5 | 2 | 75 | 50 | 38.76 | .... |
| 1.25 | 123.5 | 2 | 50 | 200 | 42.18 | .... |
| 1.5 | 127 | 1 | 75 | 75 | 9.68 | 14.50 |
| 1.5 | 127 | 2 | 75 | 75 | 54.40 | 58.52 |
| 1.5 | 127 | 3 | 25 | 25 | 91.02 | 93.72 |

An analysis of the results in Table I leads one to believe that the cane sugar solutions hydrolyze more readily than beet sugar, but from another series of experiments which we ran we would say that it depends upon the purity of the sugar used. Cane sugar is perhaps more likely to be pure and, therefore, less likely to contain negative catalyzers. Of course, if beet sugar contains impurities, one might expect it to contain a catalyzer, but such does not seem to be the case, at any rate with the samples we examined. It will be noticed that by increasing the temperature and pressure the inversion increases and by lengthening the time sufficiently 100 per cent could be produced. From the 123.5° runs it seems evident that concentration plays a part and within certain limits it might be said that the more dilute the greater the hydrolysis.

We also ran a set of experiments in which the temperature was 124° C. and the pressure 1.375 kg. We used cane sugar, beet sugar, and rock candy. To dissolve the sugar, ordinary tap water which was slightly alkaline, the distilled water already mentioned and distilled water which had been recently boiled, were used. Here we found that in each case where the tap water was used that the hydrolysis had been retarded very considerably and the resulting solution was brown, showing considerable caramelization; this was not shown in any of the other runs. The beet sugar showed the same amount of inversion as the cane (both of these samples were different from the material used in the first set of experiments), and the rock candy showed considerably greater inversion in every case. This would seem to indicate that the purer the sugar the greater the inversion.

The inversion is undoubtedly due to the hydrogen ion concentration of the solutions and we had hoped to make such measurements. Kullgren[1] states that the inversion of a sugar solution may be almost completely accounted for by the degree of dissociation of water and sugar with the rise of temperature.

We believe that a concentration of 1 sugar : 5 water will give the most satisfactory results when a pressure of 1.375 kg. and a temperature of 124° C. is used; the time can be adjusted to suit the needs. Since a syrup containing 85 sugar : 100 water is usually needed in preserving and the amount of invert sugar in the syrups on the market is about 50 per cent then a more dilute solution might be started with, the inversion run to 90 per cent or more if desired and the necessary sugar to bring it up to the proper concentration added later. It is necessary to avoid too great concentration when inverting and also too great a temperature and pressure or there will be some caramelization, a thing which, of course, must be avoided. It is obvious that the manufacturer in making these invert sugar solutions must choose sugar and water with considerable care.

LABORATORY OF FOOD AND DRUG ANALYSIS
UNIVERSITY OF MICHIGAN ANN ARBOR

[1] *Z. physik. Chem.*, **41**, 415.

## REDUCTION OF COPPER OXIDE IN ALCOHOL VAPOR IN REDUCING SUGAR DETERMINATIONS AND COPPER ANALYSIS

By A. Wedderburn

Received January 14, 1915

In the usual gravimetric invert sugar determination, the reduced copper is weighed as $Cu_2O$ or after ignition as CuO. In weighing either oxide there is always some doubt as to the accuracy of the result. It is difficult to dry the cuprous oxide with certainty that some oxidation does not occur and further the oxide is liable to be contaminated with organic matter, giving a high result. If ignited to the higher oxide, great care is necessary that the oxidation be complete and that the crucible be not held in the reducing flame, the action of which would cause a partial reduction. Even if the cuprous oxide is heated in a muffle furnace considerable time and care are necessary to insure a complete oxidation to CuO. The hygroscopic nature of cupric oxide makes it difficult to weigh with accuracy. In the hands of the ordinary laboratory assistant I have found a difference of as high as 12 mgs. after careful re-ignition of the weighed cupric oxide.

The ideal method is to weigh the copper in the metallic state. In accurate work the metal is obtained by the electrolytic method or by reducing the oxide in hydrogen. Both of these methods require considerable manipulation and time, also special apparatus not available in most sugar-house laboratories.

With the purpose of simplifying the electrolytic method and avoiding the use of expensive platinum cathodes, I made some experiments in electrolytically depositing the copper directly from alundum crucibles on copper cathodes, with partial success. I found some difficulty in cleaning the copper cathodes perfectly, prior to weighing. Mr. G. L. Spencer[1] advised that the copper could be readily cleaned by heating to redness and immersing in strong alcohol. This suggestion led to the reduction method described below.

The cleaning action of the alcohol is merely the reduction of the film of oxide to metallic copper and it interested me to know to what extent a precipitate of copper oxide could be reduced by the same means. A precipitate of cuprous oxide was collected on an

[1] Chief Chemist of the Cuban-American Sugar Company.

alundum crucible, washed with hot water, the crucible heated to redness and immersed in 95 per cent alcohol. The reduction was complete, the deposit of metallic copper adhering very firmly to the walls of the crucible. A number of trials with solutions of known strength gave very accurate results, but the shock to the crucibles was too great, many of them cracking after being used two or three times.

To avoid the breakage of crucibles the reduction was next tried in the vapor of alcohol and with entire success. The details of the method follow.

Collect the suboxide of copper on an alundum filtering crucible, using Spencer's filtering funnels with suction. Thoroughly wash with hot water followed by alcohol. Heat the crucible to redness a sufficient time to burn off any organic matter that may accompany the copper oxide. Allow the crucible to cool until the redness just begins to disappear and then immerse it in an atmosphere of alcohol vapor as follows:

Bend the wire ends of a small pipe stem or silica covered triangle so as to form a tripod support for the crucible and set the tripod on the bottom of a 400 cc. beaker, preferably of metal. Put into the beaker sufficient strong alcohol (denatured alcohol will answer) to cover the bottom to the depth of about 1 cm. and cover the beaker with a watch glass. Heat the alcohol to boiling and continue heating until the vapors begin to condense on the under side of the cover glass, then place the hot crucible on the support above the alcohol and replace the cover glass. If the crucible is too hot the alcohol may take fire but the flame may be readily extinguished by blowing directly on top of the cover glass, and no harm is done. Allow the alcohol to continue to boil a moment after putting in the crucible, then remove the beaker from the source of heat. The heat radiated from the crucible will prevent any further condensation of alcohol on the cover glass. The crucible should remain in the covered beaker until cooled to a temperature a little above that of the alcohol vapor to prevent oxidation of the copper. About 3 or 4 minutes is sufficient. It may then be taken from the beaker and the cooling be finished in a desiccator, preliminary to weighing. If the crucible is quite cold when taken from the beaker it should be moistened with a little pure alcohol and this be burned, holding the crucible in an upright position. After the alcohol burns off the crucible is ready for cooling in the desiccator. A porcelain Gooch may be used if preferred.

The reduction to metallic copper is almost instantaneous and is complete. The results are identical with those by reduction in hydrogen, closely approximating the electrolytic method.

This method may be used in copper analysis, the separations being made in the usual way and the copper collected in any form readily burned to the oxide. If in form of copper sulfide the precipitate forms in clots and is burned to the oxide with difficulty. It is preferable to dry the sulfide, roast it gently, and then with a glass rod flattened at one end, crush it to a powder. The rod should be wiped off with a piece of ashless filter paper and the paper burned in the crucible. The heating may then be continued to drive off all sulfur and the oxide reduced in alcohol vapor.

THE CUBAN-AMERICAN SUGAR COMPANY
CENTRAL "TINGUARO," PERICO, CUBA

## THE DETERMINATION OF LINT IN COTTONSEED-MEAL

By R. N. BRACKETT
Received January 7, 1915

While at first sight it might appear an easy matter to determine the amount of lint in cottonseed-meal by purely mechanical means, it has been found impracticable to do so with any degree of accuracy. The following chemical method of estimating the lint was worked out and found to give very satisfactory results:

As preliminary to the work it was first ascertained that alkali and acid of 1.25 per cent strength, as used for crude fiber[1] determinations, was practically without action on lint.

A sufficient amount of cottonseed was then freed from lint by first picking and finally singeing the last portions carefully to avoid injury to the seed. The seeds were then cut open and the meats removed completely from the hulls.

Crude fiber[2] was prepared from both the hulls and the meats, by the method above referred to. The crude fiber thus prepared was treated, in 0.2-gram portions side by side with the same weight of lint, on a boiling water bath, with 25 cc. of a solution of zinc chloride for three minutes, the time required to dissolve the lint. In this way the action of the zinc chloride[3] solution on the crude fiber was determined, and the necessary correction made in carrying out a determination of lint in ordinary cottonseed-meal. The zinc chloride solution was prepared by dissolving metallic zinc in concentrated hydrochloric acid, concentrating until the solution solidified on cooling, and then adding twice the weight of 40 per cent hydrochloric acid. On treating the crude fiber and lint with the zinc solution, the contents of the beakers were stirred vigorously during the three minutes necessary to dissolve the lint, and filtered hot through weighed porcelain Gooch crucibles with asbestos mats; the residues in the case of the fibers were washed with 25 cc. of the zinc solution, then with water and finally with a little 95 per cent alcohol dried and weighed.

EXAMPLE—On treating 0.2-gm. portions of (*a*) crude fiber from hulls, (*b*) crude fiber from meats, and (*c*) "crude fiber" from a cottonseed-meal, with 25 cc. of a zinc chloride solution for three minutes, the amount dissolved was as follows: (*a*) 0.0687 g., (*b*) 0.0678 g. and (*c*) 0.1000 g. The correction was, therefore, 0.06825 gram. Hence the amount of lint in the "crude fiber" from the cottonseed-meal was 0.1000 − 0.06825 = 0.03175 gram. But the

[1] Methods of Analysis, A. O. A. C., *Bull.* **107**, revised, p. 56.

[2] This crude fiber includes ash ingredients of the fiber. The ash is, however, so small in amount as to be negligible, unless a large proportion of hulls is contained in the cottonseed-meal. Only in the latter case would it be necessary to take the ash of the fiber into account in calculating the amount of lint in the meal.

[3] "Cross Bevan's Method for Cellulose" Cohn's "Tests and Reagents," p. 52.

meal, on analysis, gave 10 per cent of "crude fiber," which gives 1.5875 as the per cent of lint in the cottonseed-meal, since 2 grams of the cottonseed-meal contained 0.03175 gram lint.

To further test the method the following mixtures were made:

(*a*) 1 gm. of cottonseed-meal with 0.1 gram of lint.

(*b*) 1 gm. of cottonseed-meal with 0.2 gram of lint.

The crude fiber and lint amounted in (*a*) to 0.2001 gram and in (*b*) to 0.3032 gram. The factor for a new zinc chloride solution based on the use of 50 cc. for three minutes was 0.05125 gram.

| | (*a*) | (*b*) |
|---|---|---|
| Crude fiber and lint | 0.2001 g. | 0.3032 g. |
| Crude fiber residue | 0.0393 | 0.0323 |
| | 0.1608 | 0.2709 |
| Correction | 0.05125 | 0.05125 |
| Lint | 0.10955 | 0.21965 |
| Hence, per cent lint in mixture | 9.96 | 18.30 |
| Calculated per cent lint in mixture | 10.53 | 17.99 |

The method as given was worked out under the immediate direction of Assistant Professor J. H. Mitchell by two students of the last senior class, as a thesis. With more careful work and experience, no doubt much more accurate results could be obtained.

At the commencement of the work Schweitzer's reagent (an ammoniacal solution of copper hydroxide) was tried, but the solution as prepared by the students failed to dissolve lint.

Acknowledgments are due Mr. Mitchell for supervising the work, and to Messrs. J. M. McIntosh and E. R. Gilmore, the two students, for their careful and faithful prosecution of the work.

CLEMSON AGRICULTURAL COLLEGE
CLEMSON COLLEGE, S. C.

## SOME IMPORTANT CONSTITUENTS IN THE FRUIT OF THE OSAGE ORANGE

By J. S. McHargue

Received February 8, 1915

The Osage orange (*Maclura pomiferum*) is a small tree which, when first discovered, was growing wild in the southwestern portion of the United States between the Arkansas and Missouri rivers. This particular section of the country was for many years the home and hunting grounds of the Osage Indians. To them this tree was of economic importance for two reasons—from the trunk they made bows which possessed superior elasticity, and from its fruit they obtained a juice which possessed all the necessary adhesive properties for making their war paint. On account of this association with this tribe of Indians and from the resemblance of the fruit to that of the true orange, the tree has received the popular name of Osage orange, although there is no botanical relation between the two plants.

The chief source of value of this plant to the white man has been, first, for growing rural hedges, and secondly, for a crude yellow dye which is obtained from the roots. Owing to its adaptability to the climatic conditions existing in the Mississippi valley it may be found growing in almost any part of this area today, although its use as a hedge is being abandoned.

Through Central Kentucky many farmers have allowed their hedges to go untrimmed or permitted the plant to grow in out-of-the-way nooks until no small area is covered with this tree. The young tree grows rapidly on good land and the female trees begin bearing large quantities of fruit at from six to ten years of age.

At maturity the fruit has a greenish yellow color, an average diameter of $3^1/_2$ inches and an average weight of one to one and a half pounds. The fruit, or hedge balls, as they are commonly called, consists of a dense pear-shaped core at the center from which radiate rather long, irregular sized cells that terminate in an enlarged or club form, thus making an irregular surface. The cells are made up of two parts, the milk sacks and the seed sacks. The milk sacks form about two-thirds of the entire length of the cell and extend to the surface. The seed sacks lie beneath the milk sacks and are attached to the core at their base. The milk sacks contain a milky, mucilaginous fluid which in the ripe fruit is neutral to litmus, reacts only slightly with a tincture of guaiacum for oxidases, has an insipid taste and an odor similar to that emitted by the crushed twigs of cedar.

In 1912 considerable interest was aroused through newspaper dispatches emanating from Professors Emerson and Roess of the University of Kansas, who stated that they had discovered in the fruit of the Osage orange a new and cheap source of India rubber. This announcement, according to Fox,[1] created considerable interest among the rubber factories generally and perhaps more in particular among those at Akron, Ohio. Accordingly, Fox read a report of his previous investigations on the Osage orange before The Eighth International Congress of Applied Chemistry, at New York, in 1912. His investigations show that the Osage orange does not contain rubber of any commercial importance.

So far as the literature shows, the above summarizes the work that has thus far been done on the Osage orange from any standpoint.

Recently there appeared, in one of our leading farm journals, an inquiry as to the chemical composition of the Osage orange. This paper also stated that certain farmers in Illinois had been feeding the oranges to their stock and found that they ate them with considerable relish.

In order to find out more definitely concerning the composition of this fruit, a number of oranges were collected in November of 1914 and analyzed (see Tables I and II).

The oranges were prepared for analysis as follows: the outside milky cells were pared off to the seeds; the part containing the seeds was pared off to the core, and each portion dried and kept separately. After drying, the milky portion was ground fine for analysis.

The acetone extract is a brownish, semi-solid resin, at ordinary temperature.

The oranges contain a rather large amount of oval-shaped seeds, the kernels of which are approximately $^3/_8$ in. long and $^1/_8$ in. thick. They are easily separated from the hulls when dry. Kernels were separated from the hulls and dried at 100° C.

[1] Orig. Comm. 8th Inter. Cong. App. Chem., Appendix, pp. 593-597

The oil from the kernels has a viscosity slightly less than that of either refined cottonseed oil or linseed oil. It absorbs its maximum amount of oxygen in

TABLE I—ANALYSIS OF THE OSAGE ORANGE (PERCENTAGES)

| | |
|---|---|
| $H_2O$ in ripe fruit | 80.00 |
| Gums and resins in dry pulp (acetone extr.) | 29.30 |
| Nitrogen in dry pulp | 2.81 |
| Protein in dry pulp (N × 6.25) | 17.56 |
| N in pulp after acetone extraction | 3.42 |
| Protein in pulp after acetone extraction (N × 6.25) | 21.34 |
| Oil in seed (ether extr.) | 42.04 |
| N in oil-free meal | 10.80 |
| Protein in oil-free meal (N × 6.25) | 67.50 |

| MINERAL CONSTITUENTS | Dry pulp | Dry pulp after extracting with acetone | Oil-free meal |
|---|---|---|---|
| CaO | 0.16 | 0.23 | 0.24 |
| MgO | 0.20 | 0.28 | 0.73 |
| $K_2O$ | 3.82 | 5.40 | 1.32 |
| $Na_2O$ | 0.13 | 0.18 | 0.19 |
| $P_2O_5$ | 0.67 | 0.94 | 0.60 |
| Ash (crude) | 6.60 | 9.33 | 4.60 |

from fifteen to twenty hours, at 100° C. and thickens to a resin-like mass. Data obtained by analysis are given in Table II with those of oils having similar specific gravity, iodine numbers and saponification values as given in Allen's "Commercial Organic Analysis."

TABLE II—ANALYSES OF OSAGE ORANGE SEED OIL AND SIMILAR OILS

| | Specific gravity | Iodine number | Saponification value | Saponification equivalent |
|---|---|---|---|---|
| Osage orange seed oil | 0.929 | 134–136 | 192 | .... |
| Linseed oil | 0.931–0.941 | 175–201 | 190–201 | .... |
| Sunflower seed | 0.924–0.926 | 123–136 | 188–193 | .... |
| Cottonseed oil | 0.922–0.925 | 108–110 | 191–196 | .... |
| Peanut oil | 0.917–0.921 | 85–103 | 190–197 | 291.97 |

From the analyses in Tables I and II it may be seen that the pulp and seed of the Osage orange contain valuable feed, fertilizer, oil, and resin constituents. The dried pulp of this fruit contains 29.30 per cent resins and gums and in addition, more nitrogen and more than twice as much potash as wheat bran.

From the seed a new oil is obtained which has not been previously described. This oil has a light lemon color, a viscosity below that of refined cottonseed and linseed oils, a very pleasant odor and an insipid, oily taste. Its physical properties, such as specific gravity, iodine number, saponification value and oxygen absorption rate, etc., show that it is a semi-drying oil belonging to the linseed oil class. The yield of this oil is equal to that of linseed and peanut, and 1.7 times that of cottonseed.

The analysis of the oil-free cake shows that it contains 10.80 per cent of nitrogen, which is equivalent to 67.50 per cent of protein. This is 1.8 and 1.5 times more nitrogen than is contained in linseed and cottonseed meal, respectively. Meat scrap contains about 1 per cent more nitrogen than the oil-free cake of Osage orange seed.

It is also well known that the wood of the Osage orange possesses excellent properties of elasticity, durability and fineness of grain. These valuable properties, in connection with that of the fruit, should make this tree a possible economic factor in the reforestation of abandoned farm lands. It is also quite likely that the foliage of this tree would possess an additional fertilizing value with respect to nitrogen and potassium over many of our common forest trees.

This tree, under favorable conditions, produces a trunk two feet in diameter, and grows to a height of sixty feet; during its period of growth the female tree produces many tons of fruit. Therefore, it is quite probable that with due care and intelligence this tree could be made the source of a profitable industry through the utilization of its timber and the different products of its fruit.

KENTUCKY AGRICULTURAL EXPERIMENT STATION
LEXINGTON

## ETHER-SOLUBLE MATTER IN THE NITROGEN-FREE EXTRACT OF FEED-STUFFS

By J. B. RATHER[1]

Received October 27, 1914

It has long been known that the extraction of dried samples of plant and animal products with ether for 16 hours, as in the determination of fat, does not completely remove ether-soluble material. The extraction has, however, been considered complete enough for practical purposes. Any ether-soluble matter in excess of that obtained from the usual ether extract, after deducting any possible nitrogenous matter and ash, would fall within the group known to agricultural chemists as "Nitrogen-free extract."

Browne[2] states that upon pepsin digestion of steer feces and water digestion of molasses feeds, etc., considerable material is rendered soluble in ether, in excess of the ordinary ether extract.

Fraps and Rather[3] show that chloroform extracts from hays and fodders, previously extracted with ether, more or less material which is soluble in ether. Generally this is considerably less than the previous ether extract of the same samples.

### EXPERIMENTAL

Twelve samples of concentrated feeding-stuffs and twelve samples of hays and sheep excrements from them were studied.

#### AMOUNT OF ETHER-SOLUBLE MATTER IN THE NITROGEN-FREE EXTRACT

The determinations listed below were made and the results recorded in Table I.

1. ETHER EXTRACT—The material soluble in ether, the "crude fat," was determined by the official method[4] of the A. O. A. C.

2. ETHER-SOLUBLE MATTER IN ALCOHOLIC SODA EXTRACT—This is the sum of the unsaponifiable matter, fatty acids, and saponified residue, of the alcoholic soda extract of these samples determined by the alcoholic soda method.[5]

3. ETHER-SOLUBLE MATTER NOT DIRECTLY EXTRACTED BY ETHER—This is the remainder obtained by subtracting the results by (1) from (2).

4. ETHER-SOLUBLE NITROGEN × 6.25—The samples were extracted with ether and the ether-soluble matter obtained in the residue, by the alcoholic soda method. Nitrogen was determined in this by the Kjeldahl method. The factor 6.25 was used because that is the factor with the aid of which the ordinary nitrogen-free extract is obtained, and not because any of the

[1] Under the general direction of G. S. Fraps, chemist. Abstracted by the author from Texas Experiment Station, *Bull.* **169**.

[2] Proc. 20th Conv. A. O. A. C.

[3] Texas Experiment Station, *Bull.* **162**.

[4] (U. S. D. A., Bureau Chemistry, *Bull.* **107**, revised.)

[5] THIS JOURNAL, **7** (1915), 218.

nitrogen was thought to be present in the form of protein.

5. NITROGEN-FREE EXTRACT—The percentage of nitrogen-free extract was obtained in the usual manner by subtracting the sum of the percentages of protein, ether extract, crude fiber, water and ash from 100 per cent. The analyses were furnished through the courtesy of Dr. G. S. Fraps.

6. ETHER-SOLUBLE MATTER IN THE NITROGEN-FREE EXTRACT—This represents the difference between the results by (3) and (4) above, calculated in percentage of nitrogen-free extract.

TABLE I—PERCENTAGE ETHER-SOLUBLE MATTER IN FEED-STUFFS BY VARIOUS METHODS

| | | Ether Soluble | | | | N-Free Extract | |
|---|---|---|---|---|---|---|---|
| No. | Materials Tested | Ether extr. | In alc. soda extr. | Soluble matter not directly extracted by ether | N × 6.25 | Amt. found by diff. | Ether soluble matter in |
| 1 | Wheat shorts | 3.79 | 5.38 | 1.59 | | 57.65 | 2.76 |
| 2 | Corn chops | 4.31 | 4.79 | 0.48 | | 68.01 | 0.71 |
| 3 | Cottonseed-meal | 15.23 | 15.15 | 0.00 | | 52.00 | 0.00 |
| 4 | Rice bran | 7.75 | 9.66 | 1.91 | | 49.70 | 3.84 |
| 5 | Milo maize chops | 3.22 | 3.32 | 0.10 | | 68.70 | 0.15 |
| 6 | Cold-pressed cottonseed | 7.26 | 7.81 | 0.55 | | 31.70 | 1.74 |
| 7 | Kafir chops | 3.20 | 3.68 | 0.48 | | 68.74 | 0.70 |
| 8 | Corn bran | 8.59 | 9.06 | 0.47 | | 61.23 | 0.77 |
| 9 | Red rice | 1.64 | 2.36 | 0.72 | | 67.30 | 1.07 |
| 10 | Wheat bran | 4.10 | 5.67 | 1.57 | | 51.07 | 3.07 |
| 11 | Wheat bran | 7.63 | 8.38 | 0.73 | | 53.17 | 1.14 |
| 12 | Rice polish | 10.38 | 11.49 | 1.11 | | 57.76 | 1.92 |
| 13 | Tobasa grass | 0.92 | 2.62 | 1.70 | 0.19 | 46.18 | 3.27 |
| 14 | Excrement from 13 | 1.06 | 3.50 | 2.14 | 0.22 | 43.04 | 4.46 |
| 15 | Prairie hay | 2.30 | 3.89 | 1.59 | 0.24 | 47.82 | 2.82 |
| 16 | Sudan grass | 1.46 | 3.23 | 1.17 | 0.16 | 48.15 | 3.34 |
| 17 | Excrement from 15 | 2.83 | 6.28 | 3.42 | 0.24 | 43.28 | 7.35 |
| 18 | Excrement from 16 | 1.90 | 5.73 | 3.83 | 0.21 | 47.40 | 7.64 |
| 19 | Sudan straw | 1.44 | 3.69 | 2.25 | 0.24 | 47.12 | 4.77 |
| 20 | Sorghum hay | 1.83 | 3.32 | 1.50 | 0.24 | 46.25 | 2.72 |
| 21 | Excrement from 19 | 1.71 | 5.37 | 3.66 | 0.24 | 43.81 | 7.81 |
| 22 | Moth bean hay | 1.55 | 3.98 | 2.43 | 0.28 | 34.85 | 6.17 |
| 23 | Excrement from 20 | 1.78 | 5.82 | 4.04 | 0.74 | 43.50 | 8.74 |
| 24 | Excrement from 22 | 3.03 | 7.01 | 3.98 | 0.37 | 29.14 | 12.39 |
| | Average for concentrates | 6.01 | 6.81 | 0.80 | | 58.17 | 1.49 |
| Average for hays and excrements | | 1.82 | 4.53 | 2.71 | 0.24 | 42.96 | 5.97 |

The ether-soluble matter in the alcoholic soda extract in excess of that in the ether extract, varies in the concentrates from zero in cottonseed-meal to 1.91 per cent in rice bran, and averages 0.80 per cent. In the hays and excrements from them, it varies from 1.50 per cent in sorghum hay to 4.04 per cent in excrement from sorghum hay, and averages 2.71 per cent, about 150 per cent of the average for the ether extracts of the same samples (see Table I, column 1).

In calculating the ether-soluble matter of the nitrogen-free extract, we have assumed that the ether-soluble matter of the concentrates in column 3 in the table contained no nitrogen. The material may not be completely nitrogen-free, but if it had as much nitrogen, relatively, as the extracts of the hays, which derive their nitrogen in part at least from chlorophyll, the average nitrogen content would be only 0.07 per cent calculated as protein.

The ether-soluble matter in the nitrogen-free extract of the concentrates varies from zero in cottonseed-meal to 3.84 per cent in rice bran and averages 1.49 per cent. The ether-soluble matter in the nitrogen-free extract of hays and excrements from them varies from 2.72 per cent in sorghum hay to 12.39 per cent in excrements from moth bean hay, and averages 5.97 per cent.

## THE NATURE OF THE ETHER-SOLUBLE MATTER IN THE NITROGEN-FREE EXTRACT

By subtracting the percentages of the various constituents of the ether extract from those of the ether-soluble portion of the alcoholic soda extract (results are given in a preceding article) and calculating the remainder in percentage of nitrogen-free extract, the general nature of the ether-soluble portion of the nitrogen-free extracts of these samples may be determined. This has been done and the averaged results are shown in Table II:

TABLE II—PERCENTAGE COMPOSITION OF ETHER-SOLUBLE CONSTITUENTS OF THE NITROGEN-FREE EXTRACT

| | Concentrates | | | Hays and Excrements | | |
|---|---|---|---|---|---|---|
| Determination | Max. | Min. | Av. | Max. | Min. | Av. |
| Unsaponifiable | 22 | 0 | 2 | 15 | 0 | 3 |
| Total fatty acids | 100 | 71 | 98 | 44 | 17 | 30 |
| Saponified residue | 49 | 0 | 0 | 80 | 40 | 67 |

While the minimum figure is given in Table II as zero, in fact some of the results were negative. The averages shown were obtained from the algebraic sums of these differences.

In the concentrates the ether-soluble matter in the nitrogen-free extract consists on an average almost entirely of fatty acids. The variations are considerable in case of the saponified residue and the unsaponified matter.

In the hays, and excrements from them, the principal constituents of the ether-soluble matter in the nitrogen-free extract consist of saponified residue (including chlorophyll products) with some fatty acids and a little unsaponifiable matter, probably wax alcohols.

## THE UTILIZATION VALUES OF THE ETHER-SOLUBLE MATTER OF NITROGEN-FREE EXTRACT

Digestion experiments on the six hays studied above were made with sheep.[1] The results are shown in Table III:

TABLE III—PERCENTAGE UTILIZATION VALUES OF SOME ETHER-SOLUBLE CONSTITUENTS OF THE NITROGEN-FREE EXTRACT

| | Maximum | Minimum | Average |
|---|---|---|---|
| Fatty acids | 36.7 | 0.0 | 11.2 |
| Saponified residue | 37.8 | 12.6 | 21.7 |
| Ether extract | 59.5 | 19.3 | 35.5 |

In the hays examined the fatty acids had a utilization value of zero in four cases, and averaged only 11.2 per cent available. The saponified residue was utilized to a greater extent, with an average of 21.7 per cent. These figures are considerably lower than the average for the utilization of the ether extract ("crude fat") of the same hays (35.5 per cent). The fatty acids in the nitrogen-free extract of the hays examined were only slightly available to sheep, and the saponified residue was utilized only about 60 per cent as well as the ether extract of these hays.

## SUMMARY

The nitrogen-free extract of twelve concentrated feeding-stuffs contained from 0 to 3.84 per cent of ether-soluble material, and averaged 1.49 per cent. The nitrogen-free extract of six hays and six excrements from them contained from 2.72 per cent to 12.39 per cent of ether-soluble material, and averaged 5.97 per cent.

In the concentrates examined, this ether-soluble material consisted on an average of 2 per cent un-

[1] For the method of conducting the experiments see Texas Experiment Station, *Bull.* **147**.

saponified and 98 per cent fatty acids. In the hay and excrements from them it consisted on an average of 3 per cent unsaponified, 30 per cent fatty acids, and 67 per cent saponified residue.

The fatty acids in the nitrogen-free extract of six hays were utilized by sheep, 11.2 per cent on an average, and the non-fat organic acids 21.7 per cent. Of the same hays 35.5 per cent of the ether extract ("crude fat") were utilized.

TEXAS EXPERIMENT STATION
COLLEGE STATION, TEXAS

## COMPOSITION OF CERTAIN FISH FERTILIZERS FROM THE PACIFIC COAST AND THE FERTILIZER VALUE OF DEGREASED FISH SCRAP

By JOHN R. LINDEMUTH[1]

Received February 4, 1915

The availability of the fish waste of the Pacific Coast as a fertilizer is one of the investigations now being carried on by this Bureau in its search for possible sources of fertilizer material under the direction of Dr. F. K. Cameron. In this connection Dr. J. W. Turrentine, during the summer of 1913, visited the fishing and fish-canning industries along the coast of California, Oregon, Washington, and Alaska. The results of his investigations appeared as a bulletin of this Department. In conjunction with this work a number of samples of fish scrap prepared from various fish were collected and sent to this laboratory for analysis.

The list comprises samples of the raw cuttings from Humpback salmon, the prepared scrap from Humpback, Chinook salmon, Sardine, Tuna, Whale, and Dogfish. The Humpback cuttings from Alaska were made up of the raw heads, fins, tails and roe. They were shipped in a sealed tin box which was broken open in transit. Formaldehyde had been added to prevent decomposition but some pieces of the scrap were badly decomposed, while others were in a fairly good state of preservation. The altered pieces were separated as far as possible and discarded.

TABLE I—ANALYSES OF SAMPLES OF THE RAW MATERIAL PRODUCED AS WASTE IN THE MECHANICAL DRESSING OF "HUMPBACK" SALMON
Material Taken from the Floor of the Cannery of the Pure Food Fish Co., Ketchikan, Alaska, July, 1913

| | Per Cent Calculated to Basis of Wet Scrap | | | | | Per Cent Calculated to Moisture-Free Basis | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Moisture | Nitrogen N | Phosphoric acid $P_2O_5$ | Bone phosphate $Ca_3(PO_4)_2$ | Oil | Gallons Oil per Ton | Nitrogen N | Phosphoric acid $P_2O_5$ | Bone phosphate $Ca_3(PO_4)_2$ | Oil |
| Roe (1/2 male and 1/2 female) | 68.7 | 3.68 | 1.08 | 2.35 | 3.18 | 8.24 | 11.76 | 3.44 | 7.50 | 10.16 |
| Heads | 63.2 | 2.65 | 1.54 | 3.36 | 13.70 | 35.51 | 7.20 | 4.18 | 9.13 | 37.22 |
| Fins and tails | 63.26 | 3.11 | 2.20 | 4.80 | 11.16 | 28.94 | 8.46 | 5.98 | 13.06 | 30.37 |
| AVERAGE | 64.6 | 3.02 | 1.59 | 3.46 | 10.43 | 27.05 | 8.65 | 4.44 | 9.70 | 28.74 |

The samples of dry scrap were collected from the respective manufactories and were shipped in canvas sample sacks. Methods of preparation of fish scrap are described in *Bulletin* **2** of this Department.[2]

METHODS OF ANALYSIS—The methods of analysis in the main were the same as described by the author in a joint article with E. G. Parker, of the Bureau staff, on the subject, "Some Analyses of Fish Scrap."[3] Before analysis the samples were ground to a powder that would pass a sieve of 16 apertures per linear inch. Samples of 2 grams each were then dried for about 5 hours or more, according to the kind of fish, in a vacuum oven at a temperature ranging between 75° and 85°. Some types of fish require longer drying than others to remove all the moisture and secure a constant weight. The loss in weight was recorded as moisture. In the case of the sample of raw Humpback cuttings, moisture was determined before grinding by drying to a constant weight in a water-oven. In this operation it is probable that some of the lower volatile oils were lost. In fact, the point where all the moisture is removed without any loss of oil has been very hard to establish, and further work on this subject, together with a study of extraction agents, is expected to be done in the near future by the author. Oil was determined by extracting with ether a 2 gram sample which had been previously dried to constant weight. Nitrogen was determined according to the official method by Mr. T. C. Trescott, of the Bureau of Chemistry. Phosphoric acid was determined by the official gravimetric method. The results appear in Tables I and II.

On the basis of the analysis reported in Table I the value of the raw cannery waste is derived below.

The percentage of nitrogen, 3.02, is equivalent to 3.67 per cent ammonia, $NH_3$. This, in the retail market, may be expected to bring $3.20 per unit; bone phosphate is valued at 10 cents per unit, and oil at 30 cents per gallon. Then:

| | |
|---|---|
| 3.67 per cent $NH_3$ at $3.20 per unit | $11.74 |
| 3.46 per cent bone phosphate at 10 c. per unit | 0.35 |
| 27.05 gallons oil at 30 c. per gallon | 8.12 |
| TOTAL VALUE PER RAW TON | $20.21 |

By present methods in vogue, the manufacturers of fertilizer and oil from this material expect to recover about $15.00 in values. Present methods, then, can be considered as only 75 per cent efficient. In further substantiation of this conclusion are the results published by Thomas[1] quoted below:

"The averages of all experiments show the following facts: Each ton of salmon offal treated produced 800 lbs. of mixed oil and fertilizer. Of this amount 200 lbs. was salmon oil and 600 lbs. oil-free fertilizer. The average analysis of the fertilizer thus produced was:

Ammonia.....14.3 per cent Bone phosphate... 13.0 per cent

"Estimating the 200 lbs. of oil as being 25 gal., at a price of $0.32, which seems a fair average, we have then for each ton of offal treated an oil value of $8, and, estimating the value of a unit of ammonia at $3.20 and bone phosphate at 10 cents per unit, we have a fertilizer value at:

| | | |
|---|---|---|
| 14.3 per cent ammonia at $3.20 | $45.76 | TOTAL |
| 13 per cent bone phosphate at $0.10 | 1.30 | $47.06 per ton |

"Then at 600 lbs. of fertilizer of this quality to the short ton of offal treated, we have $47.06 × 0.3 = $14.12, the fertilizer

[1] Scientist in Fertilizer Investigations, Bureau of Soils, U. S. Dept. of Agriculture.

[2] *Bull.* **2**, Bureau of Soils, U. S. Dept. Agr.

[3] THIS JOURNAL, **5** (1913), 388.

[1] A. M. Thomas, "Waste in Salmon Canning Industry," *Pacific Fisherman*, [2] **12** (1914), 26.

value of one ton of offal, which gives an available value for one ton of offal of:

Fertilizer.. $14.12 Oil . . . $8.00 TOTAL VALUE . $22.12."

In Table I the averages are calculated by doubling the percentages given under heads, since the heads constitute approximately twice as much of the bulk of the scrap as either the roe or the fins and tails. The number of gallons of oil per ton of wet scrap was computed from the percentages of oil, using 0.925 as the sp. gr. of fish oil.

Table II gives the analyses of the samples of prepared scrap. Samples 6 to 10 are of the most important fish, outside of salmon, used in the fertilizer industry on the Pacific Coast. The whale scrap results compare favorably with those given by H. T. Offerdahl-Tarvik[1] of a general whale fertilizer containing 10 to 12 per cent nitrogen and 14 to 15 per cent phosphoric acid, and also with the results given by Stockhardt.[2] Analyses of dog fish were made by the Pacific Products Company of Port Townsend, Washington, on some scrap taken a few days later from the same bin as Sample 10. The results reported by them compare favorably with those of the author and are as follows in percentages:

$NH_3$, 15 $P_2O_5$, 3.6 Moisture, 8 Oil, 6.8

The two samples of an English product were examined for comparative purposes. The quantity of the samples, however, was inadequate for complete analysis, and the percentages are low because the samples contained a large quantity of sand or crushed quartz. Similarly a sample of unedible shark from the Atlantic Coast was examined. In this case the livers alone are used for their oil and the remainder thrown away.

TABLE II—PERCENTAGE ANALYSES OF PREPARED FISH SCRAP

| No. | LOCATION AND COMPANY | DESCRIPTION | N | $P_2O_5$ | Moisture | Oils(a) |
|---|---|---|---|---|---|---|
| 1 | Klawack, Alaska North Pacific Fishing and Trading Co. | Sample from trial run with steam drier | 9.39 | 5.32 | 5.36 | 14.96 |
| 2 | Anacortes, Wash.: Robinson Fisheries Co. | Dry scrap from steam drier | 8.26 | 7.91 | 5.21 | 17.36 |
| 3 | Anacortes, Wash.: Russia Cement Co. | Dry scrap from hot-air drier | 9.49 | 9.26 | 5.26 | 8.32 |
| 4 | Seattle, Wash.: Brandel Chemical Co. | Dry scrap from steam drier | 8.76 | 7.00 | 3.91 | 20.02 |
| 5 | Astoria, Ore.: DeForce Oil Works | Dry scrap from hot-air drier | 7.63 | 12.08 | 5.11 | 10.96 |
| 6 | Monterey, Cal.: Monterey Packing Co. | Sardine scrap | 7.97 | 7.11 | 5.57 | 8.42 |
| 7 | Victoria, B. C.: Canadian North Pacific Fisheries, Ltd. | Whale meal | 11.59 | 0.94 | 5.41 | 12.70 |
| 8 | Victoria, B. C.: Canadian North Pacific Fisheries, Ltd. | Whale bone-meal | 3.01 | 26.08 | 2.53 | Trace |
| 9 | San Pedro, Cal.: San Pedro Fertilizer Co. | Tuna scrap | 8.54 | 7.25 | 4.21 | 13.27 |
| 10 | Port Townsend, Wash.: Pacific Products Co. | Dog-fish scrap | 12.15(b) | 3.59 | 6.35 | 7.89 |
| 11 | London, E. C.: H. Wiskemann Wool Exchange | Fish meal | 6.54 | 4.78 | ... | ... |
| 12 | London, E. C.: H. Wiskemann Wool Exchange | Meat meal | 8.57 | 4.56 | ... | ... |
| 13 | Key West, Florida | Shark waste | 9.34 | 1.99 | 13.83 | Trace |

(a) More accurately, ether extract. This consists principally of oils.

(b) Equivalent to 14.77 per cent ammonia, $NH_3$.

CHARACTER OF PRODUCT—The scrap produced from salmon waste is of a very high quality, and is open to criticism, from a fertilizer point, only on the fact of its high content of oil. This amount of oil does have a marked influence on the fertilizing properties of the scrap as is shown in the following pot experiment work. It is further disadvantageous in that it is so much inert material of no fertilizer value. However, the fact that the oil, of high value if extracted, here plays the rôle of a worthless diluent of a less valuable product, has not as much bearing on the value of the scrap as a fertilizer as it has on the economy of the process by which the material is prepared.

COMPARISON WITH MENHADEN SCRAP—For the sake of comparison between the salmon and menhaden scrap, Table III is reprinted from the analyses appearing in "Some Analyses of Fish Scrap."[1]

The salmon scrap has a lighter color and a more pleasant odor than the menhaden scrap. This, again, possibly does not concern the fertilizing value, though there is a possibility that it may affect its demand in the trade. It is said that some agriculturists appraise the value of fertilizer materials by the disagreeableness and strength of their odor. On the contrary, it is a better established fact that considerable prejudice exists against fish scrap on the part of common carriers and the public in general because of its odor. Since nothing is to be lost and something is to be gained by reducing the disagreeable odors of fish fertilizers, the point mentioned is favorable to the salmon scrap. The better smell of the latter is due most probably in greatest measure to the fact that it is dried at moderate temperatures and is not scorched, as inevitably must happen in the hot air driers as now operated on the Atlantic Coast. It is also true that the menhaden scrap is dried in a stream of hot gases generated in a soft-coal fire; the soot from this undoubtedly contributes likewise to the dark color of the product.

Another point of difference between the salmon and menhaden scrap is introduced by the occasional acidulation of the latter. The addition of sulfuric acid to the scrap is practiced most generally to disinfect the undried but freshly cooked and warm "pomace," and to render it unfit as a breeding place for flies. This is resorted to, as a rule, only when the scrap is being produced at a rate greater than that at which it can be dried. The acidulation frequently is followed by drying. The addition of sulfuric acid to the scrap is supposed to be beneficial in that it "fixes the ammonia" and renders soluble the phosphoric acid of the calcium phosphate constituting the bones. While it induces a disintegration and pulverization of the scrap, and enables the producer to sell the bone phosphate present as soluble phosphoric acid, at the same time it acts as a diluent of slight (if any) fertilizer value, with no rating on a fertilizer basis.

In the foregoing comparison of scrap from salmon and menhaden, respectively, it is not intended that the idea shall be conveyed that the menhaden scrap for fertilizer purposes is inferior to that from the salmon. It is believed that the ammonia and phosphate of the one is as valuable as that of the other.

FISH SCRAP AS CATTLE AND POULTRY FEED—To

[1] *Ber. d. deutsch Pharm. Ges.*, **23** (1913), 558-559.

[2] *Chem. Ackersmann*, **16** (1870), 52.

[1] *Loc. cit.*

discuss fish scrap from any point of view other than that of fertilizer perhaps is beyond the province of this paper. It should be pointed out here, however, that in connection with such fertilizer materials as dried blood, abattoir tankage of high-grade, cotton-seed-meal, and fish scrap, it is better agricultural practice to feed these to stock, provided, of course, that all barn-yard manures be conserved carefully, than to apply them directly to the soil. It can be taken as thoroughly well established that both the nitrogen and the phosphoric acid, after performing their rôle in the life processes of the adult animal, are eliminated. Then the high food value of these rich foods is utilized and at the same time the fertilizing elements are still available for use on the growing crops. From the point of view of cattle and poultry feed, the salmon scrap must be considered superior to the menhaden. In the first place the acidulated scrap is totally unfit for feeding purposes. Its use in that manner undoubtedly would result in disaster. And in smaller degree, the greater care expended in drying the salmon scrap makes it a more desirable article of food. In fact, when the nature of the raw materials and the sanitary conditions under which it is treated, obtaining in certain manufactories, are considered, it might also be regarded as fit for man's consumption. It would be interesting to learn whether the oil remaining in the salmon scrap is not of a more digestible nature than that in the menhaden scrap. No experimental data is at hand in substantiation of such a belief; but such appears plausible when it is recalled that the salmon oil is light and sweet and partakes more nearly of the nature of the edible oils, while that from menhaden is dark, heavy and viscous and has a disagreeable odor. There are no differences in the methods of rendering sufficiently great to account for the difference in the natures of the respective oils; their differences must be regarded as inherent.

The subject of the suitability of fish scrap for cattle and poultry feed and the experiments performed relating thereto have been discussed in an earlier publication of this Department and therefore will not be repeated here. In all of the experiments, records of which have come to the attention of the writer, the results have been affirmative and of such a nature as to justify the further exploitation of this food material for that purpose. The reader interested in this phase of the subject is referred to *Bulletin* **2**, U. S. Department of Agriculture, "The Menhaden Fish Fertilizer Industry of the Atlantic Coast."

OIL—The literature contains little having to do with salmon oil. The amount actually produced, 286,000 gallons, is too small to give it very great importance in the industries. It is rated, however, as a high-grade fish oil. The market price, 30 cents per gallon, against 23 cents for menhaden oil as quoted in 1912, is sufficient evidence of that fact. There is no reason to doubt that it is destined to play an important part as an animal oil when the salmon scrap industry is fully developed and there is enough oil available to make its study and exploitation profitable.

In the absence of more detailed information concerning the physical and chemical properties of salmon oil, it must suffice to say that it is merely a high-grade fish oil. The crude salmon oil is lighter in color than, perhaps, the refined menhaden. Its properties, as now understood, adapt it to the uses to which menhaden oil has been successfully applied, conspicuous among which is its utilization as a lubricant, and especially in the paint and enamel industries.[1]

GLUE—Fish glue made from salmon is regarded as low-grade and of proportionately slight value. In this particular it differs markedly from that prepared from cod skins. It is applied, with success, to the preparation of "sizings" and allied materials.

POT EXPERIMENTS—Series of pot and plot experiments were undertaken by J. J. Skinner, of this Bureau, to determine whether the residual oil in the fish scrap had an injurious effect on the fertilizer value, and the preliminary results are so very interesting from several standpoints that he has been kind enough to allow me to publish them in part. Fish scrap is undoubtedly an efficient fertilizer as shown by the accompanying photographs and green weights. In every case where scrap was applied there was a decided increase in growth and when oil-free scrap was added a still greater growth was noticeable. This residual oil appears to have a large influence on the fertilizer properties and surely warrants further study and a consequent investigation of the efficiency of present methods of removing the oil.

The effect of these fish scrap fertilizers in soils was tested by growing wheat plants in the treated soil in paraffined wire pots. The plants grew from May 5th to 28th. The paraffined wire pot method is described in *Circular* **18** of this Bureau. Fish scrap was added at the rate of 700 lbs. per acre and duplicates were made in every case. There were two types of soil used, the one a loam and the other a sandy loam. The analyses of the fish scrap samples used are given in Table IV.

TABLE III—MENHADEN SCRAP

| No. | Location and Company | Description | Per cent N | $P_2O_5$ | Moisture | Oils |
|---|---|---|---|---|---|---|
| 1 | Kilmarnock, Va.: Eubanks Tankard Co | Dry scrap (from 6 sacks) | 8.93 | 6.17 | 6.48 | 5.91 |
| 2 | Taft, Va.: Taft Fish Co. | Dry scrap (sample from 525 tons) | 8.96 | 7.75 | 6.18 | 6.81 |
| 3 | Irvington, Va.: Carter's Creek Fish Guano Co | Dry scrap, dried in hot air and steam driers (from one sack) Fall product | 7.70 | 5.22 | 11.68 | 6.62 |
| 4 | Cape Charles, Va.: Atlantic Fish & Oil Co. | Dry scrap, ground (from 3 sacks) | 9.29 | 6.12 | 7.86 | 5.38 |
| 5 | Cape Charles, Va.: Atlantic Fish & Oil Co. | Dust from grinders | 8.80 | 5.21 | 7.17 | 7.55 |
| 6 | Beaufort, N. C.: Beaufort Fish Scrap & Oil Co. | Dry scrap, hydraulic presses, sample from heap | 8.22 | 5.95 | 6.13 | 8.57 |
| 7 | Morehead City, N. C.: R. W. Taylor | Dry scrap from open heap | 8.49 | 5.95 | 9.12 | 8.23 |
| 8 | Morehead City, N. C.: Chas. S. Wallace | Scrap, dry, from hydraulic presses | 7.76 | 9.65 | 8.15 | 7.56 |
| 9 | Lenoxville, N. C.: C. P. Dey | Ground scrap, sun-dried, hydraulic presses. Sample from heap | 7.81 | 5.85 | 7.46 | 7.89 |
| 10 | Lenoxville, N. C.: C. P. Dey | Scrap, dry, ground, hydraulic presses. Sample from heap | 8.29 | 9.00 | 7.00 | 5.40 |
| | AVERAGES | | 8.43 | 6.69 | 7.72 | 6.99 |

[1] For a brief discussion of menhaden oil see U. S. Dept. Agr., *Bull.* **2**, p. 46, *et seq.*

The green weights of the plants are given in Table V. It will be noticed that the Hagerstown loam was the better producing soil. The tuna scrap was not

TABLE IV—PER CENT ANALYSES OF SAMPLES USED IN POT EXPERIMENTS

| FISH | N | $P_2O_5$ | Moisture | Oil |
|---|---|---|---|---|
| Salmon | 9.39 | 5.32 | 5.36 | 14.96 |
| Sardine | 7.97 | 7.11 | 5.57 | 8.42 |
| Tuna | 8.54 | 7.25 | 4.21 | 13.27 |
| Menhaden | 8.22 | 5.95 | 6.13 | 8.57 |

very effective in the case of the Orangeburg sandy loam but shows much better results when added to the Hagerstown loam.

TABLE V—GREEN WEIGHTS (GRAMS) OF WHEAT PLANTS

| LOAM USED | Hagerstown | Orangeburg sandy |
|---|---|---|
| Soil untreated | 2.45 | 1.65 |
| Soil + Salmon fish scrap—oil-free | 4.00 | 3.15 |
| Soil + Salmon fish scrap | 3.05 | 2.05 |
| Soil + Sardine fish scrap—oil-free | 3.25 | 3.04 |
| Soil + Sardine fish scrap | 2.55 | 2.70 |
| Soil + Tuna fish scrap—oil-free | 3.52 | 2.00 |
| Soil + Tuna fish scrap | 3.25 | 1.90 |
| Soil + Menhaden fish scrap—oil-free | 3.60 | 2.70 |
| Soil + Menhaden fish scrap | 3.10 | 2.50 |

REMOVAL OF RESIDUAL OIL—The recovery of the residual oil can undoubtedly be accomplished by an extraction with gasoline, similar to the process now in vogue in the degreasing of garbage tankage. In this process the tankage is put in a large cylindrical tank and washed with gasoline until the gasoline drawn off is colorless. The residual gasoline is driven off by

FIG. I—HAGERSTOWN LOAM AND OIL-FREE FISH SCRAP
1—Untreated Soil
2—Soil + Oil-free Salmon Scrap
3—Soil + Oil-free Sardine Scrap
4—Soil + Oil-free Tuna Scrap
5—Soil + Oil-free Menhaden Scrap

steam, and the gasoline and oil separated by distillation. The equipment consists of one rotary percolator or washing tank, one condenser, one still for distilling the gasoline from the oil, one oil-finishing tank, two separating tanks for separating the solvent from water, one heater for heating solvent, three pumps, the necessary storing tanks for storing the finished oil and gasoline, two conveyors (one for delivering the material to the percolator and the other for removing the same), boilers, motors, piping, etc.

The removal of the residual oil in fish scrap will not only increase to a great extent its value as a fertilizer, as shown in the preceding experiments, but will seemingly also more than pay for itself in the oil recovered.

The following estimates of the cost of degreasing menhaden scrap have been made. Consideration has been given to the oil recovered only and not to the enhanced value of the fish scrap. These figures are based on works data obtained in the degreasing of garbage tankage. The data have been secured through the kindness of Mr. T. D. Banks, of the Municipal Reduction Plant of Columbus, Ohio, and Mr. W. J. Springborn, of the New Bedford Extractor Company, of New Bedford, Mass. Both estimate the outlay for buildings and equipment to be $25,000 for a plant with a capacity of about 10 tons per day. To house the degreasing plant a fire-proof

FIG. II—ORANGEBURG SANDY LOAM AND OIL-FREE FISH SCRAP
1—Untreated
2—Soil + Oil-free Salmon Scrap
3—Soil + Oil-free Sardine Scrap
4—Soil + Oil-free Tuna Scrap
5—Soil + Oil-free Menhaden Scrap

building would probably be regarded as essential. The cost of this would be determined by local conditions. For a fish scrap plant it would not be necessary to erect a building as expensive as that required by a municipal garbage reduction plant such as that made the basis of the above estimate.

The operation of the plant would require the services of two men, who during the actual operation would devote all of their time thereto; if the steam requisite is supplied from the boilers already installed and operated, only a portion of the fireman's time need be charged to the degreasing plant. In the degreasing of garbage tankage the loss in gasoline averages 6 gallons per ton of product while the bulk of the gasoline is redistilled and used over and over again. The following estimate of the operating expenses of an eight-hour day may then be made:

| | |
|---|---|
| One operator, 25 cents an hour | $ 2.00 |
| One laborer, 20 cents an hour | 1.60 |
| 60 gallons of gasoline | 7.20 |
| 3 tons of coal | 4.50 |
| 1/5 of fireman's time | 0.32 |
| Repairs and miscellaneous expenses | 1.00 |
| TOTAL PER DAY | $16.62 |
| TOTAL PER TON | 1.66 |

Interest on investment, $25,000, at 6 per cent, is $1,500, or per ton, on basis of 1,000 ton season's out-

FIG. III—ORANGEBURG SANDY LOAM AND FISH SCRAP WITH AND WITHOUT OIL
1—Untreated Soil
2—Soil + Oil-free Sardine Scrap
3—Soil + Sardine Scrap Containing Oil
4—Soil + Oil-free Salmon Scrap
5—Soil + Salmon Scrap Containing Oil

put, $1.50. It should be recalled in this connection that the outlay for equipment and building may be reduced materially below this figure. Hence the total cost of degreasing would be $3.16 per ton.

Since the analyses of dried menhaden scrap made in this Bureau show the average content of oil to be approximately 6.99 per cent, it may be taken that each ton of scrap would yield 139.80 lbs. of oil, which, at 7.71 lbs. per gal., is equivalent to 18.13 gals. per ton. This at 23 cents per gallon[1] has a value of $4.17 per ton. The cost of production being $3.16, the profit per ton in oil recovered would be $1.00, or for the season's production of 1000 tons, $1,000.

If such a process were applied to scrap from salmon which, it is recalled, contains 12.69 per cent oil, the profit would be $6.72 per ton, on the basis of the same operating expenses as above and of 30 cents per gallon for oil. Since the output of the individual plants on the Pacific Coast is not, on the average, 1,000 tons per season, central receiving stations could be erected in the various sections and the degreasing done there.

All the above estimates show that the oil recovered would pay for the process without any consideration being given to the enhanced fertilizer value of the product. When, however, this feature is considered, it is seen from the preceding pot experiments that on the average the fertilizing qualities of the fish scrap are increased by approximately 23 per cent.

### CONCLUSIONS

The fish waste of the Pacific Coast is very high in fertilizer value. It averages higher than menhaden in its contents, as follows:

MENHADEN: Nitrogen, 8.43 per cent; phosphoric acid ($P_2O_5$), 6.69 per cent; and oil, 6.99 per cent.

SALMON, ETC.: Nitrogen, 9.31 per cent; phosphoric acid ($P_2O_5$), 6.72 per cent; and oil, 12.69 per cent.

The menhaden industry is much larger and older, but there is no doubt but that the salmon scrap industry will grow rapidly and soon equal the menhaden. This is especially true because of the increasing demands for nitrogenous fertilizers and the availability of salmon cannery waste.

The American Fertilizer Handbook for 1914, in reviewing the fish scrap fertilizer industry, gives the following conclusions: "Probably the most important feature to the fish manure business during the past year was the unusually large number of new companies formed to operate in this line. The industry, which was only a few years ago a comparatively unimportant one, is now one that is attracting the attention of financial men generally."

BUREAU OF SOILS, WASHINGTON, D. C.

## NOTES ON THE COLORIMETRIC DETERMINATION OF PHOSPHORUS IN SOIL EXTRACTS

By C. E. MILLAR AND F. A. GANGLER

Received March 3, 1915

The colorimetric method for the determination of phosphorus suggested by Veitch[2] and perfected by Schreiner and Brown[1] has been used to some extent for a number of years. Little or no data where this method has been applied to soil solutions have been published and the general feeling has prevailed that it was somewhat inaccurate in such work.

The writers were in need of a reliable method for determining small amounts of phosphorus in soil extracts and consequently an investigation of this method was undertaken. A series of tests emphasized the precautions brought out by Veitch: (1) Use filter paper as free of silica as possible such as Schleicher and Schüll's No. 589. (2) Use exact amounts of nitric acid and molybdate solution. The use of a poorer grade of paper caused a reading almost double that obtained when blank determinations were run with the better paper. By varying the amount of nitric acid it was found that quite a distinct color could be almost entirely dissipated. Varying amounts of molybdate solution also affect the color.

With the greatest care in the purification and use of all reagents it was found impossible to get blank determinations without a trace of color and in consequence a small factor of correction was used.

The samples of soil were taken with a 1 in. soil tube to a depth of 3 ft., every foot composing a separate sample. The samples were rubbed through a 1/4 in. sieve and the soil thoroughly mixed by rolling in an oil cloth. The sample was then quartered with a large spatula and two 100-gram samples weighed out. Each sample was obtained by taking portions from opposite quarters. Each 100-gram sample was rubbed with 500 cc. of water for 3 minutes in a mortar. After standing for 40 minutes the suspension was filtered in a Chamberland filter: 50 cc. of the filtrate were taken for analysis. This procedure gave two solutions from separate portions of a well mixed sample. The duplicates shown in Table I are determinations on these separate solutions and do not represent determinations on different portions of the same solution.

TABLE I PARTS PER MILLION $PO_4$ IN FILTRATES FROM SOILS

| Plot No. | Depth Feet | $PO_4$ in duplicates | | Plot No | Depth Feet | $PO_4$ in duplicates | | Plot No. | Depth Feet | $PO_4$ in duplicates | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 3.00 | 3.00 | 6 | 1 | 0.75 | 0.50 | 10 | 1 | 2.50 | 2.00 |
| | 2 | 3.00 | 3.00 | | 2 | 1.00 | 1.00 | | 2 | 2.50 | 2.50 |
| | 3 | 3.00 | 3.50 | | 3 | 1.25 | 1.25 | | 3 | 2.50 | 2.50 |
| 2 | 1 | 5.00 | 4.50 | | | | | 11 | 1 | 1.25 | 1.25 |
| | 2 | 3.50 | 4.00 | 7 | 1 | 2.00 | 2.50 | | 2 | 1.25 | 1.25 |
| | 3 | 2.50 | 2.50 | | 2 | 2.50 | 2.00 | | 3 | 1.50 | 1.50 |
| 3 | 1 | 2.50 | 2.50 | | 3 | 2.00 | 2.00 | 12 | 1 | 0.50 | 0.50 |
| | 2 | 2.50 | 2.50 | | | | | | 2 | 0.50 | 0.50 |
| | 3 | 1.50 | 1.50 | 8 | 1 | 2.50 | 3.00 | | 3 | 0.75 | 0.75 |
| 4 | 1 | 2.00 | 2.00 | | 2 | 2.00 | 2.50 | 13 | 1 | 0.00 | 0.00 |
| | 2 | 2.00 | 2.00 | | 3 | 2.00 | 2.00 | | 2 | 0.25 | 0.25 |
| | 3 | 2.00 | 2.00 | | | | | | 3 | 0.50 | 0.50 |
| 5 | 1 | 1.00 | 1.00 | 9 | 1 | 2.50 | 2.50 | 14 | 1 | 1.00 | 1.00 |
| | 2 | 0.75 | 0.75 | | 2 | 2.50 | 2.00 | | 2 | 1.25 | 1.25 |
| | 3 | 1.00 | 1.25 | | 3 | 2.50 | 2.50 | | 3 | 1.25 | 1.25 |

From Table I it would appear that if sufficient care is given to the purity of reagents and to the measuring out of all reagents, determinations of small amounts of phosphorus may be made in soil extracts with considerable accuracy.

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[1] This figure is the normal price quoted, but during the last two years the price has advanced rapidly because of poor fishing seasons. The catch in 1913 was only 60 to 70 per cent of the normal, and figures available thus far for this year show the catch to be still lower. At the present time crude menhaden oil is scarce, and the little that is obtainable brings from 37 to 39 cents a gallon. If these prices were applied to the above estimates, the profit would be increased greatly, but since they are not normal, it would be unfair to make general statements based upon them

[2] *J. A. C. S.*, **25** (1903), 169.

[1] *J. A. C. S.*, **26** (1904), 1463.

## A NOTE ON THE FORMATION OF TRI-CALCIUM PHOSPHATE ON MIXING GROUND LIMESTONE WITH ACID PHOSPHATE

By R. N. Brackett and Benjamin Freeman

Received January 4, 1915

About two years ago one of us, while visiting a fertilizer plant, was attracted by a large pile of ground limestone, which, upon inquiry, was found to be used as a filler in preparing lower grade acid phosphate from higher grade. It appeared somewhat strange that manufacturers should deliberately revert the water-soluble phosphoric acid, which they had been at so much pains and expense to produce. Besides, it seemed not improbable that there would be some insoluble phosphoric acid formed with a consequent danger of the manufacturer falling below his guarantee of available, if he took no account of this possibility. The chemist of the plant stated, however, that there was no such danger, as he had tried experiments and did not find any insoluble phosphoric acid formed.

In a recent discussion of the advisability of using ground limestone as a filler in fertilizers carried on in Atlanta, Ga., and published in "The American Fertilizer" during the past two years, the statement has been made that no insoluble phosphoric acid is produced on mixing ground limestone with acid phosphate.

In view of these statements, and because we had not been able to find any published experiments giving figures, it seemed worth while to make a carefully conducted set of experiments to determine whether any insoluble phosphoric acid is produced and, if so, whether the amount would be sufficient to endanger an available phosphoric acid guarantee. In the spring of 1913, therefore, we procured 100 lbs. each of acid phosphate and ground limestone, and after making a careful analysis of each, prepared mixtures as follows:

| No. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Lbs. acid phosphate | 14.0 | 15.5 | 17.0 | 10.0 |
| Lbs. ground limestone | 6.0 | 4.5 | 3.0 | 10.0 |

The materials were, after grinding separately, weighed as accurately as possible on a grocer's scale, mixed thoroughly on paper and finally in wooden boxes; the contents of the boxes were then run through a small grinder, and sacked. Samples were drawn from the sacks with an Indiana fertilizer sampler, such as is used by our Fertilizer Inspectors in taking samples. The 4- or 5-pound sample thus drawn was quartered down to about 8 oz. and bottled for analysis.

On making the mixtures a considerable rise of temperature was noted, though it was not measured. Evolution of carbon dioxide took place immediately and continued for many days, as was shown by connecting a bottle of one of the mixtures with a bottle containing lime-water. This experiment was not carried to completion, owing to an unavoidable accident. The mixtures were analyzed at set intervals as shown below.

| Acid Phosphate | Per cent | Ground Limestone | Per cent |
|---|---|---|---|
| Total phosphoric acid | 16.84 | Lime | 43.62 |
| Water-soluble phosphoric acid | 13.55 | Phosphoric acid | Trace |
| Insoluble phosphoric acid | 1.33 | | |

Percentage Analyses of Mixtures

| Mixture | No. 1 W-S | No. 1 Ins. | No. 2 W-S | No. 2 Ins. | No. 3 W-S | No. 3 Ins. | No. 4 W-S | No. 4 Ins. |
|---|---|---|---|---|---|---|---|---|
| April 21st, immediately after mixing | 6.15 | 1.07 | 8.30 | 1.15 | 10.50 | 1.24 | 2.40 | 0.83 |
| May 10th | 3.05 | 1.30 | 5.84 | 1.26 | 8.66 | 1.37 | 0.99 | 0.98 |
| June 12th | 3.31 | 1.39 | 6.39 | 1.66 | 8.15 | 1.59 | 1.10 | 1.11 |
| Sept. 13th | 3.38 | 1.46 | 3.31(a) | 1.33 | 8.05 | 1.46 | 0.87 | 1.08 |

(a) This is probably an error as an analysis in November, 1913, gave about five per cent water-soluble.

All figures are the mean of closely agreeing duplicates.

These results seem to warrant the following conclusions:

I—Tri-calcium phosphate is produced on mixing acid phosphate and ground limestone.

II—The formation of the tri-calcium phosphate begins immediately on mixing, but increases slightly on standing, showing that the amount formed is a function of both time and temperature.

III—Considering the closeness with which manufacturers guarantee today, it appears necessary that the formation of insoluble in such mixtures be taken account of in making guarantees.

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# LABORATORY AND PLANT

## APPARATUS FOR THE DETERMINATION OF SULFUR IN GAS[1]

By E. R. Weaver and J. D. Edwards

Received April 8, 1915

The sulfur apparatus which is shown in the accompanying illustration is the same in principle as the well-known Drehschmidt apparatus and its many modifications, the gas being burned and the oxides of sulfur collected by passing the products of combustion through an alkaline absorbing solution. The novel features of the apparatus illustrated are the burner and the combustion chamber.

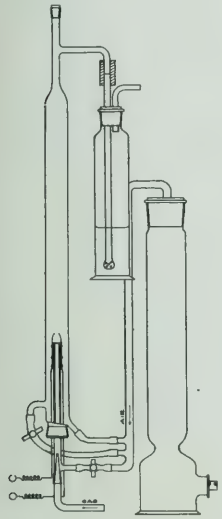
The burner is similar to one described in a technological paper of this Bureau.[2] The method of igniting the gas and the arrangement of the secondary air inlets, however, are different. The platinum spiral which was heated to incandescence in order to ignite the gas has been replaced in the new type of burner with a pair of platinum terminals forming a spark gap. The inconvenience caused by the occasional burning out of the platinum wire is thus avoided. The platinum terminals are sealed to the porcelain burner tube by means of "sealing in" glass. Only a short length of platinum wire is necessary, nickel leads being soldered to the platinum terminals, just below the point where the latter are sealed to the porcelain tube. The stopper which closes the lower end of the combustion chamber also serves as a connector, the porcelain burner tube and the glass T piece being firmly fastened into it by means of Khotinsky or sealing wax. Tke small tip through which the gas enters just above the primary air inlet is also

[1] Published by permission of the Director of the Bureau of Standards.

[2] "Determination of Sulfur in Illuminating Gas," McBride and Weaver, *Tech. Paper* No. 20, Bureau of Standards.

held in with Khotinsky cement. The tip can be easily removed for cleaning, or tips of various sizes adapted to the gas to be burned can be inserted. The air necessary for complete combustion after being purified by passage through the large soda lime tower is supplied to the flame in two portions. The primary air is drawn in by the gas as it passes through the small tip; the secondary air enters through the two inlets at the side of the combustion chamber.

The combustion chamber, made of Jena glass tubing, is about 360 mm. long and about 25 mm. in internal diameter. The narrow tube at the top may be used for introducing water when it is desired to rinse out the apparatus; when in operation this tube is closed with a small cork. Satisfactory drainage is provided by the sloping layer of paraffin or sealing wax covering the stopper at the bottom. When the burner is lighted the secondary inlet air keeps the base of the apparatus cool, but the rest of the combustion chamber up to the side tube is heated so that no condensation takes place on the walls. For that reason it is usually unnecessary to rinse out the combustion chamber. By means of a cork connector the first of a series of wash bottles is attached to the apparatus. Only one wash bottle is shown in the illustration, but three are usually required for satisfactory operation. In order that the suction may pull the gas steadily through the wash bottles it is necessary that the end of the inlet tube of the first bottle be perforated with a number of small holes. With a single, large opening the operation of the burner is not steady.



Experience has shown that combustion of the sulfur to oxides is incomplete when the flame, because of too little primary air, is smoky or even strongly luminous without smoke, as well as when the supply of secondary air is not sufficient. This latter condition is shown by a flame with an indefinite or "ragged" outline. When the gas and air entering the burner are so regulated that the flame is non-luminous and clear-cut, combustion is complete and the results obtained have been more concordant than those obtained with any other apparatus in use in this laboratory.

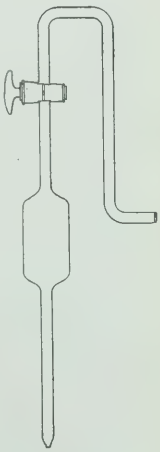
The advantages of the apparatus are its small cost, simplicity of construction, and the fact that the difficulty of lighting and regulating the burner usually experienced in the use of apparatus of this type is entirely overcome. The platinum wires become heated by the gas flame and prevent the flame from going out when the pressure fluctuates. With a single adjustment it has been found possible to keep the flame burning with gases varying in composition from pure hydrogen to pure acetylene and at pressures ranging from two to ten inches of water. Of course, combustion was not complete with such extreme variations. It is, however, easy to adjust the apparatus to burn completely any gas which can be burned in any Bunsen-type burner.

Bureau of Standards
Washington, D. C.

## A MODIFIED PIPETTE

By Sidney Born
Received February 1, 1915

The accompanying sketch shows a form of pipette which has been found very useful in our laboratory. It is made by fusing a stopcock and a piece of bent glass tubing to a pipette. The advantages over the ordinary pipette are:



1. Safety—There is no danger of sucking up acid or dangerous liquids.

2. Ease of Manipulation—The stopcock ensures tighter closing and greater accuracy than use of a finger.

3. Accuracy—The line of demarcation is level with eye when using.

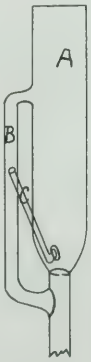
4. The pipette can be carried around full without losing any liquid.

Laboratory of the Wm. J. Lemp Brewing Co.
St. Louis

## AN APPARATUS FOR THE CONTINUOUS EXTRACTION OF A LIQUID BY ANOTHER, AND HEAVIER LIQUID

By Isidor Greenwald
Received March 23, 1915

The need of a convenient apparatus for the continuous extraction of a liquid with another, heavier liquid, has been felt for some time. The apparatus shown in the accompanying sketch is simple, compact and can readily be made by any glass-blower at little cost. For use, some of the extracting liquid is placed in the tube *A*. The liquid to be extracted is then added until the extracting liquid is forced up the tube *C* almost to its opening into *B*. The apparatus is then connected, in the usual manner, to a flask containing the extracting fluid and to a condenser. With the apparatus shown, chloroform extracted the caffeine from a 2.5 per cent solution within three hours. For substances extracted with difficulty, the apparatus may be made in a narrower, and longer, form. The apparatus may be modified by the use of ground-glass or mercury-sealed connections and also by the insertion of a stopcock in either *A* or *C* for the purpose of removing a sample of the extracted, or the extracting, fluid.




Harriman Research Laboratory
Roosevelt Hospital, New York

# ADDRESSES

## SANITARY FEATURES OF THE LOS ANGELES AQUEDUCT[1]

By E. O. Slater

A paper upon this subject is of special interest at this time because of the recent termination of two suits brought to enjoin the Los Angeles Bureau of Water Works and Supply from delivering water from the Aqueduct to consumers in Los Angeles, alleging that it is unsafe and unfit for human consumption.

It is not the purpose of this paper to review the testimony presented in the suits, but rather to endeavor to present the salient sanitary features of the system. While time did not permit of a long series of examinations, and although several special studies, such as effect of holding samples, effect of pressure upon bacteria, etc., were made and are not presented here, the results of the principal sanitary studies made to date of this water system are given in this paper.

The examinations were made in September, October, and November, 1914, and January, 1915.

### DRAINAGE BASIN

The Aqueduct receives water from the Owens River, and from creeks, wells and springs west of the Aqueduct between the intake and Haiwee Reservoir.

The headwaters of Owens River consist of several creeks, the most important of which is Deadman Creek, having its source in the Sierra Nevada Mountains on the east slope of San Joaquin Peak, at an elevation of about 11,000 ft. It flows through Long Valley, and in its course is fed by several creeks. The area of this portion of the drainage basin is 444 sq. mi. There are no permanent inhabitants in this region. During the summer months campers and cattlemen frequent the place, and several thousand head of cattle are pastured on the grassy meadow land during the warm months.

The river leaves Long Valley by way of the Owens River gorge. Stream gaugings at the mouth of this gorge show an average flow of 295 cu. ft. per second, from 1903 to 1908, inclusive. The river then flows through Round Valley, and in an easterly direction across the northern end of Owens Valley. Turning south near Laws, a railway station, it flows about three miles east of Bishop, and continues in a southerly direction about 65 mi., emptying into Owens Lake.

The only industries in all this region are agricultural and stock-raising and the most thickly settled part of the district lies about Bishop, a town of about 1,300 inhabitants, which is sewered, the sewage passing through a septic tank, and the effluent emptying into a slough which flows sluggishly toward Owens River, empties into the river during the flood season, but disappears before reaching the river the rest of the year. Bishop is the only sewered town in the drainage basin. About 14 mi. south of Bishop and 3 mi. west of Owens River is located the town of Big Pine, having about 300 inhabitants.

The Owens River between the intake and the gorge receives the drainage from an area of 737 sq. mi. west of the river, which area contains a majority of the inhabitants within the drainage basin. While the Inyo Mountain region east of the river has an area of 1922 sq. mi., there is very little drainage, and the district is sparsely populated because of lack of water.

The Aqueduct intake is about 40 mi. north of Owens Lake. A low diverting dam extending across the river controls the water entering the Aqueduct. The total area tributary to the Aqueduct south of the intake is 479 sq. mi. This region is very sparsely populated. Independence, lying 2 mi. west of the Aqueduct with a population of about 280, is the only town, and there are a few large stock ranches.

South of the intake and west of the Aqueduct there are several creeks which had an average total discharge for the years 1906, 1907 and 1908 of 198 cu. ft. per second, of which about 50 per cent is discharged into the Aqueduct. In this area also, Black Rock Spring has a constant flow of 18 cu. ft. per second into the Aqueduct. The unlined Aqueduct receives considerable water from the underdrainage. Test wells have been sunk and it is estimated[1] that 140 cu. ft. per second may be developed from underground storage.

The records of the gauging station at Charlie's Butte on the Owens River, about 3 mi. north of the intake, show an average of 442 cu. ft. per second for the years from 1904 to 1911, inclusive. The high water period in this region is in midsummer and is caused by the melting of the snows in the high Sierra Nevada Mountains. The rushing torrent of water coming from the melting snows is discharged over large deltas of coarse material, a great portion of the water disappearing beneath the surface of these fans and again emerging in springs further down near the river, or coming to the surface of the valley floor, is lost by evaporation and transpiration. This has a great leveling effect upon the discharge of the flood waters.

Owens Valley is cut off from the supply of moisture on the east and south by a long stretch of desert, and on the west by high mountains. The moisture-laden winds from the Pacific Ocean lose much of their moisture in passing over the Sierra Nevada Mountains before reaching the Owens Valley Region. The result of these conditions is the heavy precipitation near the top of the range, while desert conditions prevail in the valley only a few miles to the east. The precipitation varies almost directly with altitude over most of the western portion of the drainage basin under consideration. It varies from about 5 in. in the valley at elevations from 3700 ft. to 4000 ft., increasing to about 40 in. at 12,000 ft. The precipitation in the eastern portion of this basin is slight.

While the precipitation in this region occurs over a short period, the snows in the mountains act as a storage reservoir, the water from the melting snow furnishing a run-off over a relatively long period of time. This enables the engineers in charge to predict from four to six months in advance the amount of water that will become available for storage in Haiwee Reservoir. This is an important feature in this system, for it allows time for the development of the wells and for the pumping of the well-water in the region near Independence.

Studies of the supply of surface water available for storage in Haiwee Reservoir show that during years of normal rainfall the reservoir can be maintained half full while supplying a constant draft of 420 cu. ft. per second. These same studies show that in the period of most severe drought during the 10 years on record, 1904 to 1914, namely the years of 1912 and 1913, the wells would be called upon to supply 32,500,000,000 gallons during 14 months, or an average supply of 120 cu. ft. per second.

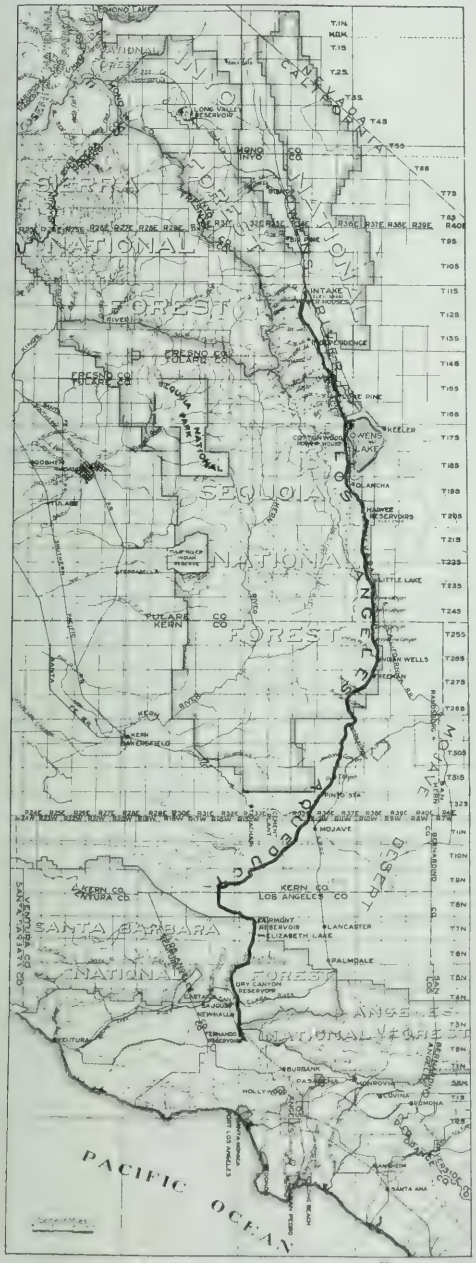
The total area tributary to the Aqueduct is 2782 sq. mi. and the population is 4775, making an average population of 1.7 persons per sq. mi. Of this area 12.7 per cent is agricultural land and 4.3 per cent of the area is irrigated. Irrigation is probably nearer its ultimate acreage in this section than in any other mountainous section of the state, and it is safe to state that there will never be a marked increase of population within the drainage area.

[1] Presented before the Southern California Section of the American Chemical Society, Los Angeles, April 15, 1915.

[2] Manager Smith, Emery & Company's Los Angeles Laboratories.

[1] See U. S. G. S. Water Supply Paper 294.

The temperature of this basin is subject to great and sudden changes, due to the wide variations in altitude. The regions




MAP OF THE LOS ANGELES AQUEDUCT AND ADJACENT TERRITORY

of agricultural land have hot summer weather, the temperature often exceeding 100° F., and cold winters, the mean temperature of the months from November to March, inclusive, usually being below 50° F.

PHYSICAL FEATURES OF THE AQUEDUCT

The Aqueduct intake on the Owens River is at an elevation of 3812 ft. For 21 mi. below the intake the Aqueduct is fenced, open and unlined, with a capacity of 900 cu. ft. per second. Its bottom is about 8 ft. below the natural ground level, and it is in this section that the normal water level is above the bottom of the Aqueduct, so that water seeps into it.

From the north end of the Alabama Hills to Haiwee Reservoir, 40 mi., the Aqueduct is fenced, open and concrete lined, with a capacity of 900 cu. ft. per second. A waste gate is located at the beginning of this section, and another one where Cottonwood Creek reaches the Aqueduct about 16 mi. north of Haiwee Reservoir. Through these gates undesirable water can be wasted.

The Aqueduct discharges water into the north end of Haiwee Reservoir. This reservoir, the most notable feature of the Aqueduct from a sanitary standpoint, is 7.5 mi. long, has a capacity of 20,843,000,000 gallons, has steep sides, is located in an almost rainless region, receives practically no water from its own natural basin, which is entirely uninhabited; when half full it is divided into three basins by very narrow constrictions, and when full it is divided into two basins. Its total area when full will be 2100 acres. It has a maximum depth of 81 ft. and an average depth of 30 ft. During the period of this investigation it was half full.

The effluent of Haiwee Reservoir is controlled by gates at varying elevations in a concrete tower. After passing through a short tunnel, the water is discharged into a temporary, open, concrete-lined canal, 2 mi. long, of 420 cu. ft. per second capacity. It is planned to replace this open canal with pipe for power development. From here the water flows through covered conduits, tunnels, syphons and flumes of 420 cu. ft. per second capacity, for 135 mi., and discharges into Fairmont Reservoir. At present the crest of Fairmont dam is at an elevation of 3024 ft., and the reservoir has a capacity of 1,890,000,000 gallons. It is planned to raise this dam to elevation 3035 ft., a total height of 115 ft., for power development. This acts as a safeguard, as a storage reservoir, and as a means for regulating the fluctuations of draft through the power plants to be located below in San Francisquito Canyon. The natural drainage basin of this reservoir is uninhabited.

From here the water is carried through Elizabeth tunnel, 26,870 ft. long, with a capacity of 1000 cu. ft. per second. The capacity is large in this section to accommodate the draft at the peak load of the power plants. At present the water discharges from this tunnel into San Francisquito Canyon and flows down it for 9 mi., but in a few weeks tunnels will be complete so that the water will flow directly through tunnels into Dry Canyon Reservoir, with a capacity of 342,000,000 gallons. This reservoir will serve to regulate the irregular flow that will be discharged through the power plants to be located in San Francisquito Canyon. It is 17 mi. between Fairmont and Dry Canyon Reservoirs. The natural basin of Dry Canyon Reservoir is uninhabited.

Tunnels and syphons, 12 mi. long, of 420 cu. ft. per second capacity, carry the water to the "Cascades" 1020 ft. long, located near San Fernando. These cascades serve to aerate the water. From here a fenced, open, concrete-lined canal 8775 ft. long carries the water to San Fernando Reservoir outlet tower. The San Fernando dam, one of the largest hydraulic earth fill dams in the world, will not be complete for another year. The water is carried by a steel syphon of 150 cu. ft. per second capacity, 12 mi. to Upper Franklin Canyon Reservoir. This reservoir has a capacity of 42 million gallons and its basin is uninhabited. Lower Franklin Reservoir, two miles below,

is not completed. At present the water flows from Upper Franklin Reservoir directly to the distributing mains at Third Street and Western Avenue, a distance of about 12 mi.

### BACTERIOLOGICAL EXAMINATIONS

The samples were iced and shipped to the laboratory so that they were plated within 48 hours and usually within 24 hours from the time of sampling. They were taken and examined in duplicate.

The samples were plated in standard agar using $^1/_2$, $^2/_{10}$ and $^1/_{10}$ cc. dilutions, and lactose-bile fermentation tubes were inoculated with $^1/_{10}$, 1 and 10 cc. of water sample. The tubes showing acid and gas formation were inoculated on to litmus-lactose agar or endo plates, and characteristic colonies fished and transplanted to peptone solution for indol production, nitrate solution for nitrate reduction, lactose milk for acid and clot, and gelatine for liquefaction. In Table I, the count is given as the average number of colonies per cc. on the six plates after incubation at 37° C. for 48 hours, and in the column "*B. coli* Group, cc" the smallest sample giving characteristic tests for *B. coli* is reported.

TABLE I BACTERIOLOGICAL EXAMINATIONS OF AQUEDUCT WATER

| DATE SAMPLED | 9/3–14/14 1st sampling | | 9/15–18/14 2nd sampling | | 9/23–26/14 3rd sampling | | 9/27–29/14 4th sampling | | 10/12–16/14 5th sampling | | 11/15–18/14 6th sampling | | 11/19–21/14 7th sampling | | 1/22–23/15 8th sampling | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Count | *B. coli* Group | Count | *B. coli* Group | Count | *B. coli* Group | Count | *B. coli* Group | Count | *B. coli* Group | Count | *B. coli* Group | Count | *B. coli* Group | Count | *B. coli* Group |
| WHERE SAMPLED | Per Cc. | Cc. | Per Cc. | Cc. | Per Cc. | Cc. | Per Cc. | Cc. | Per Cc. | Cc. | Per Cc. | Cc. | Per Cc. | Cc. | Per Cc. | Cc. |
| Intake of Aqueduct | 140 | 0.1 | | | 3200 | 0.1 | | | 6100 | 0.1 | 3430 | 1 | 2260 | 1 | | |
| Conduit at Alabama waste gate | 160 | ... | | | 4600 | 0.1 | | | 5300 | 0.1 | 2210 | 10 | 1530 | 1 | | |
| Inlet, Haiwee Reservoir | 105 | ... | 170 | | 2100 | | | | 2100 | 1.0 | 1790 | 10 | 1740 | 10 | 40 | |
| Constriction in Haiwee Reservoir | 140 | 0.3 | 160 | | 2000 | | 1800 | | 1000 | 10.0 | 840 | 10 | 900 | | | ... |
| Outlet, Haiwee Reservoir | 60 | ... | 65 | | 1800 | | 1500 | | 1300 | | 750 | | 830 | | | |
| Inlet, Fairmont Reservoir | 84 | ... | 4000 | 0.1 | 1300 | | 1700 | | 1700 | | 600 | | 870 | | 36 | |
| Outlet, Fairmont Reservoir | 150 | ... | 4500 | | 1500 | | 1900 | | 2500 | | 600 | | 710 | .10 | 52 | |
| Inlet, Dry Canyon Reservoir | 300 | ... | 4000 | | 8000 | 10.0 | 6500 | 10 | 3200 | 0.1 | 830 | .10 | 880 | | 68 | |
| Outlet, Dry Canyon Reservoir | 200 | ... | 1000 | 0.5 | 7500 | | 6200 | | 3100 | 1.0 | 620 | | 950 | | 1460 | 10 |
| Cascades | 525 | ... | 580 | | 6700 | | 7400 | | 2800 | 10.0 | | | | | | |
| Sar. trap at San Fernando Dam | 375 | ... | 2000 | | 8200 | | 7500 | | | | 630 | | 730 | | 335 | |

At first glance, the most striking feature of the bacteriological counts is the variation in total counts at a given station. This is caused by the fact that the end of the vegetative season comes suddenly in this region and that it and the fall "turnover" of the reservoir water took place during the period of examination.

The finding of *Bacillus coli* in samples taken at the inlet of Dry Canyon Reservoir is attributed to contamination in San Francisquito Canyon, where a road crosses the creek channel thirty-three times. The absence of *Bacillus coli* in all samples smaller than 10 cc. and in the great majority of 10 cc. samples taken below Franklin Reservoir, indicates that the two weeks' storage in Dry Canyon and Upper Franklin Reservoirs purified the water. As noted above, this is a temporary condition and there will be no chance for pollution to enter the water after leaving Haiwee Reservoir, except the accidental pollution by stragglers about the small reservoirs, which is guarded against by caretakers.

Below Dry Canyon Reservoir, the finding of *Bacillus coli* in occasional samples may be attributed to ducks, which were numerous on these reservoirs during the time of our work. In order to prove that the duck carried *Bacillus coli*, the fecal matter of duck killed on these reservoirs was examined and found to contain 50,000,000 typical *Bacillus coli* colonies per gram.

During the period of examination, the effluent from Haiwee Reservoir was 50 cu. ft. per second. It is estimated that the full capacity of 420 cu. ft. per second will not be required for 10 years. But it is the policy of the Water Department to always keep Haiwee Reservoir half full, thus providing at least 30 days' storage. Carefully prepared statistics for the ten years from 1904 to 1914 indicate that this storage can be provided when the constant effluent of Haiwee Reservoir is 420 cu. ft. per second, even through periods of drought, by the aid of pumped water.

The self-purification of stored water is a generally accepted principle. This knowledge has been made certain through the excellent work of Professors Russell, Jordan and Zeit at the time of the Chicago drainage canal case, and the more recent work of Dr. A. C. Houston.

The period of storage required to accomplish self-purification depends upon conditions. Two weeks' storage under the normal conditions at Haiwee Reservoir would doubtless serve to purify the water, and it is a certainty that thirty days' storage will produce an epidemiologically sterile water. Under present conditions, the Aqueduct water will be subjected to 470 days' storage. It is estimated that for the next five years the draft will not exceed one-half the capacity of the system, during which period the water will be subjected to 120 days' storage. When operating full capacity the storage period will be 65 days, thus providing a good margin of safety.

The chief argument of plaintiffs in the cases referred to in the introduction of this paper was that water would be carried from inlet to outlet of Haiwee Reservoir in as short a time as 3 days, by winds. This argument was based upon the work of Ackermann, at Owasco Lake, N. Y. It is not to be expected, however, that sufficient ice will form on Haiwee Reservoir to break up and be carried across the reservoir. Furthermore, the constrictions and the tortuous shape of the reservoir make it impossible that this action could take place.

TABLE II SANITARY CHEMICAL ANALYSES OF AQUEDUCT WATER
Results in Parts per Million

| Date sampled | 11/17/14 | 11/20/14 | 11/16/14 | 11/15/14 | 11/12/14 |
|---|---|---|---|---|---|
| Where sampled | Intake of Aqueduct | Haiwee Reservoir between | S. Haiwee Reservoir surface near tower | Dry Canyon Res. inlet | Franklin tunnel South Portal |
| Color | 10.0 | 20.0 | 20.0 | 10.0 | 22.0 |
| Turbidity | 2.0 | 3.0 | 6.0 | 2.0 | 2.0 |
| Dissolved solids | 320.0 | 220.0 | 250.0 | 440.0 | 430.0 |
| Volatile and organic matter | 100.0 | 80.0 | 60.0 | 100.0 | 80.0 |
| Chlorine | 15.0 | 15.0 | 23.0 | 50.0 | 48.0 |
| NITROGEN AS: | | | | | |
| Free ammonia | 0.040 | 0.048 | 0.270 | 0.110 | 0.046 |
| Albuminoid ammonia | 0.054 | 0.100 | 0.260 | 0.102 | 0.200 |
| Nitrites | Trace | 0.006 | 0.007 | 0.002 | 0.001 |
| Nitrates | 0.083 | 0.076 | 0.083 | 0.670 | 0.340 |
| Oxygen consumed | 2.80 | 2.52 | 3.80 | 2.80 | 2.40 |
| HARDNESS: | | | | | |
| Permanent | 12.0 | 15.0 | 14.0 | 50.0 | 35.0 |
| Temporary | 89.0 | 80.0 | 91.0 | 134.0 | 140.0 |
| Total | 101.0 | 95.0 | 105.0 | 184.0 | 175.0 |

TABLE III INDUSTRIAL ANALYSIS OF AQUEDUCT WATER
Results in Grains per U. S. Gallon

| Date sampled | 9/26/14 | 9/26/14 | 8/24/14 |
|---|---|---|---|
| Where sampled | Intake to Aqueduct | Aqueduct at Alabama waste gate | Aqueduct at Franklin Canyon power house |
| Silica | 0.75 | 0.59 | 0.80 |
| Iron and aluminum oxides | Trace | Trace | Trace |
| Calcium carbonate | 6.55 | 4.92 | 5.85 |
| Calcium sulfate | 0.51 | 0.46 | 1.02 |
| Calcium chloride | None | None | None |
| Magnesium carbonate | 1.73 | 1.67 | 2.59 |
| Magnesium sulfate | 0.36 | 0.36 | 1.64 |
| Magnesium chloride | None | None | None |
| Sodium carbonate | 2.60 | 1.58 | 1.24 |
| Sodium sulfate | 1.74 | 1.79 | 5.54 |
| Sodium chloride | 2.51 | 2.03 | 5.41 |
| Volatile and organic matter | 5.03 | 4.56 | 8.07 |
| Total solids | 21.78 | 18.36 | 32.16 |

### CHEMICAL ANALYSIS

Since our time was limited and there seemed but little need

for chemical analysis at the trial, we did only enough work to give us an insight into the character and amounts of dissolved substances in the water. The sanitary chemical analyses, Table II, and the mineral analyses, Table III, indicate that the water being delivered through the Aqueduct is softer and contains less solids than the water from the present Los Angeles River supply. Also, it is to be expected that when the more soluble salts are leached from the reservoir beds and the concrete, and the water is not run through San Francisquito Canyon, the water will contain less solids than at present.

### BIOLOGICAL EXAMINATION

To conclude this paper without reference to this subject would leave it incomplete. Yet there has been no systematic work done to date which will warrant a public statement. It is to be expected that algae will flourish in the reservoir water during the summer months. The system does not provide for filtering the water, but chemical treatment of the stored water is contemplated. Aeration is provided at present with the "Cascades" near San Fernando.

### CONCLUSION

A conclusion of this subject can best be made by stating the quality of water delivered through the Aqueduct to the consumer. A portion of the decision of Judge Lewis R. Works, rendered after hearing expert testimony for forty actual trial days in the above cases, states this ably and concisely, as follows:

"The scientific principles governing the selection and operation of a water system intended to furnish a domestic supply from surface streams requires a treatment of the water in order to rid it of the contamination which is inevitably incident to such a source of supply. This treatment consists in either the use of chemicals, the installation of infiltration plants, or in the storage of the water in reservoirs for a period of time requisite to its purification.

"If it be granted that the waters of Owens Valley are contaminated like all other surface waters, the density of population of its drainage area being the true index of contamination, and if it be granted that, for that reason, those waters would not be proper for domestic use at the intake of the Los Angeles Aqueduct, in the valley, does it follow that the water has not been purified when it reaches the point of delivery in Los Angeles, two hundred and eighty-six miles from the intake? In other words, is the water, during its transmission from the intake to the city, subjected to either of the methods of treatment above mentioned as requisite to the purification of a surface water supply?

"Ninety miles from the Aqueduct intake is located Haiwee Reservoir. From the outlet of that reservoir to Los Angeles is one hundred and ninety miles. During this progress over that distance, the water supply is halted, even if briefly, in Fairmont, Dry Canyon and Franklin Reservoirs, three other basins having some value for storage purposes.

"A large portion of the testimony during the trial has been directed to the question of the efficacy of the entire system mentioned, and especially of Haiwee Reservoir, as a purifying agency, and many experiments have been conducted in the waters of the reservoir in order to determine the problem. It is not necessary now to state the nature of these experiments, nor to analyze the theories and arguments advanced by the various expert witnesses who have testified concerning them. It is sufficient to say that the great weight of the evidence demonstrates that Haiwee Reservoir is remarkably efficient as a great purifying unit in the Aqueduct system. This immense basin is over seven miles in length, with that distance between its inlet and outlet, and impounds, for a long period of time, certainly not less than thirty days, all waters which enter it. The reservoir is peculiarly adapted to the use for which it was principally designed. One of the leading expert witnesses in the case characterizes it as unique among the storage reservoirs of the world. Being in a region in which there is a rainfall of not to exceed five inches per annum, a region of porous, sandy soil, and entirely uninhabited, it is the recipient of no run-off from its own water-shed and it is therefore free from the contamination of such a run-off. The only influent of the reservoir is the Los Angeles Aqueduct, containing waters brought from the Owens River. The intake gates on the river may be closed at will and there are frequent waste gates along the course of the Aqueduct, from the river to the reservoir, through which the waters of the great ditch may be entirely cast away. These instrumentalities conduce to a perfect control of the Haiwee influent and the waters may be diverted and wasted in periods of flood or at any other time of possible undue contamination from whatever cause.

"This peculiarly advantageous location of Haiwee is mentioned in passing, only, as the period of storage, which is allowed by its size and shape, is alone sufficient to guarantee to the people of Los Angeles a positive immunity from dangers residing in the waters before they leave Owens Valley, conceding that such dangers are there present, and without regard to the use of the waste gates mentioned, which furnish but an added factor of safety to a system safe enough without them."

TABLE IV—TIME FACTOR IN SELF-PURIFICATION OF AQUEDUCT WATER

Rates of Forward Travel of Water Estimated with Haiwee Reservoir 1/2 full and Other Reservoirs 2/3 Full

| FROM | TO STATION AT | TIME IN TRANSIT OR STORAGE IN DAYS: With maximum flow | 272 m. g. d. draft | 136 m. g. d. draft | With present flow |
|---|---|---|---|---|---|
| Intake of Aqueduct | Cottonwood Creek | 0.907 | 1.242 | 1.565 | 2.930 |
| Cottonwood Creek | Intake, Haiwee Reservoir | 0.279 | 0.362 | 0.465 | 0.798 |
| Intake, Haiwee Reservoir | Outlet, Haiwee Reservoir | 38.300 | 38.300 | 76.600 | 402.500 |
| Outlet, Haiwee Reservoir | Inlet, Fairmont Reservoir | 1.549 | 1.549 | 1.888 | 3.098 |
| Inlet, Fairmont Reservoir | Outlet, Fairmont Reservoir | 4.750 | 4.750 | 9.500 | 47.900 |
| Outlet, Fairmont Reservoir | Inlet, Dry Canyon Reservoir | 0.113 | 0.113 | 0.138 | 0.226 |
| Inlet, Dry Canyon Reservoir | Outlet, Dry Canyon Reservoir | 1.050 | 1.050 | 2.100 | 10.600 |
| Outlet, Dry Canyon Reservoir | Inlet, San Fernando Reservoir | 0.139 | 0.139 | 0.169 | 0.278 |
| Inlet, San Fernando Reservoir No. 1 | Outlet, San Fernando Reservoir No. 1 | 11.992 | 11.992 | 23.975 | 0.055(a) |
| Outlet, San Fernando Reservoir No. 1 | Inlet Upper Franklin Reservoir | 0.106 | 0.106 | 0.106 | 0.775 |
| Inlet, Upper Franklin Reservoir | Outlet, Upper Franklin Reservoir | 0.718 | 0.718 | 0.718 | 2.154 |
| Outlet, Upper Franklin Reservoir | Inlet, Lower Franklin Reservoir | 0.008 | 0.008 | 0.008 | |
| Inlet, Lower Franklin Reservoir | Outlet, Lower Franklin Reservoir | 6.180 | 6.180 | 6.180 | 0.174(a) |
| Outlet, Lower Franklin Reservoir | Third St. & Western Ave., Los Angeles City | 0.080 | 0.080 | 0.080 | |
| | Total | 66.171 | 66.589 | 123.492 | 471.488 |

(a) Reservoirs by-passed at present.

## THE REVIVAL OF THE USE OF NATURAL DYESTUFFS[1]

By EDWARD S. CHAPIN

Imagine, if you can, the following situation: The supplies of artificial dyestuffs have become exhausted. The European blockade of embargo, call it what you will, has continued in uninterrupted force. Capital has been too timid to manufacture artificial dyestuffs in this country. This situation we will

[1] Address before the 98th Meeting of the National Association of Cotton Manufacturers, Boston, April 28 and 29, 1915.

now consider. "Nothing but black and white," says one; "The country will have to wear white," cries another; a third asserts: "The mills of the country will have to shut down!" What is the truth? The truth is that natural dyestuffs can keep the mills of the Nation in operation, producing a diversification of shades and giving fast colors.

This paper does not propose to consider the question of the relative merits of natural dyestuffs *versus* artificial dyestuffs. The present is no time for controversy. It demands coöperation and construction. We must remember that before the days of the modern artificial dyes people wore colored garments. Ladies were gay and gallants tried to please long before Perkin discovered mauve. A careful reading of any of the works of the masters of detailed description of the past century—of Dickens, Thackeray, Victor Hugo, or Goethe—will reveal interesting evidence of color and colored fabrics. Even more so the standard text-books on dyeing, of fifty or seventy-five years ago, consider the whole range of the spectrum. It is truly remarkable the multi-colored and fast effects that the dyers of the old school achieved with limited means and facilities. It is quiet within the memory of many of this audience, when the earlier aniline colors were distrusted by the general public because of their comparative fugitiveness, and it took much industrious advertising and scientific development of new and better products to overcome this prejudice.

The dyers and chemists of today are in a position to secure with natural dyestuffs better results than the dyers of former days. The forms of natural dyestuffs were not so perfect formerly as today. Then the dyer was forced to use the dyestuffs in the form of chips or ground bark or ground leaves; today he has ready at hand the essential coloring matter of the natural dyestuffs in the form of extracts, pastes, or powders, and in many instances the coloring matters have been worked up by chemical treatment so that they dye more readily and give brighter and faster results. The march of chemical and mechanical science contributes to the solution of the task. Chemical science in recent years has found the exact chemical composition and nature of the natural dyestuffs, so that they can now be dyed most intelligently and in accordance with the highest development of the theory and the practice of dyeing. New and improved chemicals and dyeing assistants are at the disposal of the dyer. New forms of dyeing apparatus and improved mechanical devices help further. Improved dyeings are to be expected in response to persistent and intelligent work, and during the past months such results have been secured in many instances.

### AVAILABLE NATURAL DYESTUFFS

For the dyeing of cotton the following natural dyestuffs are available: logwood, fustic, bark or quercitron, flavine, hypernic and the various redwoods, catechu or cutch, gambier, sumac, madder, Persian berries, and indigo. Of these dyestuffs all except madder, Persian berries, and indigo are available in large quantities.

Logwood is the product of a large tree known botanically as *Hematoxylon campechianum*, which grows abundantly in the West Indies and Mexico. The supply of logwood is not petering out as some have erroneously imagined; the logwood forests have not all been cut off There are well-nigh limitless virgin forests of logwood in Haiti, Jamaica and Mexico. Reforestation and cultivation are the simplest of operations. The logwood tree is a veritable weed—it spreads itself; twelve years alone elapses between the seed and the tree ready for cutting for commercial purposes. Cultivation consists in keeping the forests thinned out, so that the luxuriant tropical growth will not form an impenetrable jungle. It may fairly be said that never before has there been available more logwood than today.

Fustic, also known as old fustic, Cuba wood and yellow wood, comes from a tree known botanically as *Morus tinctoria* or *Maclura tinctoria*. It is a native of Brazil, Mexico, and several of the West Indian Islands. Quercitron bark is the inner bark of a species of oak, the *Quercus nigra* or *Quercus tinctoria*, a native of America. It grows abundantly in Pennsylvania, Georgia, and the Carolinas. Flavine is the name given to a preparation of quercitron bark. It contains the principal coloring matter of quercitron bark, quercetin, in nearly chemically pure state. Hypernic is the name given to the color extracted from the various soluble redwoods. These are principally Brazil wood, peach wood, sapan wood, and lima wood. Brazil wood grows in the forests of Brazil. Peach wood is a native of Mexico. Sapan wood grows in Siam, Japan, and the East Indies. Lima wood is imported from Peru. Catechu or cutch and gambier closely resemble each other in properties. They are obtained from various species of acacia, areca, and uncaria, growing in India. Sumac consists of the leaves, leaf-stalks and small twigs of several species of *Rhus*. This shrub is remarkably common and widely spread, growing in Sicily, Tuscany, France, Spain, Algeria, Canada, and the United States, particularly in Virginia.

The various regions from which these natural dyewoods come are with unimportant exceptions outside the inhibiting influence of the war. Accordingly, they are all available. Even prior to the war these dyestuffs were in large general use—much more extensively than is generally realized—so that the present additional demands from the textile mills find an industry well fitted to take on extra burdens and to perform needed services.

### BLACK DYEING OF COTTON

Black is the color most widely demanded by the trade, and will accordingly first engage our attention. For black dyeing logwood has been and still is the most generally all-round useful black dyestuff. It can be used not only for the coloring of cotton but also of wool and silk and a great variety of fibers. There are three methods of applying logwood on cotton: (1) the stuffing and saddening; (2) the bluestone soda ash; (3) the mordanting methods.

### THE STUFFING AND SADDENING METHOD

In this method of dyeing, the cotton, as piece goods, yarn, or raw stock, is first impregnated with the logwood by passing it through or boiling it in a concentrated logwood extract solution; it is then dried or whizzed to fix the logwood or remove an excess not taken up by the fiber; finally it is passed through a bath of chemicals, usually chrome, or chrome and bluestone, or copperas, to develop the black. Two illustrations of this process will be given: one on piece goods, and the other on raw stock.

LOGWOOD BLACK ON PIECE GOODS—This process makes use of two boxes and has been in constant successful use for the past four years in the dyehouse of a large producer of black dyed cotton piece goods.

The apparatus consists of a stock tank for the logwood liquor and a logwood dye-bath, three sets of drying cans, a stock tank for the chrome liquor and a chrome bath, a steam box, a wash mangle, and a washer. The logwood box and the chrome box are provided with guide rolls, and above the center of each box are three squeeze rolls. The guide rolls and the squeeze rolls are so related that the cloth in its passage through both the logwood and the chrome baths is twice immersed and twice squeezed.

The dry bleached pieces are run into the dye-bath and over the first four rolls, squeezed and given a second run in the dye-bath over the second four rolls, followed by another squeeze. From the dye-bath the pieces are dried over three sets of drying cans. The passage through the chrome bath follows imme-

diately and here, as in the dyeing, there are two immersions and two squeezes. After the chroming, the goods are steamed, and then washed. The washing is very thorough, first by passage through a wash mangle, and then through a washing machine. After washing, the goods are again dried and then finished.

| Stock Liquor | Chrome Liquor |
|---|---|
| 125 gallons water | 125 gallons water |
| 110 lbs. logwood extract, 51° Tw. | 49 lbs. bichromate soda |
| 5 gallons acetic acid No. 8 | 3 lbs. soda ash, 58° |
| Temperature of dye-bath—near boil | Time of immersion—about 2 seconds |
| Time of immersion—10 seconds | Time of steaming—about 10 seconds |

The speed of the machine, 45 to 50 yards a minute, corresponds to a production of about 3,000 yards an hour; but a speed of 75 yards to the minute (4,500 yards an hour) is possible.

The goods are used as linings for suitings, overcoats, and the like, where a black is needed that will not stain white when wet hot-pressed. The logwood process is preferred because of the low cost of production, and the excellent fastness of the result.

LOGWOOD BLACK ON RAW STOCK—The following method is being employed in a Klauder-Weldon dyeing machine, coloring 1,000 pounds of cotton to a batch.

Run for one hour at a boil in a 10 per cent solution of logwood extract, prepared by dissolving 10 pounds logwood extract 51° Tw. to every 12 gallons of water. This solution will stand 4° Tw. at 70°. Take out of machine and whizz. Repack in machine, and strike with 4.5 per cent bluestone and 1.5 per cent soda chrome. Run in striking bath 1¼ hours; wash well. Soap in a 0.5 per cent solution of soap; wash and dry. The logwood bath is saved and brought up to 4° Tw. for further dyeings. This method gives a remarkably full and rich black on stock of excellent fastness to fulling and of moderate fastness to light.

### THE BLUESTONE SODA ASH METHOD

The bluestone soda ash method of dyeing cotton, or the ash black as it is commonly called, is a favorite method because of its simplicity.

The following recipe is a slight modification of a bluestone soda ash logwood black formula used in a large mill for the coloring of raw cotton, and illustrates well the general principles and practice that are obtained in the successful dyeing of cotton with logwood in the single bath:

| Dye-Baths for 100 Lbs. Raw Cotton | Starting bath Lbs. | Second bath Lbs. | 3rd or standing bath Lbs. |
|---|---|---|---|
| Logwood extract, 51° | 60 | 40 | 20 |
| Soda ash, 58° | 6 | 4 | 3 |
| Bluestone | 3 | 2 | 1.5 |

Boil 1½ hours. Throw out the stock and allow to drain. Oxidize for two hours, or until the full shade is developed, turning occasionally.

After the standing bath is obtained, enter the first lot for a second dip in the standing bath. After this, one immersion is usually sufficient. If extra heavy shades of black are required, give two immersions or increase the amount of dyestuff and chemicals in the standing bath. If a jetter shade of black is desired, use an ounce of cutch extract for every pound of logwood extract. Some dyers find it advantageous to use also an ounce of sumac extract for every pound of logwood extract.

The bluestone soda ash logwood black can be utilized for the dyeing of other forms of cotton, as cotton yarn, cotton warps and the like; and for the dyeing of a wide variety of cotton fabrics. The following series of formulae are taken from practice:

DYEING COTTON YARN For dyeing cotton yarn, black dye is usually preferred. Black dye is a logwood extract, which contains a proportion of tannin-bearing material, such as chestnut extract It gives a very good deep black at an exceedingly low cost.

| Dye Baths for 100 Lbs. Cotton Yarn | Starting bath Lbs. | Second bath Lbs. | Third or standing bath Lbs. |
|---|---|---|---|
| Black dye | 50 | 25 | 20 |
| Soda ash | 20 | 8 | 3 |
| Blue vitriol | 10 | 4 | 1.5 |

Boil 1½ to 2 hours, lift and oxidize 2 or 3 hours. By after-treating with 1 per cent chrome at 150° to 160° for 20 minutes, the fastness to washing is made excellent.

DYEING COTTON WARPS—For 650 pounds warp, prepare a bath containing:

130 lbs. logwood extract, 51 ° 18 lbs. soda ash 12 lbs. blue vitriol

Give four runs, boiling. Sadden in another tub with 6 lbs. copperas, at 120° F.; finish. This gives a very good black.

The following recipe is an example of a successful application of the use of salt in the bluestone soda ash logwood black. A Klauder-Weldon machine was used in dyeing.

For 800 pounds raw cotton prepare a starting bath containing:

370 lbs. logwood extract, 51° 18 lbs. soda ash
18 lbs. blue vitriol 10 lbs. common salt

Boil the cotton for 2 hours. Oxidize for 2 hours. Afterwards wash in:

8 lbs. soap 15 lbs. sal soda
5 lbs. common salt 1 qt. ammonia

Dissolve the chemicals for the washing in about three-quarters of a barrel of water, and feed onto the cotton at 120°. Continue washing one-half hour.

For a standing bath, gradually reduce the amount of dyestuff and chemicals above given during four or five baths to one-half the quantities.

The bluestone soda ash logwood black can be used for all purposes where fastness to fulling is not required. It is faster to light than the stuffing and saddening black.

### THE MORDANT METHODS

By mordant methods is meant those methods in which the mordant is fixed on the cotton previous to the logwood treatment. Two of these methods will engage attention: (1) the iron; (2) the chrome.

1. THE IRON MORDANT BLACK—The iron mordant logwood black has always been employed when a black of special fastness to fulling and light is required. The following recipe is for coloring warps in a four-box machine:

LOGWOOD BLACK ON WARPS—Boil up 25 per cent extract of sumac in the boxes, run in the yarn, and leave over 1 day (36 hours, or more). Treat to two runs in clear lime-water, followed by two runs in pyrolignite of iron, 3° Tw.

In practice the volume of liquor in the iron liquor machine is so small that the readings of the hydrometer are not of much value. It is best to add between 20 per cent and 25 per cent iron liquor, one-half before each run, and to squeeze the warps lightly. Much of the liquid is removed from the bath, and it is generally necessary to add some water on every set. Wait twenty to thirty minutes before washing. Then treat to 1 run in clear lime-water and wash again.

15 per cent conc. extract logwood; 3 per cent conc. extract fustic; 1 per cent copper sulfate

Add one-half the logwood and one-half the fustic, bring the temperature of the bath to 140° F., and make one run. Add the remainder of the logwood and fustic, raise the temperature to 170° F., and make one run. Raise the temperature to a boil and make six runs. Add the copper sulfate in solution, half on the fifth and half on the sixth run, there being eight runs in all. Then wash with 1 run.

One per cent potassium bichromate

Add one-half the bichromate to make one run at 180° F. Add the remainder and make one run at the same tempera-

ture. Wash with 2 runs. Finish with 3 per cent lard oil and 3 per cent soft soap (one run).

The above process can be shortened considerably with equally satisfactory results, by the use of the machinery constructed for the dyeing of sulfur colors. These machines give longer immersions than the old Scotch tubs, and have heavier nips.

FOUR BOX MACHINE

First run: First box: 50 per cent sumac extract, 180° F.; nip. Second box: 30 per cent nitrate of iron; cold; nip. Third box: Lime solution; cold; nip. Fourth box: Water.

Second run: Three boxes of logwood, 30–40 per cent to each box, boiling. Fourth box: Wash.

Practically the same processes may be used for pieces.

2. THE CHROME MORDANT BLACK—The chrome mordant black came into being in response to the request to dye logwood blacks on raw stock in a vacuum dyeing machine In this machine the methods above described, except the iron mordant method, do not give any results at all.

The use of a chrome mordant to develop and to fix logwood on wool is a well-known dyeing process. It yields blacks of excellent fastness to fulling, light, and various other agencies, and of exceptional beauty. The idea to adapt this method of dyeing wool to obtain equally fast and handsome results on cotton has long been alluring. Various methods of mordanting the cotton with chrome that have been tried in the past have not met with wide or permanent success.

The trouble has always been either that the chrome would not go on the cotton fiber or was deposited so loosely that in washing it nearly all came off.

These difficulties have recently been overcome by the use with the chrome of a compound (invented by a well known chemist) which causes the chrome to exhaust onto the cotton and to be deposited so firmly that even severe washing will not strip it off.

The preliminary studies for the practical use of this new method of mordanting cotton were made in the model laboratory of the American Dyewood Company. This laboratory is fully equipped with small size dyeing machines of latest invention. Through the courtesy of Mr. W. A. Mitchell the work has passed beyond the laboratory stage. Mr. Mitchell generously offered the use of the dyehouse of the Massachusetts Cotton Mills for trials on a practical scale; and the results obtained in the laboratory of the American Dyewood Company have thus had the benefit and the test of the splendid personnel and equipment of Mr. Mitchell's plant.

The following recipe was employed in the coloring of 150 pounds of raw cotton in a vacuum dyeing machine:

BLACK ON RAW COTTON—After loading the machine, fill with water and bring to a boil. Boil ten minutes to ensure thorough wetting out of the cotton. Add 6 lbs. of soda chrome dissolved in three pails of water, and after the chrome liquor has well circulated, add slowly 3 lbs. of chrome assistant dissolved in 2 pails of cold water. Boil one hour; wash. Fill the machine with water and bring to a boil. Prepare a half barrel of logwood extract liquor 15° Tw. containing 10 per cent fustic, and six pails of clear lime-water. Boil the logwood liquor well. Add slowly to the machine, and boil one hour. Wash. Strike cold with 1 lb. of bluestone and 8 oz. of chrome. Wash and finish as usual. Soaping improves the beauty of the shade, but is not essential.

The more concentrated the chrome liquor the more quickly the cotton takes up the chrome and the less the time required for boiling. From two-thirds to five-sixths of the chrome is exhausted on the fiber. The logwood liquor is not exhausted, but should be run off and kept for use in subsequent baths. The heavier the black required, the more concentrated should be the logwood liquor.

This process gives a black of excellent fastness to fulling and to light. The stock cards readily and the feel is especially satisfactory.

The process has been tried practically only on raw cotton. It has given good results in the laboratory on yarn and pieces. As the coloring of raw cotton in a vacuum dyeing machine is the hardest test of a process, there is good reason to believe that the new chrome mordant method can be adapted in practice to the coloring of the other forms of cotton and in the various other dyeing apparatus.

3. FASHION SHADES ON COTTON—Next in importance to black come the fashion shades. Many artificial colors are so brilliant that the great fear of many people has been that without these the consuming public could not be satisfied. A few illustrations will show that besides blacks the natural dyewoods can be made to yield a wide variety of fashion shades.

In dyeing the fashion shades, the stuffing and saddening method and the mordant method are applicable.

CATECHU OR CUTCH AND GAMBIER BROWNS—These valuable dyestuffs yield browns of specially pleasing tone and satisfactory fastness. The following recipe represents the method of dyeing a medium shade of cutch brown on pieces in a jigger:

For 100 lbs. of goods use 50 lbs. of good extract cutch. Enter goods nearly at a boil. Add the color in two ends. Then add 5 lbs. of bluestone. Bring to a boil, and boil one hour; shut off steam and allow to run from one-half to three-quarters of an hour. Draw off liquid and run in 2 lbs. of chrome. Run twenty minutes at 140° F. Rinse and dry. For a standing bath the amount may be reduced one-third. Gambier may be used in place of cutch and acts similarly.

For the toning of browns, fustic, bark and flavine are available as yellows, and hypernic as a red. Logwood, sumac, and copperas can be used for darkening.

Two illustrations follow: a light, bright brown dyed in a four-box machine, and a dark brown dyed in a jigger.

LIGHT SHADE OF BRIGHT BROWN—Prepare gambier, bark, and chrome solutions at 10° Tw. The gambier and the bark are divided between the first two boxes. Use fifteen pails of gambier and nine pails bark. The third box contains cold water, and the fourth box the chrome. Use eight quarts of chrome liquor. After leaving the chrome bath the goods are well washed in a water mangle. Repeat the process. Dry and size.

DARK BROWN—Prepare a solution in the jigger containing for 100 lbs. of goods: 10 lbs. hypernic crystals; 5 lbs. logwood extract, 51° Tw.; 15 lbs. extract of fustic, 51° Tw.; and 15 lbs. extract of bark, 51° Tw. Add the color in two ends. Boil one-half hour; shut off steam. Add 1 lb. of bluestone. Run fifteen minutes. Add 2 lbs. chrome. Run fifteen minutes. Wash.

The use of logwood for blacks has so overshadowed the other natural dyestuffs that the thought of violets, oranges, reds, bright yellows and blues does not come easily to mind when natural dyestuffs are mentioned. For this particular purpose, the new mordant process is especially adapted. On the table, in addition to sample dyeings of the other processes described, are a range of bright fashion shades colored by the new mordant process from natural dyestuffs.

In discussing this process earlier in the paper, mention was made only of the ability of the new assistant to exhaust chrome on the fiber. This chemical is also able to fix other mordants—aluminum sulfate, tin crystals, copperas, and blue vitriol, on cotton, and so firmly that washing will not strip the mordants. These mordants then react with the natural dyestuffs to produce a diversification of shades. Thus fustic on a tin or aluminum mordant produces brighter yellows than on a chrome mordant. Logwood on a tin mordant gives violet to bordeaux shades of excellent brightness.

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# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

## THE CHEMICAL TRADE OF THE UNITED STATES IN 1914

The following list of the imports and exports of chemicals and related products to and from the United States in 1913 and 1914, taken from the *Z. angew. Chem.*, **28** (1915), III, 125, shows clearly the effect of last year's economic depression and the war. Of 118 items of imports, 70 show a decrease in value from last year. The total imports of "chemicals, drugs, dyes and medicines", according to official federal statistics, fell from $101,300,000 in 1913 to $87,700,000 in 1914, a decrease of 13.4 per cent. Of this amount $49,400,000 represented duty-free imports in 1914 as against $62,200,000 in 1913; dutiable imports amounted to $38,300,000 in 1914 and $39,100,000 in 1913.

| IMPORTS | 1913 1000 lbs units | 1913 $1000 units | 1914 1000 lbs. units | 1914 $1000 units |
|---|---|---|---|---|
| CHEMICALS | | | | |
| Potassium carbonate | 21,437 | 653 | 15,891 | 387 |
| Potassium hydroxide, not in sticks[1] | 6,326 | 246 | .. | .. |
| Potassium hydroxide with not over 15 per cent $Na_2OH$ | 2,364 | 89 | 7,197 | 287 |
| Potassium cyanide | 1,023 | 144 | 1,246 | 180 |
| Potassium chloride | 427,524 | 7,120 | 337,081 | 5,741 |
| Potassium sulfate | 79,076 | 1,633 | 72,528 | 1,569 |
| Potassium nitrate, raw | 9,877 | 263 | 2,230 | 73 |
| All other potash salts, dutiable | 6,115 | 555 | 5,214 | 482 |
| Sodium cyanide | .. | .. | 2,423 | 367 |
| Sodium nitrate (1000 tons) | 626 | 21,631 | 544 | 15,229 |
| All other soda salts, dutiable | 11,176 | 325 | .. | 629 |
| The same, duty-free | .. | .. | .. | 26 |
| Ammonium chloride | 9,019 | 466 | 7,842 | 395 |
| Ammonium sulfate | 116,562 | 3,957 | 148,242 | 4,476 |
| Arsenic compounds | 6,688 | 286 | 4,079 | 165 |
| Chloride of lime | 61,605 | 510 | 34,540 | 333 |
| Potassium citrate | 3,301 | 500 | 4,359 | 725 |
| Iodine | 240 | 526 | 463 | 951 |
| Magnesite, not purified | 335,868 | 1,669 | 241,166 | 1,298 |
| Carbolic acid | 7,502 | 558 | 6,902 | 394 |
| Oxalic acid | 7,423 | 365 | 8,165 | 423 |
| Other acids, dutiable | .. | 533 | .. | 1,147 |
| Other acids, duty-free | .. | 383 | .. | 242 |
| Sulfur, raw (1000 tons) | 14 6 | 278 | 22 8 | 410 |
| Sulfur ore with over 25% S (1000 tons) | 849 | 3,611 | 977 | 4,706 |
| Tartar | 29,066 | 2,780 | 27,436 | 3,028 |
| DRUGS AND MEDICINES | | | | |
| China bark | 2,809 | 307 | 3,945 | 538 |
| Quinine sulfate and all other China bark products (1000 oz.) | 2,971 | 562 | 2,968 | 703 |
| Opium, at least 9 per cent morphine | 553 | 2,391 | 416 | 1,976 |
| Medicinal preparations | .. | 1,430 | .. | 753 |
| Fusel oil or amyl alcohol | 5,983 | 1,087 | 3,531 | 525 |
| Hops | 7,313 | 2,946 | 7,483 | 2,584 |
| Licorice root (1000 tons) | 49 7 | 1,775 | 51 6 | 1,872 |
| Vanilla beans | 1,034 | 2,530 | 835 | 2,184 |
| Mineral water (1000 doz. qts.) | 1,188 | 993 | 951 | 874 |
| DYES AND TANNING MATERIALS | | | | |
| Alizarine and alizarine dyes | 5,918 | 1,493 | 4,249 | 1,217 |
| Coal-tar dyes | .. | 7,111 | .. | 6,845 |
| Paints, pigments and lacquers | .. | 2,160 | .. | 2,243 |
| Indigo | 8,345 | 1,138 | 7,927 | 1,189 |
| Aniline salts | 4,479 | 322 | 2,245 | 181 |
| | 1000 ton units | | 1000 ton units | |
| Logwood | 38 | 469 | 41 | 522 |
| Quebracho wood | 80 | 985 | 72 | 919 |
| Other dye woods | 6 | 86 | 8 | 123 |
| Mangrove bark | 11 | 250 | 6 | 150 |
| | 1000 lb. units | | 1000 lb. units | |
| Sumach | 9,863 | 218 | 13,533 | 337 |
| All other tanning materials | .. | 401 | .. | 456 |
| Dye and tanning extracts: | | | | |
| From quebracho | 85,718 | 2,321 | 114,326 | 3,100 |
| All others | 8,513 | 314 | 8,380 | 270 |
| Lead pencils | .. | 599 | .. | 567 |
| GUMS AND RESINS | | | | |
| Camphor, raw, natural | 4,190 | 1,118 | 3,488 | 950 |
| Camphor, refined and synth | 644 | 211 | 1,054 | 369 |
| Chicle | 13,401 | 5,120 | 5,897 | 2,178 |
| Copal, Kauri and Dammar | 31,709 | 3,193 | 28,647 | 2,963 |
| Gambir (*Terra japonica*) | 16,330 | 658 | 13,706 | 494 |
| Shellac | 20,463 | 3,058 | 19,637 | 3,027 |
| Other resins, duty-free | .. | 1,615 | .. | 1,172 |
| Other resins, dutiable | .. | 269 | .. | 828 |
| RUBBER AND RUBBER SUBSTITUTES | | | | |
| Balata | 1,509 | 797 | 2,015 | 880 |
| Gutta-percha | 4,870 | 2,130 | 2,276 | 790 |
| Guttaballetong | 36,421 | 1,766 | 18,664 | 857 |
| Gutta percha | 873 | 500 | 1,923 | 337 |
| Caoutchouc | 118,881 | 76,821 | 143,065 | 70,473 |
| Caoutchouc waste | 36,748 | 3,193 | 19,119 | 1,387 |
| Substitutes | .. | 97 | .. | 63 |

[1] To October 3, 1913.
[2] From October 4, 1913.

The list of exports is based on export manifests and is not as accurate as the list of imports. Under the official class "chemicals drugs, dyes and medicines," the values for the exports of 1914 and 1913 are given as, respectively, $29,000,000 and $26,800,000, 1914 thus showing an increase of 8.2 per cent. This increase, taken together with the fact that of 73 items, 54 show a falling off, indicates that there is a concentration of effort towards exporting certain classes of goods; the exports of gasoline show an increase, for example, of over $2,400,000, gas and fuel oil more than $8,000,000, cartridges, $3,500,000, etc.

| IMPORTS | 1913 1000 lb. units | 1913 $1000 units | 1914 1000 lb. units | 1914 $1000 units |
|---|---|---|---|---|
| FERTILIZERS | | | | |
| Guano | 19 | 538 | 26 | 763 |
| Kainite | 466 | 2,207 | 330 | 1,581 |
| Salts | 223 | 2,150 | 168 | 1,843 |
| Bone meal and ash materials | 35 | 837 | 36 | 891 |
| All other fertilizing materials | .. | 4,996 | .. | 5,055 |
| OILS, WAXES, ETC | | | | |
| Ethereal oils: | | | | |
| Oil of lemon | 371 | 721 | 486 | 897 |
| Other ethereal oils, duty-free | .. | 2,804 | .. | 26 |
| Other ethereal oils, dutiable | .. | 1,196 | .. | 2,063 |
| Plant oils | | | | |
| Cocoa butter | 4,413 | 1,223 | 1,244 | 349 |
| Coconut oil | 72,196 | 6,258 | 58,012 | 5,147 |
| Cottonseed oil | 11,407 | 724 | 16,017 | 869 |
| Linseed oil | 162 | 87 | 580 | 263 |
| Chinese nut oil | 5,678 | 2,370 | 4,018 | 1,503 |
| Peanut oil | 1,502 | 1,038 | 982 | 675 |
| Olive oil, for technical use | 564 | 369 | 748 | 475 |
| Olive oil, for domestic use | 5,179 | 6,777 | 6,718 | 8,421 |
| Rapeseed oil | 1,149 | 712 | 1,490 | 732 |
| Palm oil | 54,072 | 3,631 | 49,092 | 3,155 |
| Palm nut oil | 27,746 | 2,445 | 21,089 | 1,869 |
| Soya bean oil | 14,221 | 693 | 12,555 | 657 |
| | 1000 gal. units | | 1000 gal. units | |
| Animal oils | 751 | 305 | 1,893 | 684 |
| Codliver oil | 1,582 | 530 | 1,459 | 464 |
| All others | | | | |
| Mineral oils | | | | |
| Raw mineral oil | 713,100 | 10,945 | 910,351 | 10,023 |
| Benzine, gasoline etc | 15,483 | 1,472 | 12,751 | 1,121 |
| All others | 2,777 | 580 | 1,345 | 357 |
| | Pounds | | Pounds | |
| Mineral wax | 7,255 | 555 | 6,812 | 442 |
| Vegetable wax | 5,294 | 1,146 | 5,160 | 1,099 |
| Sulfur oil (olive residues) | 10,450 | 717 | 13,045 | 853 |
| All other similar oils and fats | 8,444 | 439 | 11,665 | 530 |
| | 1000 ton units | | 1000 ton units | |
| MISCELLANEOUS | | | | |
| Asbestos | 87 | 1,929 | 64 | 1,408 |
| Asbestos products | .. | 390 | .. | 360 |
| Graphite | 26 | 2,110 | 20 | 1,398 |
| Coke | 94 | 443 | 121 | 556 |
| | 1000 lb. units | | 1000 lb. units | |
| Mica | 2,887 | 981 | 846 | 205 |
| | 1000 oz units | | 1000 oz. units | |
| Platinum, unworked | 51 4 | 1,929 | 32 1 | 1,155 |
| Platinum, in blocks, sheets, etc. | 66 6 | 2,960 | 40.2 | 1,780 |
| Platinum, crucibles, dishes, etc. | .. | 105 | .. | 39 |
| | 1000 gal. units | | 1000 gal. units | |
| Coal tar preparations, neither dyes nor medicinal, dutiable | .. | 782 | .. | 1,118 |
| Coal tar preparations, neither dyes nor medicinal, duty-free | .. | 1,035 | .. | 256 |
| Creosote oil | 69,022 | 4,081 | 48,839 | 3,024 |
| | 1000 lb. units | | 1000 lb. units | |
| Glue | 9,530 | 907 | 20,652 | 1,637 |
| Glue, raw materials | .. | 1,852 | .. | 2,081 |
| Perfumes and toilet articles | .. | 2,034 | .. | 2,360 |
| Horse hair, artificial | .. | 107 | .. | 90 |
| Silk, artificial | | | | |
| Thread, etc | 2,305 | 2,877 | 2,923 | 3,655 |
| Other forms | .. | 655 | .. | 412 |
| Soap, Marseilles | 4,552 | 348 | 4,289 | 345 |
| Soap, all other | .. | 402 | .. | 503 |
| Photographic paper | .. | 1,275 | .. | 1,122 |
| Photographic films and plates | .. | 1,056 | .. | 1,898 |
| Explosives and fireworks | .. | 723 | .. | 628 |
| Matches | .. | 758 | .. | 911 |
| Gelatine | 2,015 | 624 | 2,541 | 750 |
| Glycerine, raw | 38,270 | 4,695 | 24,787 | 3,123 |
| | 1000 piece units | | 1000 piece units | |
| Electric lamps | | | | |
| Arc lamps | 2 4 | 43 | 0 3 | 5 |
| Carbon filament lamps | 1 011 | 64 | 562 | 33 |
| Metal filament lamps | 5 688 | 481 | 7,243 | 628 |

| EXPORTS | 1913 | | 1914 | |
|---|---|---|---|---|
| | 1000 lb. units | $1000 units | 1000 lb. units | $1000 units |
| Calcium carbide | 32,362 | 946 | 32,750 | 989 |
| Calcium acetate | 74,056 | 2,158 | 47,897 | 833 |
| Copper sulfate | 4,169 | 212 | 7,387 | 328 |
| Sodium compounds | ..... | .. | ..... | 735 |
| Acids: | | | | |
| Sulfuric | 9,689 | 104 | 13,176 | 140 |
| All others | ..... | 881 | ..... | 620 |
| | Tons | | Tons | |
| Sulfur, raw | 89 | 1,600 | 98 | 1,807 |
| | 1000 gal. units | | 1000 gal. units | |
| Methyl alcohol | 1,021 | 827 | 1,161 | 479 |
| Dyes | .. | 387 | .. | 538 |
| Tan bark extract | .. | 508 | ..... | 1,084 |
| | 1000 lb. units | | 1000 lb. units | |
| Ginseng | 182 | 1,480 | 155 | 1,265 |
| Roots, herbs, barks, etc. | .. | 476 | ..... | 410 |
| Medicines, patent and proprietary | .. | 6,966 | ..... | 6,521 |
| Baking powder | 2,986 | 866 | 2,858 | 779 |
| Washing powder, etc. | 11,224 | 806 | 12,683 | 933 |
| Petroleum jelly, vaseline, etc. | .. | 635 | .. | 640 |
| SOAP AND TOILET ARTICLES: | | | | |
| Toilet soaps | ..... | 2,185 | ..... | 1,801 |
| Other soaps | 55,528 | 2,672 | 59,514 | 2,863 |
| Perfumes and toilet preparations | ..... | 1,575 | ..... | 1,514 |
| Soap materials (fat, etc.) | ..... | 5,117 | ..... | 4,421 |
| EXPLOSIVES: | | | | |
| Cartridges | .. | 3,015 | ..... | 6,567 |
| Dynamite | 13,310 | 1,498 | 11,303 | 1,214 |
| Gunpowder | 1,284 | 360 | 867 | 290 |
| Other explosives | ..... | 682 | ..... | 1,967 |
| OILS: Vegetable oils, fixed and pressed: | | | | |
| Cottonseed oil | 264,779 | 17,991 | 216,309 | 14,684 |
| Corn oil | 17,789 | 1,219 | 16,204 | 1,127 |
| | 1000 gal. units | | 1000 gal. units | |
| Linseed oil | 1,591 | 784 | 266 | 154 |
| Other fixed oils | ..... | 418 | .. | 393 |
| Animal oils (total) | 2,507 | 1,250 | 871 | 542 |
| Including: Fish oil | 1,187 | 319 | 155 | 47 |
| Lard oil | 88 | 102 | 102 | 81 |
| Mineral oils: | | | | |
| Raw oil | 194,570 | 8,448 | 124,736 | 4,959 |
| Illuminating oil | 1,119,441 | 72,042 | 1,010,449 | 64,113 |
| Lubricating oil | 207,639 | 29,609 | 191,648 | 26,316 |
| Gasoline | 117,728 | 17,419 | 162,669 | 19,898 |
| Other light distillates | 70,329 | 10,674 | 47,024 | 5,391 |
| Gas oil and fuel oil | 359,009 | 9,991 | 634,297 | 18,019 |
| All others | 67,850 | 1,134 | 69,210 | 1,205 |
| Paraffin and paraffin wax | 236,046 | 8,177 | 188,823 | 6,435 |
| | 1000 lb. units | | 1000 lb. units | |
| Ethereal oils: | | | | |
| Peppermint oil | 112 | 367 | 119 | 309 |
| Other ethereal oils | .. | 254 | .. | 229 |
| | 1000 bbl. units | | 1000 bbl. units | |
| NAVAL STORES: | | | | |
| Rosin | 2,605 | 13,563 | 1,749 | 8,068 |
| Tar, turpentine and pitch | 179 | 526 | 419 | 841 |
| | 1000 gal. units | | 1000 gal. units | |
| Turpentine oil | 20,024 | 8,161 | 14,118 | 5,189 |
| | 1000 ton units | | 1000 ton units | |
| FERTILIZERS: | | | | |
| Phosphate rock: | | | | |
| High-grade hard rock | 473 | 4,735 | 282 | 2,818 |
| Land pebble | 891 | 5,255 | 681 | 3,948 |
| Other grades | 2 | 6 | 1 | 5 |
| Other fertilizers | 73 | 1,667 | 64 | 1,311 |
| MISCELLANEOUS: | | | | |
| Graphite | 5,384 | 392 | 3,921 | 277 |
| Coke | 882 | 3,310 | 592 | 2,234 |
| | 1000 lb. units | | 1000 lb. units | |
| Mercury | 86 | 44 | 108 | 71 |
| Celluloid | .. | 1,317 | .. | 1,109 |
| Caoutchouc: | | | | |
| Waste | 6,560 | 768 | 4,187 | 409 |
| Reclaimed | 4,988 | 837 | 6,250 | 872 |
| | 1000 ton units | | 1000 ton units | |
| Wood flour | 12 | 738 | 11 | 484 |
| | 1000 lb. units | | 1000 lb. units | |
| Hops | 28,701 | 7,484 | 11,056 | 2,926 |
| Glue | 2,362 | 260 | 2,248 | 243 |
| Candles | 2,083 | 253 | 3,153 | 308 |
| | 1000 piece units | | 1000 piece units | |
| Electric lamps: | | | | |
| Arc | 2 | 384 | 1 | 43 |
| Carbon filament | 1,844 | 288 | 668 | 88 |
| Metallic filament | 1,094 | 302 | 1,348 | 378 |
| | Running feet | | Running feet | |
| Photographic films for cinematograph (unexposed) | 114,124 | 3,056 | 88,401 | 2,381 |
| Other sensitized products | .. | 2,107 | .. | 1,488 |
| Vulcanized fabrics, etc. | .. | 775 | .. | 652 |
| | 1000 bbl. units | | 1000 bbl. units | |
| Cement | 2,964 | 4,271 | 2,140 | 3,089 |

| EXPORTS | 1913 | | 1914 | |
|---|---|---|---|---|
| PAINTS AND VARNISHES | 1000 lb. units | $1000 units | 1000 lb. units | $1000 units |
| White lead | 15,062 | 905 | 17,646 | 1,017 |
| Zinc oxide | 28,933 | 1,136 | 31,183 | 1,409 |
| Lampblack | .. | 170 | .. | 387 |
| Other pigments | .. | 224 | .. | 684 |
| | 1000 gal units | | 1000 gal units | |
| Ready mixed paints | 907 | 1,167 | 733 | 974 |
| Lacquers and varnishes | 1,130 | 1,107 | 864 | 834 |
| Similar products | .. | 1,819 | .. | 1,596 |
| Printers' ink | .. | 435 | .. | 421 |
| Other inks | .. | 197 | .. | 152 |
| Blacking | .. | 698 | .. | 547 |
| Pencils | .. | 711 | .. | 760 |

## THE GERMAN LEAD INDUSTRY

A number of German works, members of the German Sales Bureau for Rolled and Pressed Lead Manufacturers, have, according to *Engineering* **99** (1915), 247, formed a combine under the name of the United Lead and Tin Works, Limited, Cologne, and have also entered into an agreement with the Rhenish-Nassau Mining Company, Stolberg. A central rolling-mill will be erected in direct connection with the works. The new firm, after the erection of the central works, will remain a member of the above-mentioned sales bureau, an agreement having been arrived at to this effect. The new company, however, will not only manufacture goods for the sales bureau, but also specialties, which the different works hitherto have manufactured for their own account. The Gelsenkirchen Lead Works, which is at present idle, will be extended and maintained as a kind of center for the coal district. The capital of the new company amounts to 3,150,000 marks.

## A NEW TYPE OF OIL CARRIER, THE CYLINDRICAL TANK STEAMER "RICARDO A. MESTRES"

A new type of oil-carrying steamer has recently been built in England; in it the oil, instead of being carried in ordinary holds with straight bulkheads, is contained in large vertical cylindrical tanks, so that there is a freedom from webs and stiffeners on the internal surface, the consequence being that the process of cleansing is greatly expedited and more effective. The tanks are of sufficient capacity to take the full dead-weight load of heavy oil, and ordinary cargo or light oil can be shipped in the spaces between the outer walls of the cylindrical tank and the sides of the ship, this space being divided up into a number of compartments by water-tight bulkheads.

A vessel of this type, the "Ricardo A. Mestres," is illustrated in a recent issue of *Engineering;* she was constructed for the Transcontinental Petroleum Company, and is the third of her type to be put into service.

This vessel has a length between perpendiculars of 365 ft., a breadth extreme of 50 ft. 9 in., and moulded of 50 ft. $6^1/_2$ in., while the depth moulded is 29 ft. 3 in. She is built with a double bottom extending throughout the full length of the ship, with the usual fore peak, in which oil fuel may be carried in supplement to the oil fuel in the athwartship bunker immediately in front of the boiler compartment, which, with the engine-room, is placed in the after part of the ship. There are five tanks for the carrying of heavy oil. The forward tank has a capacity of 32,850 cu. ft., the other four of 38,025 cu. ft. each; the hold-tanks, at the side of and between the cylindrical tanks, on the port as well as the starboard side, are of a capacity each of 10,642 cu. ft. In addition, oil may be carried in the five double-bottom tanks, as marked on the longitudinal section; and these, including the accommodation of the expansion trunks formed in connection with the decks, make the total capacity of the cargo spaces up to 285,793 cu. ft. Excluding the expansion trunks, the total capacity is 263,968 cu. ft. In addition, there is bunker capacity of 26,183 cu. ft.

### TRANSVAAL GOLD-MINING

The fact does not appear to be generally recognized, according to *Engineering*, **99** (1915), 380, that since September last year the production of gold in the Transvaal has on the whole shown a greater output than in the corresponding months of the previous year. The output in October was valued at $15,100,000, as compared with $14,800,000 in October, 1913; in November at $14,800,000, as compared with $13,900,000; in December at $14,350,000, as compared with $13,900,000; in January at $14,900,000, as compared with $13,400,000; and in February at $11,500,000, as compared with $12,900,000. Transvaal gold-mining is, however, threatened with a special war tax by the South African Union.

### THE CANADIAN CHEMICAL MARKET

According to *Chemische Industrie*, **38** (1915), 74, prohibition of the exportation of chemicals from England combined with the stoppage of German exports has made Canada dependent almost entirely on American chemical products. Among those chemicals which are especially sought for in Canada are carbolic, salicylic, oxalic, citric and tartaric acids, camphor, cocaine, morphine, codeine, glycerine, hydroquinone, menthol, vegetable oils, potassium permanganate, sodium benzoate and salicylate, and santonine. The prices of these articles have reached from 200 to 900 per cent of their normal values.

### MONOPOLY FOR NITROGEN PRODUCTS IN GERMANY

The German Government has introduced a measure of great importance to the chemical industry—*viz.*, a proposal for the establishment of a trade monopoly for various nitrogen products, to remain in force until March 31, 1922 [*Engineering*, **99** (1915), 455]. After that date the Act can be prolonged by fresh legislation. The measure is described as having been due to the present emergency, and comprises: (*a*) Inorganic minerals containing nitrogen; (*b*) nitrogen products manufactured synthetically, as well as natural products; (*c*) manures, containing nitrogen, coming under (*a*) and (*b*). The monopoly will affect the different kinds of saltpeter, nitride of sodium, ammonium products, guanidine, nitric acid, etc. It will affect both the Norwegian and the Swedish industries within that branch, which have a market of some importance in Germany.

### TIN MINING IN SIAM

A feature of the tin mining industry which centers around the Straits is the increased production obtained from Siamese Malaya and Siam itself. [*Mining Journal*, 4157 (1915)] Nowhere has the tin dredging industry had so much success, and the scale of operations at the present time is the most extensive anywhere. For the last financial year, 1913–1914, eight dredges were at work, which produced black tin yielding 1,800 tons of metal from 4,700,000 yards of gravel treated. This number has been added to since, and there are now thirteen dredges at work and more under construction. Apart from the dredging industry the output of metal would probably show a declining tendency. The output for the last four years in metal is as follows:

| | | | |
|---|---|---|---|
| 1910–1911 | 4,900 tons | 1911–1912 | 5,900 tons |
| 1912–1913 | 6,600 tons | 1913–1914 | 6,800 tons |

D. G. ANDERSON

### CHINA CLAY IN ENGLAND

The present state of the China clay trade in Cornwall is, according to the *Paper Makers' Journal*, No. 3 (1915), exceedingly quiet. Comparatively little business is being done in any grade. Many of the China clay works are shut down entirely, and others are working short time.

The demand for China clay from America has fallen off considerably, and the scarcity of shipping, combined with high freights and insurance, is proving very detrimental to the home trade. The industry on the whole is badly hit, and most of the works at present working are engaged in development work. Stocks are accumulating and in many cases the drys are closed. —A.

### ENAMELLED WIRE

During the past few months enamelled wire has obtained a very great popularity for very many purposes, and considerable success has been achieved in its manufacture by way of eliminating the early defects which manifested themselves. Even now, however, there are complaints that for certain purposes difficulties arise owing to the apparent inability to coat the wires absolutely evenly with the enamel in the enamel bath. The particular complaint which has just come under notice [*Mechanical World*, 1475 (1915)] has reference to the use of this wire for telephone purposes, especially in tropical countries, but it is not altogether certain that the complaints may not be due to isolated instances rather than to there being a generally unsatisfactory result. That such wires are giving satisfaction is indicated by their use in the Post Office Telephone Department, where very stringent tests are imposed. The practice of the G. P. O. is to insist that such wires shall be able to withstand an electrical pressure of 1000 volts after immersion in caustic soda, sulfuric acid, nitric acid, and hydrochloric acid, for 48 hours, and potash for 35 minutes. It is also a fact that more than one manufacturer of telephone apparatus in which enamelled wire is used is quite satisfied with the product he is obtaining; but manufacturers of this wire will probably welcome having their attention drawn to the fact that complaints are even now made. It is suggested that simple enamel insulation is not suitable for very fine-gauged wires, and it is more or less to these that such complaints as are made relate.—A.

### LIQUID FUEL FOR INTERNAL COMBUSTION ENGINES

According to *The Engineer*, No. 3095 (1915), 408, one of the problems which will shortly have to be faced in a thorough manner by the chemists of Great Britain, is that of providing an alternative fuel for the class of engines that are now dependent for their operation on petrol and benzol. In 1914 the world's output of crude oil amounted to 57 million tons and the highest possible yield of petrol from the whole quantity is placed by Professor Lewes at 1,700,000,000 gallons, of which amount the United States, alone, last year used 1,200,000,000 gallons and Great Britain over 200,000,000.

The two fuels from which petrol is likely to receive the chief opposition in the future are, of course, benzol and alcohol. The yield of the former is, however, almost infinitesimal, and there is not much likelihood of any material increase in the production. Taken at 1.8 gallons per ton of coal, the total amount, from the whole of the coal carbonized in Great Britain last year would be only 9,000,000 gallons. That the Germans had been alive to the valuable properties of benzol is shown by the fact that nearly all the benzol produced in the coke ovens in England has been exported to Germany, chiefly for use in the dye industry.

The Germans also commenced to replace all the old beehive ovens by recovery ovens, free of cost, and took payment in benzol. Recognizing the necessity for economy in this class of fuel at the present time, the Germans are now said to be employing for military transport purposes a mixture containing 80 per cent alcohol and 20 per cent benzol, to which is added 200 grains of naphthalene. The last-named ingredient is first dissolved in the benzol, which, in turn, is mixed with the alcohol and, according to Professor Lewes, the resulting mixture gives five-sixths of the power of petrol. Unfortunately, much of the benzol now

on the market, and especially that produced by gasworks, has an injurious effect upon the engine, owing largely to the presence in it of sulfuric acid.

One of the leading motor car manufacturing firms has taken the pains to investigate the effects of poor quality benzol upon lubricating oil and has found that when sulfuric acid is present in the benzol a semi-solid deposit is formed in the crank case, due to the leakage of benzol past the pistons. This deposit consists of carbon and sulfuric acid and the acid rusts the valves and stems. The best remedies for this state of things are more thorough washing of the spirit or, failing this, the mixing of the benzol with petrol in the proportion of 65 per cent benzol and 35 per cent petrol, the alkaline ingredients in the latter neutralizing the acid content of the benzol.

Everything, however, points to alcohol as the fuel of the future. The thermal value of alcohol is only about one-half that of petrol or benzol, but whereas it is not advisable to use a higher compression pressure with the last-mentioned fuels than about 80 lbs. per sq. in., with alcohol the compression may be raised to a pressure of 200 lbs. without fear of preignition, and the quantity of air required to complete combustion is little more than one-half. Last year the Royal Automobile Club appointed a committee to investigate and report on alcohol as a fuel. The report has not yet been published, but the most important problem which this body will have to investigate is that of finding a suitable denaturant which will satisfy the excise authorities. If the efforts of this committee result in the abatement of the duty and some modification of existing restrictions on the manufacture of alcohol, capital will no doubt be readily found to provide factories for the production of the fuel in such quantities as will, at any rate, serve to prevent the further rise in price of petrol on which so much of the nation's welfare depends.—A.

## BRITISH BOARD OF TRADE

During the month of May the British Board of Trade have received enquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles:

Aluminum ware
Artificial horse hair
Belts and belting
Celluloid boxes
Slip lid zinc tins
Camel hair brushes
Bronze powder
Celluloid buttons
Case-hardening compositions
Cellulose extract
Acetate of lead
Aniline oil
Antimony oxide
Chloride of magnesite
Cresol
Phthalimide
Red phosphorus
Salicylate of soda
Salicylic acid
Zinc oxide
Collapsible tubes
Lactometers
Bismuth subnitrate
Caffein-sodium benzoate
Guaiacol
Phenyl salicylate
Sodium bromide
Fustic extract
Logwood extract
Carbon for arc lamps
Porcelain insulators
Brown ware
Lanoline
Galalith substitute
Gelatine
Lithopone
Locks for tin trunks
Mirrors
Olive oil soap
Barytes
Crude antimony ore
Sacks
Preserved egg preparation
Tanning materials
Springs (spiral steel)
Steel thimbles
Bimetallic strips for use as compensating devices in recording thermometers, in brass and 36 per cent nickel steel or similar combinations
Black-lead pencils (cheap)
Metal ink bottles for covering with leather
Nickel ink bottles for attaché cases
White glass bottles, to take screw caps
Brass-headed chair nails
Carnauba wax (fatty gray quality used in lamps)
Celluloid device for holding papers straight, for use with typewriting machines
Cast iron cylinders for carbolic acid
Celluloid in solid rods and tubes
Butyric acid, 90 per cent
Epsom salts (B. P. and commercial)
Sodium nitrate (refined)
Xylene (*o*, *m*, and *p*)
Enamelled iron clock dials
Vulcanized hair combs
Pressed bone dominoes
Glue, dry, for boot and shoe trade
Filtering pulp as used in breweries
Opal shades for electric lights
Leather and imitation leather
Machinery for making leather cloth
Machinery for molding celluloid into rings and hooks
Machinery for printing pottery transfers
Skeining machines for splitting rods
Machine for wire stitching
Malacca canes (about 15 feet long) for use as drain rods in conduit work
Metal foil—Brass foil and Dutch metal foil
Metal tubes, seamless, in very fine gauges for making hypodermic needles
Paper—cigarette paper, and paper for pottery transfers
Steel sheets coated with brass, copper and nickel
Spent animal charcoal
Thermometers (clinical and dairy)
Typewriting supplies (ribbons, etc.)
Waste liquors from wood paste
Vegetable ivory in tubes
Vulcanite beads
Tungsten powder

Firms who may be in a position to supply any of the above articles are asked to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.—A.

## IRON PRODUCTION OF THE U. S.—MAY, 1915

The total pig-iron output of the United States in May was 2,263,470 tons, or 73,015 tons a day, against 2,116,494 tons in April, or 70,550 tons a day. With 205 furnaces in blast June 1st, or ten more than on May 1st, the active capacity was 74,343 tons, against 71,385 tons one month previous. Pig-iron production is now at the rate of 27,400,000 tons a year. On April 1st it was at 26,000,000 tons, and on January 1st at 18,000,000 tons a year.

Comparison of last month's iron output with previous months of the past three years (figures here representing gross tons) is as follows, according to the *Iron Age:*

| | 1915 | 1914 | 1913 |
|---|---|---|---|
| May | 2,263,470 | 2,092,686 | 2,822,217 |
| April | 2,116,494 | 2,269,995 | 2,752,761 |
| March | 2,063,834 | 2,347,867 | 2,763,563 |
| February | 1,674,771 | 1,888,670 | 2,586,337 |
| January | 1,601,421 | 1,885,054 | 2,795,331 |
| | 1914 | 1913 | 1912 |
| December | 1,515,752 | 1,983,607 | 2,782,737 |
| November | 1,518,316 | 2,283,603 | 2,630,854 |
| October | 1,778,186 | 2,546,261 | 2,689,933 |
| September | 1,882,577 | 2,505,927 | 2,463,839 |
| August | 1,995,261 | 2,545,763 | 2,512,431 |
| July | 1,957,645 | 2,560,646 | 2,410,889 |
| June | 1,917,783 | 2,628,565 | 2,440,745 |

## OUTPUT OF PORTLAND CEMENT IN U. S.—1915

The output of Portland cement last year, according to the New York *Evening Post*, totaled 88,230,170 barrels, valued at $81,789,368. This was a decrease in quantity of 3,866,961 barrels, and a decrease in value of $10,768,249, compared with 1913. Pennsylvania and Indiana held first and second places, respectively, as producing States.

## U. S. TRADE IN APRIL

The following table from the monthly report of the Bureau of Foreign and Domestic Commerce, Department of Commerce, shows a gain in trade in all classes of merchandise.

| EXPORTS, APRIL | 1915 | 1914 | 1913 |
|---|---|---|---|
| Crude material | $ 44,355,870 | $ 37,627,006 | $ 47,556,871 |
| Foodstuffs, crude | 59,414,365 | 6,328,730 | 13,209,610 |
| Foodstuffs, partly prepared | 46,618,860 | 19,590,417 | 26,178,111 |
| Partly manufactured | 38,451,343 | 31,844,607 | 37,044,590 |
| Manufactures, complete | 90,503,475 | 62,557,755 | 70,664,000 |
| Miscellaneous | 9,693,543 | 1,021,188 | 1,580,524 |
| Total domestic | $289,037,456 | $158,969,703 | $196,233,706 |
| Foreign exp | 5,708,661 | 3,582,867 | 3,579,732 |
| TOTAL EXPORTS | $294,746,117 | $162,552,570 | $199,813,438 |
| IMPORTS, APRIL | | | |
| Crude material | 61,714,060 | $ 65,868,163 | $ 52,987,666 |
| Foodstuffs, crude | 22,685,047 | 20,414,438 | 15,991,013 |
| Foodstuffs, partly prepared | 33,806,036 | 25,064,922 | 18,243,578 |
| Partly manufactured | 19,227,750 | 27,164,602 | 29,278,333 |
| Manufactures, complete | 21,775,507 | 34,082,964 | 28,937,438 |
| Miscellaneous | 1,367,706 | 1,167,025 | 756,436 |
| TOTAL IMPORTS | $160,576,106 | $173,762,114 | $146,194,461 |

## TAR DEHYDRATION AND TOLUOL RECOVERY

The question of the dehydration of tar has lately attracted considerable attention in England, since prepared tar is being generally adopted for road construction and the light oils driven off in the process of dehydration contain all the toluol and phenol originally in the tar, products now in urgent demand for the manufacture of explosives. One ton of average crude gas-works tar yields, when dehydrated, 160 gallons of prepared tar, 30 gallons of light oils, and 10 gallons of ammoniacal liquor. An average sample of 200 cc. of the such light oil, washed with caustic soda, gave 18 per cent of tar acids; on fractionating the washed oil, the following results were obtained:

| Temp. | Per cent product | | Temp. | Per cent product | |
|---|---|---|---|---|---|
| Up to 100° C. | 35 | Benzol | 120° to 125° C. | 28 | Solvent naphtha |
| 100° to 120° C. | 10.5 | Toluol | Residue | 40.5 | Creosote |

The oil also contained 6 per cent of very good pyridine. The quantities of fuel required per ton of tar distilled are with plants actually at work, 67 lbs. of breeze or 450 cu. ft. of gas of 500 B. T. U. [*J. Gas Lighting*, 130 (1915), 330].

# SCIENTIFIC SOCIETIES

## THE SEATTLE MEETING

The 51st Annual Meeting of the American Chemical Society will be held at the University of Washington, Seattle, August 31st to September 2nd. The Hotel Frye, corner 3rd Avenue and Yesler Way, has been chosen as headquarters. Cowen Park and Ravenna cars, which pass headquarters on 3rd Avenue, lead, without transfer, to the University grounds, reaching the 40th Street entrance to the Campus in 35 minutes.

REGISTRATION will take place in the lobby of Hotel Frye on August 30th and in Bagley Hall, University of Washington, on August 31st and September 1st. All members and guests should register on arrival and are requested to secure banquet tickets on registration. Special excursions to points of interest may be arranged for at the registration desks, and guides will be provided.

PROGRAM OF MEETING

AUGUST 30, 7.30 P.M.—**Complimentary dinner to the Council,** at the Hotel Frye, by the Science Faculty of the University of Washington; followed by business meeting.

AUGUST 31, 10.00 A.M.—**Opening meeting** at Meany Hall.
**Addresses of Welcome**—HON. ERNEST LISTER, Governor of State, and PRESIDENT HENRY SUZZALO, of the University of Washington.
**Response**—DR. H. K. BENSON.
**Address, "Chemical Industry,"**—DR. LEO. H. BAEKELAND.
1.30 P.M.—**Division Meetings,** Bagley and Science Halls.
3.00 P.M.—**Complimentary Reception and Tea,** for ladies, University Campus
8.00 P.M.—**Complimentary Smoker** by Seattle Commercial Club.
8.00 P.M.—**Complimentary Organ Recital,** for ladies.

SEPTEMBER 1, 10.00 A.M. and 1.30 P.M. **Division Meetings.**
10.00 A.M.—**Complimentary automobile ride,** for ladies
4.30 P.M.—**Complimentary automobile trip** from University Campus to Hotels *via* boulevard system.
8.00 P.M.—**President's Address**—PRESIDENT CHARLES HOLMES HERTY; followed by business meeting.

SEPTEMBER 2—**Excursion on Puget Sound** for inspection of harbor facilities and the fishing industry.
8.00 P.M.—**Subscription Banquet** (Price, $3.00).
11.55 P.M.—Special train leaves Seattle for Mt. Ranier Park (See THIS JOURNAL, **7** (1915), 545).

LOCAL COMMITTEES (SEATTLE)

The following local committees are in charge of the arrangements for the meeting:

EXECUTIVE—H. G. Byers, *Chairman;* E. J. Bartells, *Vice-Chairman;* H. L. Trumbull, *Secretary;* J. E. Bell, *Treasurer;* H. K. Benson, *Councilor.*
FINANCE—H. K. Benson, *Chairman;* M. J. Falkenburg, C. A. Newhall, Rex Smith, C. E. Bogardus, H. Linton, H. Maschmedt, E. J. Bartells.
EXCURSIONS—E. J. Bartells, *Chairman;* C. E. Bogardus, E. A. Dieterle, George Grindord.
PRESS—Lee A. White, *Chairman;* E. E. Hurja, I. F. Laucks, E. O. Heinrich, Frank Sternberg.
RECEPTION AND REGISTRATION—J. H. Linton, *Chairman;* M. J. Falkenburg, H. L. Trumbull, S. C. Langdon.
BANQUET—R. W. Clough, *Chairman;* H. K. Benson, A. L. Knisely.
SMOKER—M. J. Falkenburg, *Chairman;* J. H. Linton, Rex Smith, A. Jacobson.
LADIES' ENTERTAINMENT—Mrs. C. A. Newhall, *Chairman;* Mrs. H. Maschmedt, Mrs. C. E. Bogardus, Miss Glenola Behling, Miss Ruby Clift, Mrs. Ray Clough, Mrs. H. G. Byers

RATES AT THE HOTEL FRYE (European plan) are as follows:

| | | |
|---|---|---|
| SINGLE | Without bath, $1.50 to $2.00 | With bath, $2.00 to $3.00 |
| DOUBLE | Without bath, $2.00 to $2.50 | With bath, $3.00 to $4.00 |

Rates at other hotels convenient of access are.

| | | |
|---|---|---|
| New Washington | Single, $3.00 to $5.00 | Double, $4.00 to $7.00 |
| Savoy | Single, $1.00 to $3.50 | Double, |
| Butler | Single, $1.00 to $3.00 | Double, $1.50 to $2.00 |
| Washington Annex | Single, $1.50 to $2.50 | Double, $2.00 to $4.00 |

THE ARCTIC CLUB, located across Prefontaine Square from headquarters, will keep open house to delegates with dining-room and ladies' dining-room open all day. A limited number of rooms are available, and delegates may secure the same by writing M. J. Falkenburg, Pioneer Square, Seattle.

## THE DETERMINATION OF MOISTURE IN SHELLAC

Both orange and bleached shellac give off volatile matter at temperatures approaching 100° C. Bleached shellac alters chemically at these temperatures losing its solubility in alcohol For these reasons the usual methods of determining water by heating in the air bath at 100° to 110° C. are not applicable in the analysis of shellac.

SAMPLING—Bleached shellac is sold in three forms, as hanks or bars containing approximately 25 per cent water, as ground bleached in pulverized form with about the same water content, and as bone-dry or kiln-dried shellac. The latter is prepared by drying the ground bleached shellac in the air or in vacuum driers at moderate temperatures: it may contain, depending upon the completeness of the drying and weather conditions, up to 10 per cent or more of water.

In sampling bone-dry bleached shellac a fairly large portion (about a pound) should be taken from different parts of the barrel and finely ground by running quickly through a coffee mill. No attempt must be made to sieve it. It should be rapidly mixed and transferred to a Mason jar provided with a screw cap and rubber ring seal; the jar should not be more than two-thirds full, leaving room for a thorough mixing by shaking the contents; it must be kept in a cool place and tested as promptly as possible. If too warm the shellac may become partly caked, in which case the lumps must be broken up by shaking the bottle.

In sampling bars or hanks it is recommended that a whole hank be taken. It should be crushed and ground as rapidly as possible. Ground bleached may be treated as above, bearing in mind that the large amount of moisture present makes rapid handling imperative.

MOISTURE DETERMINATION—*Method 1:* From 5 to 10 grams of the sample should be weighed in flat-bottomed dishes about four inches in diameter or in watch glasses ground to fit and provided with a clamp. The shellac is then placed in a desiccator freshly filled with concentrated sulfuric acid. The contents of the dish should be spread out in a thin layer to expose as large a surface as possible The desiccator is exhausted by a vacuum pump as completely as possible. With a good vacuum (3 mm. pressure or better) constant weight will be obtained in between 24 and 48 hours. Absolutely dry bleached shellac is quite hygroscopic and the final weight should be taken as rapidly as possible.

*Method 2:* The same results may be obtained by drying the shellac in a well ventilated air bath from 3 to 6 hours at 100°–110° F. (38°–43° C.). One or two electric light bulbs provide a convenient source of heat. The temperature should not be allowed to rise above 43° C., otherwise sintering may occur and retard drying. With poorly ventilated ovens the drying may take much longer. Completeness of drying should be ascertained by continuing the treatment to constant weight. It is recommended that analysts check the accuracy of results obtained in the oven by comparison with a test made in a vacuum desiccator before relying exclusively on the oven.

NOTE—When the determination of alcohol-insoluble matter in bleached shellac is required, the sample must be dried if in the form of bars or ground bleached, as the water present dilutes the alcohol to a point where solution may not be complete. Prolonged heating at the temperatures of 38°–43° C. stated above may render the shellac partly insoluble and it is recommended that in preparing shellac for this determination a separate portion be dried by exposure to the air in a thin layer without the application of heat

| APPROVED BY | SIGNED BY COMMITTEE |
|---|---|
| BERRY BROTHERS, INC | A. C. LANGMUIR, *Chairman* |
| KASEBIER-CHATFIELD SHELLAC CO | G. F. ASHBY |
| THE MAC-LAC CO | C. T. BRAGG |
| MARX & RAWOLLE | E. F. HICKS |
| PITTSBURGH PLATE GLASS CO | P. C. MCILHINEY |
| ROGERS-PYATT SHELLAC CO | J. W. PAISLEY |
| WM. ZINSSER & CO. | A. C. STILLWELL |

# RESULTS OF SOME CO-OPERATIVE WORK ON DETERMINATION OF SULFUR IN PYRITES; SOME OBSERVATIONS ON DETAILS OF MANIPULATION, SOURCES OF ERROR, AND ON BARIUM SULFATE AS PRECIPITATED UNDER DIFFERENT CONDITIONS[1]

By H. C. Moore

After several experiences, when we had submitted portions of the same ground laboratory sample to several laboratories for sulfur analysis, we found that a good general agreement of the results reported was quite unusual. Since it generally appeared, upon investigation, that all laboratories had followed practically the same details of analysis, the cause of these disagreements was not apparent. We then decided to make a study of this matter and the best plan seemed to be that of co-operative work on carefully prepared samples. Accordingly, two large samples were ground to pass 80 mesh and were separately mixed. Sealed portions of these samples were sent to several laboratories with the request that they determine sulfur by their usual committee on sulfur determination in pyrites, blends, etc., to the 6th International Congress of Applied Chemistry.[1] The methods followed were those of Lunge and of Silberberger. The maximum difference by each method was nearly 1 per cent.

Many investigators, and especially Allen and Johnston,[2] have pointed out several causes, or sources of error, accountable for differences in results obtained by the Lunge method. Allen and Johnston determined quantitatively the effect of these errors and found the greatest to be due to the presence of ammonium salts in the solution in which barium sulfate is precipitated. We also made a quantitative study of this error and our results, Table IV, confirm closely the results of Allen and Johnston, and show that by the modified Lunge method this error affects the results by from 0.3 to about 1.0 per cent sulfur.

We also made a study of the methods of effecting oxidation and solution of the sample (Results, Table II), and found two sources of error following the Lunge method: (1) loss of sulfur presumably by volatilization and (2) loss due to incomplete oxidation. In Sample 15,095 free sulfur separated when treated with the nitro-hydrochloric acid; in such a case another error would be introduced unless this free sulfur were oxidized and brought into solution.

TABLE I—SULFUR RESULTS REPORTED BY THE SEVERAL LABORATORIES ON THE TWO SAMPLES OF PYRITES

| Lab. No. | Analyst | Per cent S—Dry basis No. 15095 | No. 15096 | METHOD OF ANALYSIS |
|---|---|---|---|---|
| 1 | B | 38.88 | 46.91 | Modified Lunge method.(*a*) Two precipitations of iron by $NH_4OH$. Iron residue not tested for sulfur. |
| | A | 38.63 | 46.79 | |
| 2 | | 38.60 | 46.63 | Same as No. 1 |
| 3 | | 38.74 | 47.06 | Av. of several modifications of Lunge |
| 4 | | 38.93 | 46.60 | Practically same as No. 1, except iron residue was dissolved and sulfur precipitated by $BaCl_2$. |
| 5 | W | 38.73 | 47.00 | Modified Lunge. Made 2nd evaporation with $HNO_3$-HCl mixture. One precipitation of iron by $NH_4OH$. Iron residue |
| | B | 39.24 | 47.06 | not tested for sulfur. |
| | L | 39.21 | 47.34 | |
| 6 | | 39.50 | 47.63 | Lunge. $BaSO_4$ dried at 130° C. |
| 7 | A | 39.41 | 47.38 | Allen and Bishop method.(*b*) |
| | B | 39.54 | 47.40 | |
| | C | 39.43 | 47.32 | |
| 8 | | 40.00 | 47.88 | Lunge. One precipitation of iron by $NH_4OH$. Sulfur precipitated in iron residue. $BaCl_2$ solution added all at once. |
| 9 | | 39.23 | 47.62 | Modified Lunge. One precipitation of iron by $NH_4OH$. Iron residue not tested for sulfur. |
| 10 | | 39.48 | 47.63 | Method not reported. |
| 11 | | 39.55 | 47.62 | Modified Lunge. Allen and Bishop method of solution. One precipitation of iron by $NH_4OH$. Iron residue dissolved in HCl and sulfur precipitated. |
| 12 | S | 39.53 | 47.76 | Modified Lunge. One precipitation of iron by $NH_4OH$. Iron residue dissolved in HCl and sulfur precipitated. |
| | H | 39.21 | | |
| 13 | | 39.56 | 47.45 | Modified Lunge. Two precipitations of iron by $NH_4OH$. Iron residue dissolved in HCl and sulfur precipitated. Beaker containing precipitated $BaSO_4$ left on steam bath over night before filtering. |
| | | 39.54 | 47.59 | Allen and Bishop Method. |
| 14 | | 39.37 | 47.28 | Modified Lunge. One precipitation of iron by $NH_4OH$. Iron residue dissolve in HCl and sulfur precipitated |
| | | 39.21 | 47.38 | Electrochemical method of A. M. Smoot.(*c*) |
| | | 39.70 | | Method of Smoot, except cold precipitation of $BaSO_4$ according to Allen and Bishop. |
| 15 | | 39.19 | 47.19 | Modified Lunge. Two evaporations with $HNO_3$-HCl mixture. |
| | | 39.59 | 47.44 | Allen and Bishop method. |
| 16 | | 39.19 | 47.88 | Lunge method. |
| | | 39.15 | 47.87 | Allen and Bishop method. |

SUMMARY OF ABOVE RESULTS (excepting those of Laboratory 10 and 14)

| | MODIFICATIONS OF LUNGE METHOD | | ALLEN AND BISHOP METHOD | |
|---|---|---|---|---|
| | Sample No. 15095 | Sample No. 15096 | Sample No. 15095 | Sample No. 15096 |
| Max. per cent sulfur | 40.00 | 47.88 | 39.59 | 47.87 |
| Min. per cent sulfur | 38.60 | 46.60 | 39.15 | 47.31 |
| Aver. per cent sulfur | 39.18 | 47.28 | 39.47 | 47.49 |

(*a*) By modified Lunge method is meant some one of the numerous modifications. By most of these modifications $BaSO_4$ is precipitated by the slow addition of $BaCl_2$ solution.

(*b*) "An Exact Method for Determination of Sulfur in Pyrites Ore," *8th International Congress of Applied Chemistry*, **1**, 33.

(*c*) *Engineering and Mining Journal*, **94**, No. 9.

method and when reporting their results to describe briefly their details of analysis. Results have been received from seventeen laboratories and appear in Tables I, II and III; these results present about the usual disagreement.

The following laboratories and analysts participated in the work.

| | |
|---|---|
| McCandless Laboratory | Atlanta, Ga. |
| N. P. Pratt Laboratory | Atlanta, Ga. |
| Stillwell & Gladding | New York, N. Y. |
| Pennsylvania Salt Manufacturing Company | Philadelphia, Pa. |
| A. M. Smoot, Ledoux & Company | New York, N. Y. |
| W. S. Allen, General Chemical Company | New York, N. Y. |
| F. B. Carpenter, Virginia-Carolina Chem. Company | Richmond, Va. |
| W. D. Richardson, Swift Fertilizer Company | Chicago, Ill. |
| C. W. Blackman, Swift Fertilizer Company | Atlanta, Ga. |
| W. C. Dumas, A. M. Lloyd Laboratory | Atlanta, Ga. |
| C. A. Butt, International Agricultural Corporation | Atlanta, Ga. |
| F. K. Wanner, Tennessee Chemical Company | Nashville, Tenn. |
| W. D. Drummond, Planters Fertilizer & Chem. Co. | New Orleans, La. |
| Paul Rudnick, Armour Fertilizer Works | Chicago, Ill. |
| H. G. Hackman, Armour Fertilizer Works | Chrome, N. J. |
| R. Neu, Armour Fertilizer Works | Jacksonville, Fla. |
| R. D. Caldwell and H. C. Moore, Armour Fertilizer Works | Atlanta, Ga. |

Results of similar co-operative work were reported by the

[1] Presented at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915. Recommended for publication by the Committee on Research and Methods of Analysis, Division of Fertilizer Chemists.

The most general method for determining sulfur in pyrites has been either that of Lunge or some modification of this method. Allen and Johnston[3] have shown that accurate results are impossible by any modification of the Lunge method, or when barium sulfate is precipitated in solutions containing ammonium salts, unless as the result of a nice balancing of the plus and minus errors, or by applying certain empirical corrections. The fact, however, that some laboratories, by certain modifications of this method, get results which agree with those of the later and more exact methods, either that of Allen and Bishop[4] or of Smoot,[5] shows that they have employed details of analysis which have produced conditions favorable to a nice balancing of the plus and minus errors.

Laboratory 6 seems to have effected a compensation of errors

[1] Also published in *Zeit. fur angew Chemie*, **1905**, p. 449.

[2] *J. Am. Chem. Soc.*, **32** (1910), 588.

[3] *Loc. cit.*

[4] *8th International Congress of Applied Chemistry*, **1**, 33.

[5] *Engineering and Mining Journal*, **94**, No. 9.

by drying the barium sulfate at 130° instead of igniting. Our investigation shows that under certain conditions (see Table IV) very good results are obtained by this practice.

Attention is called to the results of Analyst 14, Mr. A. M. Smoot, to whom credit must be given for some very interesting observations relative to the co-precipitation of calcium sulfate with barium sulfate. He found that his results on Sample 15096 by the modified Lunge method[1] and his electrochemical method were normal, but that results on Sample 15095 by the same methods were unusual in that higher results were obtained an aliquot for analysis. The result of this procedure did not agree quite so well for some reason as those by the regular method. The method of Smoot also appears to be an excellent one except that suitable electrical apparatus is not available in all laboratories.

From the foregoing and from the results in Tables I to IV, we might conclude that the disagreement in results in Tables I, II and III is due partly to the different methods of analysis and partly to the personal factor or different ways of handling the same method.

TABLE II—RESULTS BY ANALYST A OF OUR LABORATORY

| METHOD | Per cent sulfur on dry basis No. 15095 | No. 15096 |
|---|---|---|
| (1)—Modified Lunge. 0.5-g. samples treated with 10 cc. nitro-hydrochloric acid(*a*) (also $KClO_3$ on Sample 15095) and after 15 minutes placed on steam plate and evaporated. Evaporated again with 10 cc. HCl and took up residue with 1 cc. HCl and 100 cc. water. One precipitation of iron by $NH_4OH$ and filtrate, 350–400 cc., boiled to expel excess $NH_3$ before precipitating. Iron residue dissolved in dil. HCl and sulfur precipitated | 39.19 | 47.13 |
| (2)—Same as (1) except sample and acid mixture stood one hour in cold before heating on steam plate | 39.21 | 47.16 |
| (3)—Same as (2) except sample and acid mixture stood about 12 hours in cold before heating on steam plate | 39.34 | 47.26 |
| (4)—Same as (1) except that sample and acid mixture stood from one-half to one hour cold and then after evaporation, made six successive evaporations with 5 cc. nitro-hydrochloric acid | 39.24 | 47.31 |
| (5)—Same as (3) making one extra evaporation with 5 cc. nitro-hydrochloric acid | 39.48 | 47.34 |
| (6)—Same as (5) except that sample and acid mixture stood in cold 10–15 minutes before putting on plate | ..... | 47.08 |
| (7)—Same as (1) except using Allen and Bishop method of solution | 39.21 | 47.28 |
| (8)—Allen and Bishop method | 39.57 | 47.53 |

(*a*) 3 parts by volume of conc. $HNO_3$ and 1 part conc. HCl.

by the modified Lunge method than by the electrochemical method. He then found that this sample contained a considerable amount of carbonate of lime and found on further investigation that quite an appreciable error had resulted from the co-precipitation of calcium sulfate with barium sulfate. He then combined the barium sulfate precipitates from two determinations (averaging 39.21 per cent), made by the electrochemical method and determined the per cent of CaO. His results follow:

| | | |
|---|---|---|
| Weight of the combined precipitates of $BaSO_4$ | 2.8544 grams | |
| Weight of $CaSO_4$ | 0.0478 gram | = 1.13% S |
| Weight of actual $BaSO_4$ | 2.8066 grams | = 38.55% S |
| TOTAL | | = 39.68% S |

The error therefore due to co-precipitation of calcium sulfate amounted to 0.47 per cent sulfur. He then made two determinations by the same method except that precipitation of barium sulfate was made by the method of Allen and Bishop. The results of these two determinations checked perfectly at 39.70 per cent sulfur. The two precipitates were combined and tested as before with the following results:

| | | |
|---|---|---|
| Weight of combined precipitates of $BaSO_4$ | 2.8896 grams | |
| Weight of $CaSO_4$ | 0.0136 gram | = 0.32% S |
| Weight of actual $BaSO_4$ | 2.8760 grams | = 39.50% S |
| TOTAL | | = 39.82% S |

The error in this case amounted to only 0.12 per cent sulfur, indicating that the co-precipitation of calcium sulfate is much less on cold precipitation by the method of Allen and Bishop than by hot precipitation.

Allen and Bishop showed that, by their method, 1 per cent calcium had no appreciable effect on the results. It is likely, however, that Sample 15095 contains calcium[2] in excess of this amount. At any rate, Mr. Smoot seems to have made a very interesting observation.

It will be noted from an examination of the results in Tables I, II and III that those obtained by the Allen and Bishop method are much more concordant than those obtained by the modifications of the Lunge method. The objections to the Allen and Bishop method are the large amount of barium sulfate to filter and wash; also the enormous beakers in which precipitation is made. This objection, however, we have successfully removed by using a smaller sample and correspondingly smaller beakers, as indicated under Methods 3 and 4, Table III. We also made a number of determinations by using a larger sample and after reducing with aluminum in a flask, made to volume and took

[1] *Eng. Min. J.*, **94**, No. 9.

[2] One complete analysis covering one month's shipment of this same kind of ore shows 2.48 per cent calcium.

Some chemists have claimed that some pyrites samples, even when kept in tightly stoppered bottles, undergo oxidation, thus reducing the per cent of sulfur in the sample. While this is doubtless true in some cases, yet it will hardly help to explain the disagreement of results in Tables I, II and III, since some

TABLE III—RESULTS BY ANALYST B, OUR LABORATORY

The results in this table were obtained over a period of a little over two months and several of the sealed portions of each sample were used in this work. Under Method 1, Sample 15096, for example, the first two results listed were obtained 6/4/14 and the last three results in the same list on 8/10/14. The other five results in this list were obtained between these dates. This would indicate that these samples did not change or oxidize on standing.

| METHOD | Per cent sulfur on dry basis No. 15095 | No. 15096 |
|---|---|---|
| (1)—Allen and Bishop (*a*) | 39.50 | 47.41 47.49 |
| | 39.44 | 47.41 47.45 |
| | 39.56 | 47.44 47.36 |
| | 39.54 | 47.40 47.48 |
| | 39.52 | 47.49 47.43 |
| | Av., 39.51 | Av., 47.43 |
| (2)—Allen and Bishop, except that solution was filtered from insoluble residue before reducing with aluminum | | 47.43 47.47 |
| | | 47.47 47.46 |
| | | 47.45 47.48 |
| | | Av., 47.46 |
| (3)—Allen and Bishop, except used 0.5495 gram samples. Treated with 6–8 cc. Br-$CCl_4$ mixture and then 10 cc. $HNO_3$ and evaporated. Added 10 cc. HCl and again evaporated. Treated residue with 1 cc. conc. HCl and 50–100 cc. hot water. Added 0.1 g. Al powder to reduce iron, filtered and washed. Added 2.4 cc. conc. HCl and diluted to about 640 cc. and precipitated with 50 cc. 5 per cent $BaCl_2$ sol. cold and without stirring. | 39.56 | |
| | 39.56 | |
| | 39.54 | |
| | Av., 39.55 | |

| | Dried | Ignited(*b*) | Dried | Ignited |
|---|---|---|---|---|
| (4)—Allen and Bishop, exactly like (3), except that $BaSO_4$ was dried for 8 hrs. at 130° C. and weighed before ignition. | 40.55 | 39.69 | 48.41 | 47.52 |
| | 40.51 | 39.64 | 48.61 | 47.56 |
| | 40.40 | 39.57 | 48.59 | 47.56 |
| Average, | 40.49 | 39.63 | 48.54 | 47.55 |

| | Dried | Ignited | Dried | Ignited |
|---|---|---|---|---|
| (5)—Allen and Bishop, exactly as described by author (1.3738 g.) except that $BaSO_4$ was dried for 18 hrs. at 130° C. and weighed before ignition. | 40.37 | 39.56 | 48.41 | 47.43 |
| | 40.19 | 39.45 | 48.42 | 47.46 |
| | 40.29 | 39.52 | 48.42 | 47.48 |
| | 40.23 | 39.52 | | |
| Av., | 40.27 | 39.51 | 48.42 | 47.46 |

| | Dried | Ignited | Dried | Ignited |
|---|---|---|---|---|
| (6)—Modified Lunge: 0.5495 g. sample, Allen and Bishop method of solution with final treatment like Method 1, Table II. $BaSO_4$ dried for 18 hrs. and weighed before ignition. | 39.39 | 39.07 | 47.83 | 47.31 |
| | 39.50 | 39.08 | 47.83 | 47.32 |
| | 39.63 | 39.24 | 47.85 | 47.37 |
| | 39.43 | 39 09 | 47.73 | 47.30 |
| Average, | 39.49 | 39.12 | 47.81 | 47.325 |

(*a*) *Loc. cit.*
(*b*) Ignited; heated to constant weight over high temperature burner.

of the results obtained by the Allen and Bishop method, more than a year ago, agree almost perfectly.

The fact that such disagreements in results are not unusual is a matter of considerable importance to the fertilizer industry since it is the largest single user and manufacturer of sulfuric acid.[1] This clearly proves the need of some standard method

[1] A. M. Fairlie, in "American Fertilizer Handbook," **1914**, p. 35.

for determining the sulfur in pyrites. Such a method need not be used, unless desired, but it would at least provide a basis for standardizing other methods and be the method of final reference in case of disputes.

A few observations with reference to barium sulfate may be of interest. The barium sulfate precipitates from a hot and a cold solution differ in appearance and some results would indicate that their compositions also differ. When barium sulfate is precipitated in a hot solution and especially in solutions containing ammonium salts it is very fine while barium sulfate precipitated in a cold solution, by the method of Allen and Bishop, is coarse and of crystalline form. Some results (Table IV) indicate that barium sulfate, whether precipitated in a hot or cold solution, holds water in combination. If this is true it would explain the statement of Allen and Johnston[1] that barium sulfate holds water up to 500°. We found (Tables III and IV) that when barium sulfate precipitates were dried at 130° and weighed, the results agree quite as well as when the precipitates were fully ignited and again weighed. The average loss on ignition for precipitates formed in cold solution was 2.02 per cent (average of four results) and the corresponding average loss (average of four results, Table III) for the two samples of pyrites was 2.01 per cent. The average loss on ignition for precipitates formed in a hot solution, no ammonium salts present, was 0.48 per cent (average of two results). We also found that where the precipitate had been made in hot solution and in the presence of ammonium chloride that the loss on ignition amounts to very close to 1 per cent. If it is permissible to assume that this loss in weight is due to water of crystallization, which is only an assumption, then the formula for barium sulfate precipitated in a cold solution, by the method of Allen and Bishop, would be $15BaSO_4.4H_2O$ and for barium sulfate precipitated in a hot solution, no ammonium salts present, would be $16BaSO_4.H_2O$.

TABLE IV—RESULTS BY ANALYST B, OUR LABORATORY ON $H_2SO_4$ SOLUTION

The sulfuric acid solution was standardized by titration against C. P. $Na_2CO_3$ using the same aliquot as used in (2) to (8) below. Calculating the $Na_2CO_3$ value into terms of sulfur equals 45.18 per cent S, agreeing almost perfectly with the results by the methods (1) and (2) below. Precipitates of $BaSO_4$ stood over night before filtering; they were then dried for 18 hrs. at 130° C., weighed, ignited and weighed again.

| | Percentage Sulfur Dried | Ignited |
|---|---|---|
| (1)—Aliquot of $H_2SO_4$ solution (corresponding to about 4.5 g. $BaSO_4$) diluted to 1600 cc., added 10 cc. conc. HCl, and precipitated cold without stirring, by adding 125 cc. 5 per cent $BaCl_2$ solution, as described by Allen and Bishop.(a) | 45.99 | 45.16 |
| | 45.96 | 45.15 |
| | 45.98 | 45.15 |
| Av., | 45.98 | 45.15 |
| (2)—Aliquot of $H_2SO_4$ solution (corresponding to about 1.8 g. $BaSO_4$) diluted to 640 cc., added 4 cc. conc. HCl and precipitated as in (1) with 50 cc. 5 per cent $BaCl_2$ solution. | 46.04 | 45.17 |
| | 46.11 | 45.16 |
| | 46.11 | 45.19 |
| | 46.10 | 45.19 |
| Av., | 46.09 | 45.18 |
| (3)—Same aliquot as (2) diluted to 350–400 cc. with water, heated to boiling and precipitated by adding 25 cc. hot 10 per cent $BaCl_2$ solution drop by drop, stirring continuously. | 45.29 | 45.09 |
| | 45.34 | 45.13 |
| | 45.34 | 45.12 |
| Av., | 45.32 | 45.11 |
| (4)—Same aliquot as (2), diluted to 350–400 cc. water, added methyl orange, and made neutral with NH₄OH, then added 3 drops conc. HCl and precipitated as in (3). | 45.48 | 44.90 |
| | 45.48 | 44.94 |
| Av., | 45.48 | 44.92 |
| (5)—Same as (4) except 1 g. $NH_4Cl$ was added before precipitation of $BaSO_4$. | 45.26 | 44.81 |
| | 45.16 | 44.87 |
| Av., | 45.21 | 44.84 |
| (6)—Same as (5) except that 2 g. $NH_4Cl$ were added..... | 45.26 | 44.88 |
| | 45.23 | 44.85 |
| Av., | 45.245 | 44.865 |
| (7)—Same as (5) except that 4 g. $NH_4Cl$ were added..... | 45.17 | 44.74 |
| | 45.02 | 44.63 |
| | 45.07 | 44.62 |
| | 45.12 | 44.66 |
| Av., | 45.095 | 44.66 |
| (8)—Same as (5) except that 6 g. $NH_4Cl$ were added..... | 45.11 | 44.65 |
| | 44.96 | 44.52 |
| | 44.96 | 44.53 |
| | 44.92 | 44.47 |
| Av., | 44.99 | 44.54 |

(a) "An Exact Method for Determination of Sulfur in Pyrites Ore," *8th International Congress of Applied Chemistry*, **1**, 33.

From the results of this work, the following conclusions may be drawn:

I—The disagreement of results reported by the different laboratories on these samples of pyrites, and determined by some modification of the Lunge method, is about in line with past experiences.

II—The results by the Allen and Bishop method show a much better agreement.

III—The sources of error in the Lunge method brought out in this work are (1) loss of sulfur presumably by volatilization, (2) loss of sulfur in the insoluble residue due to incomplete oxidation, (3) loss due to presence of ammonium salts, (4) coprecipitation of calcium sulfate which is greater in hot precipitation than in cold.

IV—Barium sulfate precipitated under different conditions appears, from some results obtained, to have varying compositions both physically and chemically.

The writer wishes to express here his thanks to all those who have participated in this work and especially to Mr. A. M. Smoot for the account of his interesting observations.

ARMOUR FERTILIZER WORKS, ATLANTA, GA

[1] *J. Am. Chem. Soc.*, **32** (1910), 559.

## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS SEVENTH SEMI-ANNUAL MEETING LOS ANGELES AND SAN FRANCISCO, AUGUST 18 AND 25-28, 1915

The Seventh Semi-annual Meeting of the American Institute of Chemical Engineers will be held in Los Angeles and San Francisco, California, on August 18 and 25–28, respectively. The tentative itinerary published in THIS JOURNAL, **7**, 448, has been accepted with a few minor changes. The complete program may be obtained by writing to Secretary J. C. Olsen, Cooper Union, New York City.

### PROGRAM OF PAPERS

**A New Electrolytic Process of Sewage Disposal.** J. C. OLSEN AND WM. H. ULRICH

**The Improvement of High Boiling Petroleum Oils, and the Manufacture of Gasoline as a By-Product Therefrom, by the Action of Aluminum Chloride.** A. M. MCAFEE.

**Wine Making.** ARTHUR L. LACHRAN.

**Costs as Applied to Professional Businesses.** R. A. GOULD

**Resources and Possibilities of Chemical Industry in the Southwest.** EDGAR BARUCH.

**Manufacture of Cream of Tartar.** OTTO BEST.

**Present State of the Thiogen Industry.** S. W. YOUNG.

**The Purification of Sewage by Aeration in the Presence of Activated Sludge.** E. BARTOW.

**Electrical Precipitation Method.** W. A. SCHMIDT

### PROGRAM OF EXCURSIONS

In addition to points of local and geographic interest the following plants will be visited:

LOS ANGELES—Oil-burning Power Plant; Salt Plant; Kelp Industry; Beet Sugar Factory; Orange, Walnut and Fruit Orchards; Whittier and Fullerton Oil Fields (Wells, Casinghead Gas Plants, etc.); Oxnard Beet Sugar Factory; American Olive Co. Plant; Bishop & Co. Plant (candy making, fruit preserving, etc.).

SAN FRANCISCO—Oil Gas Works (Mr. Edward C. Jones will explain the process); Vineyard and Wineries at Winehaven.

### COST OF TRIP

Transportation for entire round trip (22 days), Pullman lower berth, Grand Canyon side trip, sight-seeing trips at Colorado Springs, Pike's Peak, Santa Barbara and Del Monte, all meals on trains (estimated at $1.00 each), berth and meals on steamer, San Francisco to Astoria and Duluth to Buffalo—$249.00.

The following items are not included in the above figure: Yosemite Valley trip (meals, lodging and transportation)—$52.35; Yellowstone Park trip (meals, lodging and transportation)—$53.50; Hotel accommodation and other expenses in San Diego, San Francisco, Seattle, Butte, Anaconda, St. Paul and Duluth (17 days).

# NOTES AND CORRESPONDENCE

## CONDITIONS OF THE RUSSIAN TREASURY DEPARTMENT COMPETITION ON THE INDUSTRIAL USES OF ALCOHOL

### REAGENTS FOR DENATURING ALCOHOL

In order to encourage the wide-spread utilization of alcohol (wine spirits), for technical purposes, an international competition is announced consisting of three prizes, *viz.*, 30,000, 15,000 and 5,000 rubles ($15,000, $7,500 and $2,500) for the discovery of new denaturants or for the improvement of present denaturing processes, which, while assuring the free circulation of denatured alcohol, will make impossible its use for drinking purposes. The new denaturing agents must satisfy the following conditions:

1—The denaturing agents must convert the alcohol into a liquid which is absolutely unsuitable for drinking purposes by imparting an unpleasant taste to the alcohol or by having a violent physiological action on the organism (nausea, vomiting, diarrhea).

2—The denaturing agents must not give rise to a suffocating odor which would make the utilization of the alcohol for the needs of every-day life difficult or injurious.

3—The denaturing agents must not leave a residue after combustion nor contain substances which would be injurious to the apparatus in which the alcohol is burned.

4—Separation of the denaturing agents of the alcohol by simple means, such as removal by water, salting out, filtration through carbon, simple distillation, etc., should be impractical.

5—The primary materials used in the preparation of the denaturing agents should be among such as can be obtained in Russia in sufficient amounts.

The period fixed for the presentation of the statements of competitors expires January 1, 1916.

The statements should be presented, written in Russian or French, to the General Bureau of Indirect Contributions and the Alcoholic Commission (Glavnoé Oupravlenié Neocladnich Sborow i Casennoïj Prodagy Piteïj à Pétrograd) in packages bearing an assumed name; in a separate envelope, bearing the same assumed name, the name and address of the competitor should be indicated.

In the statement of discoveries the composition of the proposed denaturing agent, the quantity necessary per "vedro" (12.3 liters) of alcohol and its value should be stated.

Samples of the denaturing agents should be added to the statement mentioned above and the quantities of these should not be less than one kilo.

The offerings made will be examined by a Competition Commission made up of persons designated by the Minister of Finance. Included in this Commission will be representatives of the Ministries and General Bureaus interested as well as representatives of science and industry.

In case of an invention or improvement of especial value, the Commission will have the right to assign several or all prizes of the competition to one individual.

The examination of the statements presented and the assignment of prizes will take place July 1, 1916, at the latest.

The decisions of the Competition Commission will be confirmed by the Minister of Finance.

The Government reserves the right to utilize the methods of denaturing which receive the above-mentioned prizes without indemnifying the inventors in any other way.

### NEW INDUSTRIAL APPLICATIONS OF ALCOHOL

An international competition is announced to encourage the extensive development of the application of alcohol or its derivatives for heating, lighting and for the production of motor power as well as to stimulate the utilization of alcohol in the various industrial branches of chemical technology. For this purpose the following prizes are offered:

1—Three prizes of 60,000, 30,000, and 10,000 rubles ($30,000 $15,000 and $5,000) for the invention of a new process for the utilization of alcohol in the preparation of a product which would be absolutely different in nature than the alcohol used in its production. As examples of such products may be mentioned vinegar, ether, and chloroform, etc.

2—Three prizes of 50,000, 20,000 and 5,000 rubles ($25,000, $10,000 and $2,500) for the invention of a new process for the utilization of alcohol in the preparation of a product in which the alcohol or its derivatives (*e. g.*, sulfuric, ether, etc.) constitutes one of the component parts of the products or the solvent but under such conditions that the alcohol can not be recovered economically from the product in question. As examples of such products may be mentioned pharmaceutical and perfumery preparations.

3—Three prizes of 30,000, 15,000 and 5,000 rubles ($15,000, $7,500 and $2,500) for the invention of a new process for the utilization of alcohol in an industry in which the alcohol or its derivatives (*e. g.*, sulfuric, ether, etc.) would serve as the intermediary and provisional solvent or as the extractive agent or precipitant. As examples of such applications may be mentioned the production of smokeless powder, the manufacture of artificial silk, etc.

4—Four prizes of 75,000, 50,000, 30,000 and 20,000 rubles ($37,500, $25,000, $15,000 and $10,000) for the invention or improvement of apparatus for the utilization of alcohol for feeding internal combustion motors.

5—Four prizes of 75,000, 50,000, 30,000 and 20,000 rubles ($37,500, $25,000, $15,000 and $10,000) for the invention or improvement of apparatus having as their object the utilization of alcohol or its derivatives for heating.

6—Four prizes of 50,000, 30,000, 15,000 and 5,000 rubles ($25,000, $15,000, $7,500 and $2,500) for the invention or improvement of apparatus in which alcohol is used for lighting.

The period fixed for the presentation of statements of competitors expires January 1, 1916.

The statements should be presented written in Russian or French to the General Bureau of Indirect Contributions and the Alcoholic Commission (Glavnoé Oupravlenié Neocladnich Sborow i Casennoïj Prodagy Piteïj) in packages with an assumed name; in a separate envelope bearing the same assumed name, the name and address of the competitor should be given.

The statement mentioned above should contain detailed descriptions of the conditions for the application of the alcohol with figures on the economics of the application calculated on the basis of an alcohol cost of 2 copecks per unit of alcohol (123 cc. absolute alcohol at a temperature of 15.5° C.).

The statements referring to the prizes indicated in Sections 1 to 3 should include samples of the products and the amount of these should be at least one kilogram.

The statements referring to the prizes indicated in Section 4 should be accompanied by a complete motor and detailed drawings of the parts of the motor which represent the nature of the invention, at the same time indicating the necessary dimensions.

The statements referring to Sections 5 and 6 should be presented with specimens of apparatus for using the alcohol (burner distributors, aeolipiles, lanterns, lamps, etc.) and with detailed drawings showing the dimensions of the apparatus.

As regards the classes indicated in Sections 4, 5, and 6, the object of the prizes to be assigned will be (conjointly or separately) not only the inventions or improvements relative to the construction itself of the apparatus using the alcohol, but also

the mixtures of alcohol with other substances and the methods of utilization of these mixtures to increase the calorific power of the alcohol.

The samples of substances to be added to the alcohol, if not found on the Russian market, should be sent in sufficient amounts to make detailed trials; in any event, not less than five kilograms.

In estimating the improvements relating to internal combustion motors the preference in the assignment of the prizes will be given to such separate improved parts as can be readily adapted to internal combustion motors and which belong to existing types and make possible the advantageous utilization of alcohol or its mixtures in place of other kinds of fuel.

The statements presented will be examined by a Competition Commission made up of persons designated by the Minister of Finance. Taking part in this Commission will be representatives of the Ministries and General Bureaus concerned as well as representatives of science and industry.

The prizes will be assigned only to those inventions or improvements of which it may be assumed that they would imply an appreciable consumption of alcohol.

In the case of inventions or improvements of especial value the Commission will have the right to assign several or all prizes in that class to one person.

The examination of the statements made and the assignment of prizes will take place July 1, 1916, at the latest.

The decisions of the Competition Commission will be confirmed by the Minister of Finance.

The inventor reserves the right to exploit his invention and to protect it by taking out a certificate of protection.

## NOTE ON FERMENTATION OF FOODS CONTAINING BENZOIC ACID[1]

Occasionally it is observed that foods to which sodium benzoate has been added undergo fermentation. While working with apple juice during the last few seasons, sodium benzoate was added while the juice was running from the press. The juice was then transferred to casks holding 2500 gallons where it was clarified to a degree of perfect brilliancy and then drawn off into new freshly paraffined kegs. Sometimes a few of these kegs would soon show signs of a very vigorous fermentation while all of the others would remain in perfect condition for several months. Thus it appeared that there are yeasts that will grow in the presence of benzoic acid, and that such cells had found their way into the kegs that were showing evidences of fermentation. To determine this, some fresh apple juice was sterilized and the action of benzoic acid on several yeasts noted. With a pure wine yeast and Fleischmann's baker's yeast, 0.1 per cent of benzoic acid would inhibit the growth of the yeast as well as completely check the fermentation where the yeast has been permitted to become very vigorous before adding the benzoic acid (a more or less common belief prevails that benzoic acid will not prevent fermentation after the yeast has been permitted to become active). With the yeast taken from the kegs, however, 0.1 per cent of benzoic acid had no inhibiting effect whatever; 0.2 per cent had a weak retarding action, while 0.3 per cent had a complete inhibiting effect.

[1] Author's abstract of paper presented before the St. Louis Section of the American Chemical Society, March 8, 1915.

3601 Salena Street, St. Louis
March 24, 1915

Geo. Lang, Jr.

## PAPER PULP AS AN AID IN FILTRATION

To prepare the pulp, make a mixture of one part strong $HNO_3$ with four parts water in a wide mouth bottle. Add ordinary filter paper. Shake vigorously till the mixture is reduced to a fine smooth pulp. Throw the mass on a Buchner funnel, wash free of acid, then mix the pulp with water to form a thin liquid that will pour easily for use.

This pulp has been found most indispensable for the filtration of the ammonium citrate solution from the digestion of phosphates for the determination of available $P_2O_5$ which is done as follows: Fit a filter paper (9 cm. S. & S. 595) into a 2-in. filter cone. Fill full with paper pulp, and after part of the water has run through, press the mass against the sides of the cone extending above the edge of the filter paper. In filtering, the cone may be filled full, as the paper pulp prevents leaking at the top of the filter paper. The complete filtration and washing to a volume of 400 cc. or more is usually complete in five minutes or less, instead of the half an hour or more which is frequently required without the paper pulp.

If ashless paper pulp is used it may replace asbestos for use with Gooch crucibles. After ignition nothing remains but the precipitate.

University of California, Berkeley
February 8, 1915

P. L. Hibbard

## KNOWLEDGE AND RESEARCH—CORRECTION

*Editor of the Journal of Industrial and Engineering Chemistry:*

My address on "Knowledge and Research," delivered before the University of Pittsburgh, at the dedication of the new building of the Mellon Institute, and reported in your issue for April [7 (1915), 328] contains an erroneous statement, which I desire to correct; namely, I said, in passing, and by way of illustration, that Mr. Edison had received, in perfecting his inventions, certain aid from Dr. Ira Remsen. This was not true; and I wish to withdraw the statement. To go further, and explain how I was misled to make it, would be giving too much importance to a slip of memory which did not in the least affect my argument, and which is only worth notice because any error, however small, ought to be corrected at once.

29 West 39th Street, New York
April 29, 1915

R. W. Raymond

# PERSONAL NOTES

Sir Arthur Herbert Church, formerly professor of chemistry at the Royal Academy of Arts, London, and known for his contributions to chemistry and mineralogy, has died at the age of eighty-one years.

Robert Stewart, professor of chemistry in the Utah Agricultural College, has been appointed associate professor of soil fertility and assistant chief in soil fertility in the Agricultural Experiment Station at the University of Illinois.

Jacob Lund, chemist, Christiania, Norway, has received the "Polyteknisk Förening's" gold medal for his work on fats, an abstract of which may be found in *C. A.*, **8** (1915), 1516.

In an infringement suit brought by the General Bakelite Co against George J. Nikolas, of Chicago, for infringing the Baekeland patents Nos. 954,666, April 12, 1910, 1,018,385, Feb. 20, 1912, and 1,037,719, Sept. 3, 1912, decision was rendered in the United States District Court, Eastern District of New York, on June 12th, by Judge Thomas Chatfield, holding all three patents valid and infringed. The decree covers about 60 pages and carefully reviews the details of the testimony of both plaintiff and defendant, and discusses at length the prior art as disclosed in this case. The trial was held in open court under the new rules of patent practice, and lasted for 23 days, beginning on December 9, 1913. The testimony filled 1396 typewritten pages. The defendant submitted 47 prior patents and many literature references which were alleged to contain prior disclosures. All

of these citations were carefully considered by Judge Chatfield and rejected.

The June 15th meeting of the Southern California Section of the A. C. S. took the form of a joint dinner with the technical societies of Los Angeles—Civil Engineers, Electrical Engineers, Mechanical Engineers, Mining Engineers, Architects, and Engineers and Architects. The meeting was addressed by Wm. Mulholland and by Dr. James A. B. Scherer, president of Throop College of Technology, on the subject, "Service of the Technical Man to the Community."

Mr. Will H. Coghill wishes to announce that after seven years in the practice of ore testing at Chicago he has removed his laboratory to 3705 Hueco Street, El Paso, Texas, where he will continue in the same line of work.

Dr. Francis Clifford Phillips and Mrs. Phillips were the guests of honor at a testimonial dinner given on June 3rd at the German Club, Pittsburgh, Pa., by one hundred former students and friends who desired to show their love and esteem upon the occasion of Dr. Phillips' retirement from active service as professor of chemistry in the University of Pittsburgh. Dr. Phillips, who is well known professionally because of his contributions to the chemistry of gases and his active participation in the interests of the American Chemical Society, has occupied the Chair of Chemistry at Pittsburgh since 1875 and is retiring under the terms of the Carnegie Foundation. Among the speakers at the dinner were Drs. Walther Riddle, Albert E. Frost, R. B. Carnahan and J. H. James, and Professor Alexander Silverman. As an expression of their high regard for his devotion to the University of Pittsburgh, the former students of Dr. Phillips presented him with a check for $1000.00.

The annual spring excursion of the Northeastern Section of the American Chemical Society, on June the 11th, consisted of a visit to the chocolate and cocoa factory of the Walter M. Lowney Company in Mansfield, Massachusetts, followed by a dinner at the Mansfield Tavern, at which Mr. Lowney addressed the Section on the "Story of Chocolate and Cocoa." About seventy-five members and guests were present.

The Hoskins Manufacturing Company announces the appointment of Mr. W. C. Tharp as District Manager in charge of its Pittsburgh office, to succeed Mr. I. J. Shults, resigned. Mr. Tharp has formerly been associated with the Republic Iron and Steel Company, the Scientific Materials Company and the Metallurgical Testing Laboratory of Pittsburgh.

A monument to the late Professor J. H. van't Hoff was unveiled at Rotterdam on April 17th. It consists of a bronze statue, double life-size, in sitting position, and has been placed in front of the school at which Professor van't Hoff was educated.

Dr. Edward Kohman, who has been an instructor in Chemistry at Yale, has just been appointed Chief Dairy Chemist at the University of Illinois.

Albert Plaut, president of Lehn and Fink and one of the most prominent figures in this country's drug trade for many years, died in his fifty-eighth year, in New York, on June 17th.

The Spring Meeting of the American Society of Mechanical Engineers was held in Buffalo, New York, June 22nd–25th, with headquarters at Hotel Statler. An appropriate program of papers was given and excursions were conducted to Niagara Falls, *via* the Gorge Route trip, where the power plants both on the American and Canadian sides were inspected; visits were also made to the Shredded Wheat Company's factory, the Falls Chocolate Company, and various manufacturing plants in and around Buffalo.

Prof. Charles Baskerville addressed the Interstate Cotton Seed Crushers Association at their annual convention in Birmingham, May 18th, on his new process for refining vegetable oils.

John D. Lewis, manufacturer of dyestuffs at Providence, R. I., died at his home in that city on Thursday, May 20th, in his seventieth year. Mr. Lewis studied at Brown University with the class of 1868 and later entered upon the manufacture of dyestuffs with his father. In addition to his activities as a manufacturer Mr. Lewis was also the representative of several foreign dye and chemical companies.

Two anonymous gifts of $150,000 and $100,000 have been made to the Massachusetts Institute of Technology for dormitories. Funds with which to construct the mining building, some $225,000, have been offered to the Institute by Charles Hayden, '90, of Boston, and T. Coleman du Pont, '83, and S. Pierre du Pont, '90, of Wilmington, Del., past and present presidents of the du Pont de Nemours Powder Co. T. Coleman du Pont, it will be remembered, with his gift of $500,000, made the purchase of the Technology site in Cambridge possible. Charles A. Stone, '88, and Edwin S. Webster, '88, of Boston, will provide a residence for the president.

Herbert M. Wilson, engineer in charge of the Pittsburgh Experiment Station of the United States Bureau of Mines, has resigned from the government service to become the director of the Coal Mine Insurance Association. This organization is a newly formed combination of ten American and British insurance companies associated for the joint underwriting of coal-mine accident insurance.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### BUREAU OF THE CENSUS

**Cottonseed Crushed and Linters Obtained.** Preliminary Report, post-card form dated March 18, 1915. This card gives a statement of the number of establishments crushing cottonseed from the crops of 1912, 1913, and 1914 with a statement of the quantity of seed crushed and the quantity of linters obtained. The summary is as follows:

| Year | No. of cottonseed-oil mills | Cottonseed crushed Tons | Linters obtained Running bales |
|---|---|---|---|
| 1912..... | 857 | 4,579,508 | 602,324 |
| 1913 ..... | 870 | 4,767,802 | 631,153 |
| 1914..... | 880 | 5,493,899(*a*) | 772,270(*a*) |

(*a*) Includes 681,315 tons of seed estimated to be crushed and 95,360 bales of linters to be obtained after the date of the March canvass.

### BUREAU OF FISHERIES

**The Menhaden Industry of the Atlantic Coast.** Rob L. Greer. Document No. 811, Appendix III to the report of the U. S. Commissioner of Fisheries for 1914. 27 pp. Paper, 10 cents. This report gives a history and a statistical summary showing the extent of the menhaden fisheries up to the end of 1912. The methods of fishing and the apparatus employed are described and the fishing grounds and season summarized. The processes used for cooking, pressing and drying of the material as well as the properties of the oil and scrap are described in detail. Prices are given for the various parts of equipment required in each process and summaries of costs included.

### BUREAU OF STANDARDS

**Methods of Measuring the Inductances of Low-Resistance Standards.** FRANK WENNER, ERNEST WEIBEL AND F. B. SILSBEE. Scientific Paper 246. 21 pp.

**A Study of the Atterberg Plasticity Method.** CHARLES S. KINNISON. Technologic Paper 46. 18 pp. The practical significance of the Atterberg factor and the rating of clays based on shrinkage or water of plasticity are discussed. The Atterberg factor when used alone is of little significance but when coördinated with the water of plasticity, as recommended in this paper, it appears to be possible to differentiate between the non-sticky or safe working clays and the sticky varieties which are difficult to work.

### GEOLOGICAL SURVEY

**The Production of Lead in the United States in 1914.** C. E. SIEBENTHAL. Preliminary Report. 1 large sheet, dated April 2, 1915. This advanced statement is prepared in order to give at the earliest practicable date reliable figures of the lead production in the United States in 1914. The data given are prepared on confidential reports from each lead smelting and refining company in operation in the United States during that year. The import and export data are taken from records of the Bureau of Foreign and Domestic Commerce. The report shows that the production of primary refined lead (that is, lead smelted from ore) in the United States in 1914 was 542,122 short tons, or an increase of 17 per cent over the preceding year. The primary lead refined and available for consumption in the United States was approximately 450,000 tons, an increase of 7 per cent over 1913. The production of the United States in 1913 is reported as 32.4 per cent of the world production for that period. The report includes price curves for a 3-year period, giving the average weekly price of lead in New York and London. There is also included a list of all the lead smelters and refineries in the United States, Canada, and Mexico. The exports of domestic lead are reported as 20,000 tons during the period March to June, 1914 and 38,500 tons during July to December, 1914. During 1914 the imports of lead in all forms amounted to approximately 57,000,000 lbs., more than 46,000,000 lbs. coming from Mexico. These imports are less than 50 per cent of the amount for the preceding year which in turn was less than any year preceding since 1906 or earlier.

**Advance Statement of the Production of Copper in the United States in 1914.** B. S. BUTLER. Unnumbered leaflet, dated April 5, 1915. 4 pp. The production of primary and secondary copper by the regular refining plants in the United States during 1914 is given (in pounds) as follows:

| | Primary | | Secondary |
|---|---|---|---|
| | Domestic | Foreign | |
| Electrolytic | 991,573,073 | 323,358,205 | 27,702,928 |
| Lake | 158,009,748 | | |
| Casting | 21,506,325 | | 4,224,052 |
| Pig | 39,334,043 | | |
| Total | 1,210,423,189(a) | 323,358,205(a) | 31,926,980 |
| | 1,533,781,394 | | |
| TOTAL OUTPUT | | | 1,565,708,374 |

(a) The distribution of refined copper of domestic and foreign origin is only approximate, as an accurate separation at this stage of manufacture is not possible.

If the output of plants treating purely secondary material is added to the production of the regular refining companies, the contribution of domestic plants of the United States to the world's supply of copper for 1914 is found to be 1,790,000,000 lbs. In addition to the output of metallic copper the regular refining companies produced bluestone with a copper content of 8,602,861 lbs.

The apparent domestic consumption of refined new copper during 1914 was 711,600,000 lbs. If to this quantity of new refined copper is added the 256,000,000 lbs. of secondary copper and copper in alloys produced during the year, it is found that a total of about 968,000,000 lbs. of old copper was available for domestic consumption.

**The Production of Sand-Lime Brick in 1914.** JEFFERSON MIDDLETON. Separate from Mineral Resources of the United States 1914. Part II. 7 pp. Production of sand-lime brick in 1914 is summarized as follows:

| Number of active firms reporting | 68 | |
|---|---|---|
| | Common brick | Front brick |
| Quantity (thousands) | 178,352 | 11,307 |
| Value | $1,118,402 | $119,923 |
| Average price per M | $6.27 | $10.61 |
| TOTAL VALUE | $1,238,325 | |

This summary indicates that the value of the output decreased 14.5 per cent as compared with the 1913 output.

**A Gold-Platinum-Palladium Lode in Southern Nevada.** ADOLPH KNOPF. Bulletin 620–A. 18 pp. (Separate from Contributions to Economic Geology 1915.) The ore of the Boss gold mine in the Yellow Pine mining district, Clark County, Nevada, has recently been shown to be rich in platinum and palladium. The occurrence of platinum and palladium in this Nevada gold ore is of some interest, inasmuch as a review of the known distribution of platinum in veins shows that the Boss vein is one of the few primary deposits in which metals of the platinum group are present in more than traces, and, with one possible exception —the New Rambler deposit in Wyoming—it is the only primary deposit of economic importance in which these metals are the constituents of predominant value.

The report includes a description of the location, the history, the geology and the general mineralogic features of this district. Analyses of the ore are reported and there is given a general discussion of the known lode occurrences of platinum throughout the world and a comparison of the Boss deposit with those previously known.

**The Coalville Coal Field, Utah.** CARROLL H. WEGEMANN. Bulletin 581–E. Separate from Contributions to Economic Geology, 1913. Part II. Pp. 161–187. The purpose of this study was to work out in detail the rock structure, correlating so far as possible the coal beds exposed at the several localities, outlining the probable productive area, and making estimates as to the depth of the beds within it. The general character of the coal is considered and the beds are discussed by townships.

**Mineral Deposits of the Santa Rita and Patagonia Mountains, Arizona.** F. C. SCHRADER, with contributions by J. M. Hill. Bulletin 582. 373 pp. and 25 plates. The purpose of this paper is to furnish a general idea of the character, occurrence, distribution, and development of the mineral resources of a desert area comprising about 1,400 sq. mi. in Pima and Santa Cruz counties, Arizona, 26 mi. southeast of Tucson. The physiography, geology, and water supply of the area are briefly discussed and the mining districts, camps, and properties are considered in detail. The deposits include gold, silver, copper, lead, zinc, tungsten, molybdenum, and building materials. Topographic and geologic maps of the area discussed and of parts of it, maps, plans, and sections of some of the mines and their workings, and halftone plates showing geologic features, make up the illustrations.

**Geology and Coal Resources of North Park, Colorado.** A. L. BEEKLY. Bulletin 596. 121 pp. 12 plates. This bulletin describes the geography, stratigraphy, structure, and economic geology of North Park, a great natural depression in the Rocky Mountains of northern Colorado, sharply defined as a topographic unit by its prominent, almost continuous rim of mountain crests 2,000 to 5,000 ft. above the bottom of the basin. On account of its remoteness from frequented routes of travel, very little has been known of the geology of this basin until recent years. As coal is the most valuable known mineral resource of North Park, this report calls special attention to the coal deposits, discussing their occurrence and development and the production and estimated tonnage of the mines. The illustrations consist of a geologic map and sections of North Park, sections of coal beds, and photographic views of geologic features.

**Contributions to Economic Geology, 1913. Part I. Metals and Nonmetals Except Fuels.** F. L. RANSOME AND H. S. GALE. Bulletin 580. 462 pp. This bulletin is made up of 16 brief reports on investigations of mineral deposits made in 1913. In each case items of economic interest are reported, but little material of purely scientific significance is given. The more important of the reports have already been reviewed in THIS JOURNAL.

BUREAU OF MINES

**Metallurgical Treatment of the Low-Grade and Complex Ores of Utah.** D. A. LYON, R. H. BRADFORD, S. S. ARENTZ, O. C. RALSTON AND C. L. LARSON. A preliminary report issued jointly by the Bureau of Mines and the Department of Metallurgical Research of the University of Utah, Engineering Station. Technical Paper 90. 40 pp. Paper, 5 cents. The principal topics discussed in this report are the following: Methods of mining and mining conditions in Utah (gold, silver, lead, copper and zinc); situation and extent of the low-grade ores; metallurgical treatment of the ores; processes having a possible application for Utah ores; availability of certain raw materials for use as reagents; discussion of the allied problems, especially fuel supply and electric energy costs.

**Mining and Milling of Lead and Zinc Ores in the Wisconsin District, Wisconsin.** CLARENCE A. WRIGHT. Technical Paper 95. 39 pp. Paper, 10 cents. This report gives a description of the zinc and lead mining districts, the ore deposits and their field relations, together with an elaborate discussion of the mining and ore-dressing practice, and the labor, cost, accident, and other factors of operating interest.

**Permissible Explosion-Proof Electric Motors for Mines; Conditions and Requirements for Test and Approval.** H. H. CLARK. Technical Paper 101. 14 pp. Paper, 5 cents. The Bureau of Mines has applied the term "explosion proof" to motors constructed so as to prevent the ignition of gas surrounding the motor by any sparks, flashes, or explosions of gas or of gas and coal dust that may occur within the motor casing. This paper mentions the details of construction that the bureau considers essential for satisfactory service and describes tests of an explosion-proof mining-machine motor and accessories approved by the bureau.

The conditions under which motors may be labeled as approved by the Bureau are described and the "caution" and "approval" plates which are permitted are illustrated. One satisfactory make of motor has already been examined. The test proved that the protection of the motor, starting rheostat, and cable reel was adequate at the time of testing. It is, therefore, considered that with reasonable care the equipment can be maintained permanently in an explosion-proof condition. The equipment has therefore been approved by the Bureau as permissible for use in gaseous mines.

**The Condensation of Gasoline from Natural Gas.** GEORGE A. BURRELL, FRANK M. SEIBERT AND G. G. OBERFELL. Bulletin 88. 106 pp. Paper, 15 cents. "This report treats of a method for preventing some of the waste of the natural gas incidental to oil mining. This method, the condensation of gasoline from natural gas, offers to the oil operator and others a profitable means of utilizing some of the oil-well gas now being wasted. The most desired constituent of crude oil is obtained, the production of oil is not hindered, and the gas, after extraction of gasoline, can be returned to the leased area to drive pumps or into pipe lines for uses to which natural gas is ordinarily put, usually with its fuel value lessened only in slight degree."

In discussing these subjects the growth of this industry is described, and a general discussion given of the constituents of natural gas, their properties and the factors which affect the yield of gasoline from natural gas. Methods of determining the probable yield and flow of gas with the pilot tube and methods of gas analysis are described. The conditions under which the life of wells is sufficient to justify the installation of recovery plants is discussed and data are given as to methods of compression and costs both for installation and operation of the plants. Scientific data are given as to the properties of various gases and their constituents.

**A Primer on Explosives for Metal Miners and Quarrymen.** CHARLES E. MUNROE AND CLARENCE HALL. Bulletin 80. 125 pp. Paper, 25 cents. This report is an elementary discussion of combustion and explosion; blasting and mine explosives; fuse, detonators, and electric detonators; and the proper methods for the use of explosives in quarrying, excavation work, metal mining, and tunneling; including a discussion of the storage, handling, and thawing of explosives and a list of permissible explosives. The report covers metal mining and quarrying giving information which corresponds to that published in Bulletin 17 of this Bureau as applying to the coal mining industry.

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**European Markets for Fish.** Miscellaneous Series 25. 36 pp. Paper, 5 cents.

**Some Aspects of Iron and Steel Industry in Europe.** Special Consular Reports 71. 48 pp. Paper, 5 cents. (Review to be given next month.)

COMMERCE REPORTS—MAY, 1915

Ireland produces annually 47,000 tons of **salt** and imports 33,000 tons, the imports being chiefly from Spain and Italy. The chief salt works is at Antrim where there is a vein 80 feet thick, the salt being obtained partly as rock salt, and partly from brines. (P. 528.)

Export of natural **indigo** from England is now permitted. (P. 561.)

Pocahontas **coal** is about to be used on Brazilian railways. (P. 565.)

At Kingston, Canada, **talc** is quarried from open pits, and is crushed and reduced to 200 mesh, for use in **paper making** and **foundry** purposes. (P. 569.)

The American Peat Society whose object is the furtherance of the use of **peat** in this country, will meet in Detroit, September 20–22, 1915. (P. 571.)

In Moscow, there is a marked increase in the demand for chemicals including **carbolic acid and chloride of lime for disinfectants, potassium ferrocyanide, cottonseed oil, citric and acid nitrate of soda.** (P. 572.)

Argentina is having some difficulty in finding a market for **linseed, quebracho logs, bones, fertilizers, sugar and wine.** (Pp. 580–8.)

Of the large amount of **soda ash** and soda crystals made in Germany in 1913, only a small portion was exported, *viz.*, $36,000 worth to Austria-Hungary and Switzerland. (P. 588.)

A new **tin foundry** is to be erected at Santiago, Chili, to smelt Bolivian ores. (P. 594.)

Under the title **"British Solution of the Dyestuff Problem,"** commercial agent Thos. H. Norton discusses in detail the organization of "British Dyes (Ltd.)," the new company organized to develop the dyestuff industry in Great Britain. The government has subscribed nearly half the capital and also $500,000 for a research laboratory. Most of the stock has been subscribed. Shareholders will have priority in receiving available supplies. The largest existing plant, that of Read, Halliday, and Sons has been acquired. A proposal to pledge stockholders to use only dyes from the new company for five years after the war, was abandoned. The government has permitted all manufacturers to use all patents the property of persons in belligerent countries, suitable royalties to be paid after the war. All alcohol to be used in the dye industry is untaxed. Efforts are being made to coöperate with the Swiss factories. There is some criticism because there is no chemist on the Board of Directors. No

means has yet been provided for protecting the industry from German competition after the war. (Pp. 596–602.) (See also THIS JOURNAL, 7 (1915), 538.)

Owing to a greatly increased demand in England for **high-speed steels**, the price has advanced greatly, as well as that of **ferrotungsten and ferrochrome**, while **ferrovanadium** has remained stationary. (P. 609.)

An export tax on **boric acid** and **borates** has been levied in Chili. The **nitrate industry** is slowly improving. (Pp. 618–9.)

A report on the **oil, seed, and cake trade** of Hull, England, includes statistics of the manufacture and prices in 1913, 1914 and 1915, of linseed, cottonseed, castor beans, rape seed and soya beans, and the corresponding oils and cake. (Pp. 629–31.)

In order to stimulate the production of **coke oven by-products** required for **explosives, fuel,** and **fertilizer** the German government is seeking to extend the use of coke as fuel on railways and in manufacturing. (P. 637.)

Export of **coal** from Great Britain except to colonies and allies, has been forbidden. (P. 641.)

Owing to the increased price of **copper,** the mining industry of British Columbia is improving. (P. 658.)

Efforts are being made to conduct the **washing of wool** in Argentine instead of abroad, and obtain the wool-grease as a by-product. (P. 717.)

The market in China for American and other **ginseng** still continues, in spite of the conclusion of many doctors that it has no therapeutic value. (P. 728.)

The **Second Pan-American Scientific Congress** will be held in Washington, D. C., from December 27, 1915 to January 8, 1916. The United States Government has appropriated $50,000 toward the Congress. (P. 739.)

Among the principal resources of Alaska are **gold, copper, silver, coal, fish oils, gypsum, marble, and tin.** (P. 740.)

Almost no **sugar beet seed** is raised in the United States. The principal producer is Germany, which exports 30,000 tons annually. The "mother beet seed," *i. e.*, the seed used to plant beets for the production of seed, is mostly raised in Holland. (P. 750.)

Paraguay produces 70 per cent of the world's output of **"petitgrain oil,"** the essential oil extracted from the leaves of the wild orange, from $20,000 to $50,000 worth being annually exported to the United States for use as a drug. (P. 755.)

The price of **aniline dyes** in Japan is ten times the normal price. (P. 769.)

In a review of the **"Dyestuff Situation in the United States,"** Commercial Agent Thomas H. Norton states that the existing supplies are so low that the stock of foreign dyes will be practically exhausted by July 15, 1915. The two cargoes of dyes, whose shipment was permitted by the British Government, have not been sent from Germany although there is an ample stock there. While the recovery of coke oven by-products in America is being greatly increased, the demand for **benzol** and **toluol** for **explosives** is restricting the amounts available for dyes. The American output of **aniline** is now sufficient to meet the needs of the dyestuff industry. Most of the contracts are for three years, at a price to be determined by the market price. All the American dyestuff plants have enlarged their plants, and most of the important intermediates are now being made here. There is a marked increase in the demand for natural dyestuffs, especially **"quercitron"** extracted from the black oak, the only natural dyestuff indigenous to the United States. No provision has yet been made for the manufacture of **alizarin** or **synthetic indigo** in the United States. It is believed that a self-contained American coal tar industry is possible under existing tariff conditions, provided there is protection against "dumping." (Pp. 770–9.)

The world's output of **copper** in 1914 was 10 per cent less than in 1913. (P. 797.)

Japan is importing some **phosphate rock** from the Marshall Islands, now under Japan, in place of part of the American supply. (P. 811.)

STATISTICS OF EXPORTS TO THE UNITED STATES (Pp.)

FRANKFORT DISTRICT.
GERMANY—708
Chemicals
Dyestuffs
Paper
Steel and iron
Platinum
Hides
Zinc dust
Spelter
Copper
Barytes
Colors
Bronze

AUSTRIA - HUNGARY—Supplement 1*a*
Beer
Brass
Chinaware
Uranium
Earthenware
Glassware
Glue
Hops
Kaolin
Mineral water
Rennet
Mineral salts
Zinc oxide
Barium chloride
Potassium permanganate
Enamel paints
Fusible enamel
Hides
Sod oils
Steel tubing
Aluminum
Antimony
Paraffin

HAMBURG — Supplement 6*a*
Cement
Ceresin
Stearin
Paraffin
Acids
Coal tar preparations
Earthenware
Chinaware
Glassware
Metals
Essential oils
Fusel oil
Mineral oil
Palm oil
Palm kernel oil
Paints
Paper
Tar
Varnish
Wood pulp
Albumen
Sugar
Antimony
Cantharides
Carmonile
Coriander
Dyewoods
Ergot
Lycopodium
Clay
Coal, etc.
Fertilizer
Fibers
Tin
Glue stock
Wool grease
Gums
Gutta percha
Hides
Rubber
Ivory nuts
Jute and sisal
Mica
Rennet

BAVARIA—Sup. 6*b*
Aluminum powder
Beer
Brass
Bronze
Electric light carbons
Celluloid
Earthenware
Chinaware
Glassware
Gold and silver leaf
Hops
Lava stone
Paints
Paper
Burgundy pitch
Lithographic stones
Tin foil
Glue
Matches
Pumice stone
Gelatine
Manganese oxide
Rags
Steel balls

HAWAII—790
Sugar
Molasses
Hides

BRISTOL, ENGLAND—Supplement 19*j*
Animal charcoal
Ammonium chloride
Bleaching powder
Fuller's earth
Hides
Glue
Iron ore

GREECE—Sup. 7*a*
Olive oil
Soap

LIVERPOOL—Sup. 19*h*
Aluminum
Dried blood
Bones
Carbolic acid
Ammonium sulfate
Sal ammoniac
Bleaching powder
Calcium chloride
Glycerine
Gum tragasol
Soda ash
Sodium cyanide
Sodium silicate
Sodium sulfide
Coal and coke
Copper
Earthenware, etc.
Fertilizer
Fibers
Glassware
Glue
Hides
Crude rubber
Ferromanganese
Tin plate
Oil cake
Cocoanut oil
Palm oil
Palm kernel oil
Soya bean oil
Oleostearin
Paints, etc
Paper stock
Salt
Artificial silk
Tin
Wax
Potassium carbonate
Potassium chlorate
Potassium hydrate
Antimony
Tanning extracts

CANADA—767
Pulp wood

SAXONY—Sup. 6*c*
Beer
Chinaware
Earthenware
Drugs, etc.
Essential oils
Wood pulp
Bone meal
Caustic potash
Colors and inks
Fertilizer
Hides
Oil of roses
Oxalic acid
Peptomangan
Montan wax
Wool grease
Enameled ware
Tungsten powder

BRITISH HONDURAS—Supplement 21*a*
Chicle
Rubber

ONTARIO—Sup. 23*d*
Corundum
Aluminum
Asbestos
Beeswax
Bones
Brass
Carbon
Acetone
Acetic acid
Arsenic
Hydrochloric acid
Nitric acid
Sulfuric acid
Tartaric acid
Wood alcohol
Ammonium sulfate
Aniline dyes
Calcium
Casein
Creosote oil
Cobalt oxide
Fusel oil
Glycerine
Chicle
Gambier
Kauri
Calcium acetate
Menthol
Potassium hydrate
Potassium cyanide
Coal, etc.
Cyanamid
Fibers
Gold and silver
Wool grease
Hides
Rubber
Iron ore
Iron and steel
Manganese ore
Mercury
Mica
Feldspar
Nickel ore and matte
Cottonseed-oil
Oleo oil
Ketone oil
Paper stock
Platinum
Graphite
Diamonds
Silicon
Artificial silk
Marble
Pyrites
Talc
Tan bark
Tin
Wax
Zinc scrap

DEMANDS FOR AMERICAN GOODS (Pp.)

PALERMO, ITALY—870
Coal
Fuel oil

CYPRUS—871
Glass
Chinaware

TURKEY—804
Cement

ENGLAND—622
Glass:
Plate
Sheet
Flint
Bottle

CANARY ISLANDS—669
Fertilizer

IRELAND—710
Animal fats
Glue

COLUMBIA—744
Iron
Steel

CHINA—758
Paints

NOTE—The above items are for May 1 to 21 inclusive; the rest of the May reports will be covered next month

The manufacture of "asbestos slates" for roofing, has been started in Japan. (P. 813.)

The French Government has created a special bureau in the Department of Commerce to foster the production and supply of chemical and pharmaceutical products. Supplement 5*b*. (P. 15.)

Special Supplements published during the month follow. In general they contain discussions of the manufacturing and trade conditions and in most cases, import and export statistics.

Austria-Hungary—1*a*. France—5*b*. Germany — Hamburg 6*a*; Bavaria—6*b*; Saxony—6*c*. Greece — Patras — 7*a*. United Kingdom — Liverpool — 19*h*; Bristol—19*i*. British Honduras— 21*a*. Canada — Ontario — 23*d*. Canada—23*e* Cuba—25*a*. Mexico — San Luis Potosi—32*a*. Panama—35*a*. Brazil—40*a*. British Guiana—44*a* China — Hongkong — 52*a*. Australia—60*b*.

## DEPARTMENT OF AGRICULTURE

**Soils of Massachusetts and Connecticut with Especial References to Apples and Peaches.** HENRY J. WILDER. Department Bulletin 140. Contributions from the Bureau of Soils. 73 pp. Paper, 25 cents. This report is largely of agricultural interest as the character of the soil is discussed only in its relation to fruit production.

**Tests of Wood Preservatives.** HOWARD F. WEISS AND C. H. TEESDALE. Department Bulletin 145. Contributions from the Forest Service. 20 pp. Paper, 10 cents. The following summary of the investigation indicates the scope of the report.

"The practical value of a preservative depends very largely upon the conditions under which it is used, and investigations to determine its value must necessarily be broad. The following points were considered in the tests:

"1—The important chemical and physical properties of the preservative.

"2—The effect of the preservative on the strength of the wood treated with it.

"3—The ability of the preservative to penetrate and diffuse through wood.

"4—The permanency of the preservative after its injection into wood. This involves a study of its volatility and leachability.

"5—The combustibility of wood treated with the preservatives.

"6—The toxic efficiency of the preservative in preventing the growth of wood-destroying fungi.

"7—The corrosive action of the preservative on steel.

"8—The effect of the preservative on paint applied to the wood subsequent to treatment.

No systematic tests were made on the effect of the preservative as an electrolytic or in contaminating drinking water, nor were any tests made which relate to a special or limited use."

**Soil Erosion in the South.** R. O. E. DAVIS. Department Bulletin 180. Contribution from the Bureau of Soils. 23 pp. Paper, 10 cents. Only the mechanical effects and the mechanical means of prevention are discussed. The chemical influences on the soil due to erosion are not described.

**Morphology of the Barley Grain with Reference to Its Enzym-Secreting Areas.** ALBERT MANN AND H. V. HARLAN. Department Bulletin 183. Contribution from the Bureau of Plant Industry. 32 pp. Paper, 15 cents. The discussion given in this paper is of particular interest as indicating the desirable and undesirable properties of barley in connection with malting. There is included a discussion as to the source of diastatic ferments and as to the location of diastase secretion. This Bulletin is of interest to agronomists, brewery chemists, maltsters, and others.

**Loss in Tonnage of Sugar Beets by Drying.** HARRY B. SHAW. Department Bulletin 199. Contribution from the Bureau of Plant Industry. 12 pp. Paper, 5 cents. The conditions which affect the moisture content in sugar beets as well as the sugar losses which occur during storage of beets are discussed. A number of suggestions are given as to the relation of the shrinkage to the price of the beets and methods for adjusting prices on the basis of sugar making value.

**Field Studies of the Crown-Gall of Sugar Beets.** C. O. TOWNSEND. Department Bulletin 203. Contributions from the Bureau of Plant Industry. 8 pp. Paper, 5 cents. This paper is summarized as follows:

1—There are at least two distinct types of sugar-beet galls.

2—The crown-gall of sugar beets is caused by a bacterium or a number of closely related bacteria.

3—Sugar-beet galls appear to have an injurious effect upon the quality of the roots.

4—The galls themselves are low in purity and therefore detrimental in the milling processes.

5—Sugar-beet galls sometimes cause the beet roots to decay, but, so far as general field observations can determine, they do not appear otherwise to affect the tonnage.

6—This disease may be held in check by a proper system of crop rotation with grain-producing plants.

**Weeds Used in Medicine.** ALICE HENKEL. Farmers' Bulletin 188. Contribution from the Bureau of Plant Industry. 45 pp. "Some of the plants coming within this class are in many States at present subject to antiweed laws, and farmers are required to take measures toward their extermination. It seems, therefore, desirable to make these pests sources of profit where possible. In many cases, when weeds have been dug, the work of handling and curing them is not excessive and can readily be done by women and children.

"The prices paid for crude drugs from these sources are not great and would rarely tempt anyone to pursue this line of work as a business. Yet, if in ridding the farm of weeds and thus raising the value of the land the farmer can at the same time make these pests the source of a small income instead of a dead loss, something is gained. In order to help the farmer to obtain the best possible prices for such products, instructions for collecting and preparing crude drugs derived from weeds are here briefly given."

This subject is of more than usual interest under the present conditions when the drug market is so largely affected by the failure of certain European supplies.

**Leguminous Crops for Green Manuring.** C. V. PIPER. Farmers' Bulletin 278. Contribution from the Bureau of Plant Industry. 27 pp. Largely of agricultural interest.

**Cottonseed-Meal for Feeding Beef Cattle.** W. F. WARD. Farmers' Bulletin 655. Contribution from the Bureau of Animal Industry. 8 pp. The conditions under which cottonseed-meal is a valuable and economic feedingstuff are discussed, but the bulletin gives little of direct chemical interest except indicating the proper conditions for the utilization of this product of the cottonseed industry.

**Manufacture and Use of Unfermented Grape Juice.** GEORGE C. HUSMANN. Farmers' Bulletin 644. Contribution from the Bureau of Plant Industry. 16 pp. This bulletin gives instructions for making grape juice for home use as well as the directions for commercial operation.

**Effect of Fertilizers on the Physical Properties of Hawaiian Soils.** WILLIAM MCGEORGE. Bulletin 38 of the Hawaii Agricultural Experiment Station. 31 pp. Paper, 5 cents.

**Notes on Hydrocyanic-Acid Content of Sorghum.** J. J. WILLAMAN AND R. M. WEST. Journal of Agricultural Research, 4 (1915), 170–85; also available as a separate. A contribution from the Agricultural Experiment Station of the University of Minnesota.

**Effect of Soil Moisture on Changes in Surface Tension of Soil Solution Brought About by Addition of Soluble Salts.** P. E. KARRAKER Journal of Agricultural Research, 4 (1915), 186–92. A Preliminary Report.

**Manual of Procedure for Guidance of State Health, Food, and Drug Officials.** Compiled by J. S. ABBOTT. 12 pp. Obtainable only through the Bureau of Chemistry

**Rules and Regulations Governing Importation of Cotton Lint into the United States.** Adopted by the Federal Horticultural Board. Dated May 14, 1915. 10 pp. Paper, 5 cents

# BOOK REVIEWS

**Chemistry of Familiar Things.** By SAMUEL SCHMUCKER SADTLER, S.B, xiii + 320 pp. Illustrations: 23 plates and 6 figures. Philadelphia and London: J. B. Lippincott Company, 1915. Price, $1.75.

A number of books have been written for the instruction of the reader possessing little or no chemical knowledge. Some of these "demochemical" works have neither simplicity of style nor clearness of expression; in others the authors failed to exercise ingenuity in the selection of subject material, in the elimination of irrelevant matter, or in the presentation of the essentials, while still others are not free from incautious and extravagant statements, likely to create false impressions. To serve happily their intended purpose, such treatises should be entertaining in exposition; the chapters thereof should be consecutive and clear, and the points emphasized therein should be the important ones. These criteria of excellence are very exacting indeed, which accounts for both the number of popular works on chemistry which have been prepared in the endeavor to meet the requirements of the "intelligent" lay-reader and the poor reception accorded so many of these. The great difficulty has been to give a presentment of facts garbed in an interestingly attractive style, since it is quite simple, owing to the availability of the literature of chemistry, for one experienced in teaching the science and possessing mature judgment, to select suitable material; and the writings of few authors, and among these the three books of the late Dr. Robert Kennedy Duncan merit first mention, are touched with a certain largeness and attraction of form and are yet without perissology.

The twenty-two chapters of Sadtler's book deal with many diverse subjects (historical development of chemistry; the periodic system; light; heat; combustion and insulation; air, oxidation and ventilation; water; alkalies and salts; metals; gold and silver; the earth's evolution; soil and its conservation; food elements and food classes; individual foods; animal feeding; fermentation; chemistry of the body; soaps, solvents, and paints; paper and textiles; leather and rubber; silicious substances and glass; and definitions) and contain a fund of carefully selected information; but they are merely wholesome without being either artistic or adapted to arouse the reader's interest. In other words, the book will serve a useful purpose if it is read, for while the author is not literose, his composition is one of the most comprehensive popular expositions of every-day practical chemistry which has been brought to the reviewer's attention, and accuracy prevails throughout.

RAYMOND F. BACON

**Methods in Metallurgical Analysis.** By CHARLES H. WHITE. D. Van Nostrand Co. Price, $2.50 net.

Professor White has written a book that is very good of its kind, but of a kind of which we already have more than enough. Why will not some of our colleges teach analytical chemistry instead of schemes of analysis? To be sure it would involve more work for the instructors, but they are not in the least afraid of work or at all unwilling to undertake it if it will improve results. The majority of the analysts turned out yearly know only definite schemes, but are utterly lost if asked to check the accuracy of a method or to devise a new one. Routine analyses in most works are made not by chemists but by boys trained for the particular purpose and working under the direction of a chemist. To obtain suitable chemists for this purpose is very difficult, largely owing to the methods of instruction in vogue.

The book starts with a clear and very condensed statement of the definitions and descriptions of the principal operations This is followed by detailed directions for the analysis of the common metallurgical materials and products. The methods are clearly described and the illustrations are adequate. The plan of the work involves a great deal of repetition, but there is no more of this than is unavoidable under the circumstances. The methods described have the sanction of practice, nearly all being in common use, though in some cases well-known sources of error are not pointed out. For instance, the great danger of the contamination of precipitates of the hydroxides of iron and alumina with silica derived from the ammonia, or the certainty of high results in the volumetric determination of zinc when the ores contain cadmium. Where several alternative methods are given, no criticism of them is made, and their relative accuracy and suitability for different purposes is not pointed out.

Prof. White rightly insists on the necessity of testing weights and volumetric apparatus—a matter that is frequently neglected. He also repeatedly points out the necessity of standardizing volumetric solutions under identically the same conditions in all respects as are present when the unknown solution is titrated.

The book, like all of its kind, will be useful in many cases as it brings together a great deal of information now scattered through many journals and books.

GEO. C. STONE

**Leavening Agents.** By RICHARD N. HART, B.S. Published by the Chemical Publishing Company, Easton, Pa. 90 pp. 13 illustrations. Price, $1.00.

This book, in which yeast and baking powders are briefly discussed from the manufacturer's point of view, will be found helpful to any one seeking information as to the method of yeast manufacture. The work could to advantage be enlarged on the biochemical side so that the chemist having a yeast problem to investigate might be able to obtain suggestions as to how to proceed.

A little over a page is given to "Tests for Yeast," the Metzler test being proposed. This test is misleading, particularly if a flour is used having low fermenting value, or one encouraging abnormal fermentation.

A concise description of baking powders is given and the author does not hesitate to express his views on the subject. "In a baking powder it is not a question of whether alum is harmful, or phosphate and cream of tartar wholesome, but of whether their residues in bread are deleterious,"....."there is no record as yet of injurious results from using any baking powder well made by any of the standard formulae." If a writer had expressed such an opinoin a few years ago, it would have invited much controversy and some would have condemned him to the "scrap heap." Happily, however, the time has come when manufacturing problems relating to foods can be looked at from a rational view-point. Some of the subject matter in the book could have been more judiciously selected, as on page 60 the test referred to is in reality a test of recipe rather than a test of flours.

In the chapter on milk powder only meager mention is made of skim milk powder and no analyses are given. Many bakers use skim milk powder, supplying the fat in forms cheaper than the butter fat in the more expensive whole milk powders.

In the discussion of "Salt-Rising Fermentation" it is quite apparent why the culture methods have come into use with the manufacture of cleaner flours which are less likely to contain as a natural constituent the gas generating ferment.

The book is well printed on good paper and is quite free from typographical errors. It is to be commended and the author encouraged to get out a larger and more complete edition at some future time

HARRY SNYDER

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Analysis: Mikrochemische Analyse.** By P. D. C. KLEY. 504 pp. Price, $6.00. Leopold Voss, Leipzig.

**Cement: Zement und Beton im Tiefbau.** By H. GAMANN. 8vo 299 pp. Price, $2.00. Tonindustrie-Zeitung, Berlin.

**Colloids: Der Kolloide Zustand der Materie.** By LEONARDO CASSUTO. 8vo. Price, $2.00. Theodor Steinkopff, Leipzig.

**Compressed Air: Die Verwendung von Pressluft im Bergbaubetriebe.** By A. E. LIEVEHR. 8vo. 258 pp. Price, $1.25. C. Steinert, Weimar.

**Concrete: Reinforced Concrete.** By A. A. SCOTT. 8vo. 186 pp. Price, $1.00. Scott, Greenwood, London.

**Dynamometers:** By F. J. JERVIS-SMITH. 8vo. 267 pp. Price, $3.50. D. Van Nostrand, New York.

**Electricity: Mechanics of Electricity.** By F. J. B. CORDIERO. 8vo. Price, $1.25. E. and F. N. Spon, London.

**Ferromanganese: Ferromangan als Desoxydationsmittel im festen und fluessigen Zustand und das Ferromanganschmelzen.** By W. RODENHAUSER. 8vo. 127 pp. Price, $1.75. O. Leiner, Leipzig

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**Physical Chemistry: Practical Physical Chemistry.** By J. B. FIRTH. 8vo. 190 pp. Price, $0.75. Methuen and Co., London.

**Soil Analysis: Ueber die Bedeutung und die Methode der chemischen Bodenanalyse mit starker heisser Salzsaeure.** By D. J. HISSINK. 8vo. Price, $0.50. Verlag fuer Fachliteratur, Berlin.

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## RECENT JOURNAL ARTICLES

**Alcohol: Estimation of Methyl Alcohol in Presence of Ethyl Alcohol.** By G. C. JONES. *The Analyst*, Vol. 40 (1915), No. 470, pp. 218–222.

**Blast Furnace: Progress in Blast Furnace Practice.** By A. E. MACCOUN. *Iron Trade Review*, Vol. 56 (1915), No. 22, pp. 1129–1130

**Blast Furnace Plant Auxiliaries.** By J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 6, pp. 373–378

**Blowpipe Analysis: Quantitative Blowpipe Analysis in the Field.** By GEORGE DELIUS. *Mining and Scientific Press*, Vol. 110 (1915), No. 19, pp. 725–726.

**Boiler Plate: Tests on the Diagonal Strength of Boiler Plate.** By G. W. F. MACDONALD. *Power*, Vol. 41 (1915), No. 23, pp. 779–780

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**Colloids: The Action of Certain Colloids on Ions during Electrolysis.** By A. MUTSCHELLER. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 6, pp. 353–357.

**Copper: Physikalisch-Chemische Studien am Kupfer.** By ERNST COHEN AND W. D. HELDERMAN. *Journal fuer Physikalische Chemie*, Vol. 89 (1915), No. 5, pp. 638–639.

**Corrosion: Tests for Corrosion Resistance.** By DANIEL M. BUCK. *Iron Trade Review*, Vol. 56 (1915), No. 22, p. 1124.

**Corrosion: Recent Progress in Corrosion Resistance.** By DANIEL M. BUCK. *Steel and Iron*, Vol. 19 (1915), No. 18, pp. 582–586.

**Cyanide Process.** By FRANK S. WASHBURN. *The Chemical Engineer*, Vol. 21 (1915), No. 5, pp. 177–184.

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**Cyaniding Practice of Churchill Milling Co., Wonder, Nev.** By E. E CARPENTER. *Bulletin of the American Institute of Mining Engineers*, No. 102 (1915), pp. 1317–1332.

**Electric Lamp Industry.** G. F. MORRISON. *General Electric Review*, Vol. 18 (1915), No. 6, pp. 497–503.

**Electric Power Industry.** DAVID B. RUSHMORE. *General Electric Review*, Vol. 18 (1915), No. 6, pp. 427–439.

**Enamelling: Anlage und Betrieb eines Moderne Emaillierwerkes.** *Die Glashuette*, Vol. 45 (1915), No. 11/12, pp. 71–72.

**Fats: Ueber die Bestandteile tierischer Fette.** By J. KLIMONT AND K. MAYER. *Monatshefte fuer Chemie*, Vol. 36 (1915), No. 4, pp. 281–287.

**Fatty Acids: Ueber die Verbindungen des Calciums und Magnesiums mit hoeheren Fettsaeuren.** By JULIUS ZINK AND RICHARD LIERE. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 36, pp. 229–232.

**Fertilizer: A Municipal Fertilizer Plant at Los Angeles.** By BURT A. HEINLY. *Engineering News*, Vol. 73 (1915), No. 22, pp. 1063–1064.

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**Gas Reactions: Zwei Gasreaktionen.** By MAX TRAUTZ. *Zeitschrift fuer Elektrochemie*, Vol. 21 (1915), No. 7/8, pp. 118–122.

**Heat: The Difficulty of Measuring Heat.** By A. H. BARKER AND F. C. BRENDAL. *Heating and Ventilating Magazine*, Vol. 12 (1915), No. 5, pp. 21–24.

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**Mineral Acids: Bericht ueber die Industrie der Mineralsaeure im Jahre 1914.** By K. RAUSCH. *Chemiker-Zeitung*, Vol. 39 (1915), No. 54, pp. 342–343.

**Palladium: Zur Trennung von Palladium und Zinn durch elektrolytische Abscheidung des Palladiums.** By A. GUTBIER. *Zeitschrift fuer analytische Chemie*, Vol. 54 (1915), No. 4, pp. 208–213.

**Paper: Practical Aspects of Paper Testing.** *Paper*, Vol. 16 (1915), No. 11, pp. 17–18.

**Rubber: Recent Advances in the Analysis and Evaluation of Rubber and Rubber Goods.** By PHILIP SCHNIDROWITZ *The Analyst*, Vol. 40 (1915), No. 470, pp. 223–233.

**Rust Removal by Chemical Reagents.** By J. N. FRIEND AND C. W. MARSHALL. *Iron Trade Review*, Vol. 56 (1915), No. 22, pp. 1023–1024

**Selenium: Ueber die Gewichtsanalytische Bestimmung des Selens.** By A. GUTBIER AND F. ENGEROFF. *Zeitschrift fuer analytische Chemie*, Vol. 54 (1915), No. 4, pp. 193–205.

**Steam: Commercial Value of Exhaust Steam.** By A. J. JOHNSTON, JR. *Engineering Magazine*, Vol. 49 (1915), No. 3, pp. 327–335.

**Sulfur Gas Reclaiming System.** By C. B. THORNE. *Paper*, Vol. 16 (1915), No. 10, pp. 11–13.

**Thermodynamics of Saturated Vapor.** By J. E. SIEBEL. *Ice and Refrigeration*, Vol. 48 (1915), No. 6, pp. 363–366.

**Zinc: Recent Improvements in the Metallurgy of Zinc.** *Engineering and Mining Journal*, Vol. 99 (1915), No. 21, p. 896.

**Zinc Ore: Electromagnetic Zinc-ore Treatment.** By L. E. IVES. *Engineering and Mining Journal*, Vol. 99 (1915), No. 23, pp. 979–980.

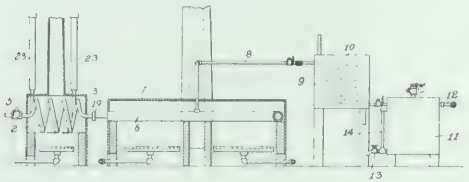
# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. Parker

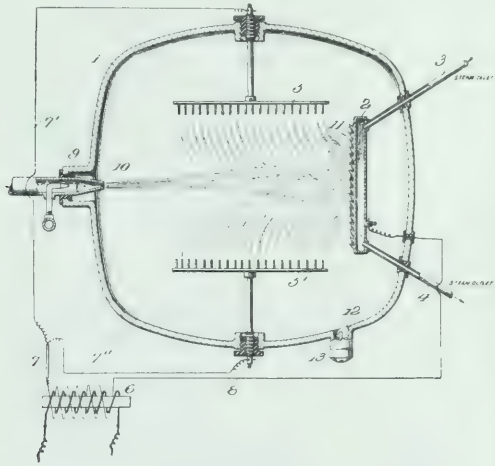
Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Treating Oil. J. A. Dubbs, Jan. 5, 1915. U. S. Pat. 1,123,502.** Finely divided particles of water are removed from emulsified oil by subjecting a body of such oil to a pressure materially above



atmospheric pressure, such pressure being produced by heating the oil to a temperature above that required for boiling water at such pressure and removing the steam and oily vapors generated during such treatment.

**Hydrogenating Fats, Oils and Waxes. T. B. Walker, Jan. 5, 1915. U. S. Pat. 1,123,962.** Hydrogenation is effected by sub-



jecting the material under treatment, in a comminuted condition, to the action of hydrogen gas under superatmospheric pressure and a catalytic body, in the presence of heat and an electric discharge.

**Magnesium Perborate. W. Weber, Jan. 5, 1915. U. S. Pat. 1,124,081.** A mixture of magnesium sulfate and sodium perborate are melted, with constant stirring.

**Electrolytically Refining Tin. G. Michaud and E. Delasson, Jan. 12, 1915. U. S. Pat. 1,124,315.** An electric current is passed from an anode of impure tin to a cathode through an electrolyte of high conductivity composed of protochlorid of tin, 100 kg.; sulfuric acid, 10 kg.; magnesium chlorid, 1 kg.; boric acid, 1 kg.; and the requisite quantity of distilled water to bring the solution up to 20° Baumé

Light Hydrocarbons, etc. **P. Sabatier and A. Mailhe, Jan. 12, 1915. U. S. Pat. 1,124,333.** Crude petroleum, heavy petroleum oils, etc., are converted into hydrocarbons distilling below 300° F. by passing their vapors over catalyzing metals in a state of division in contact with metals or alloys of metals of the nickel series maintained at a temperature varying from 300° F. to dark red and to bright red by the passage of an electric current.

**Effecting Dissociative Reactions upon Carbon Compounds. W. O. Snelling, Jan. 12, 1915. U. S. Pat. 1,124,347.** The process comprises heating a carbon compound capable of undergoing a reversible reaction in which hydrogen is one of the products and separating and withdrawing the hydrogen in an uncombined state during the progress of the reaction.

**Saturating Unsaturated Acids and Their Glycerides by Combining Them with Hydrogen. E. Utescher, Jan. 12, 1915. U. S. Pat. 1,124,560.** Hydrogenation of oil is effected by subjecting the oil to the action of hydrogen, a catalyzer and silent electrical discharges.

**Dry Fat and Oil Compounds. M. Hamburg, Jan. 12, 1915. U. S. Pat. 1,124,611.** The composition is produced by emulsifying not less than 25 parts of materials having the physical properties of oil with approximately 75 parts of highly concentrated diastatic starch conversion products without addition of a foreign emulsifying agent, and drying and granulating the resultant mixture.

**Explosive. C. A. Woodbury, Jan. 12, 1915. U. S. Pat. 1,124,679.** This is an explosive having a relatively low velocity of detonation comprising nitrate of ammonia, nitroglycerin and an absorbent, the nitrate of ammonia being in the form of relatively large globular grains.

**Extracting Potassium from Flue-Dust. S. Peacock, Jan. 12, 1915. U. S. Pat. 1,124,798.** Flue-dust containing potassium salts is treated with a solution of non-calcium phosphate to react with potassium silicates present and also with an acid to react with any potassium salts which may be mechanically held by such silicates.

**Reclaiming Rubber. H. W. Kugler, Jan. 12, 1915. U. S. Pat. 1,124,920.** Vulcanized rubber is simultaneously treated, under suitable conditions of temperature and pressure, with a carbo-cyclic amido compound, such as anilin, toluidin, xylidin, or the like and a substance capable of combining with or absorbing sulfur, such as caustic alkali solution.

**Making Arsenic and Arsenical Compounds. G. P. Fuller, Jan. 19, 1915. U. S. Pat. 1,125,086.** Arsenious acid is suspended in an aqueous solution of an alkali metal halid and subjected to electrolysis. The product of the reaction is filtered and the filtrate treated to recover its arsenical compounds.

Copper. **W. M. Page and W. Tassin, Jan. 19, 1915. U. S. Pat. 1,125,164.** Copper in a highly heated molten condition is treated with iron in excess of an amount sufficient to react with the oxygen and oxids present; the excess of iron is burned out under conditions precluding re-oxidation of the copper.

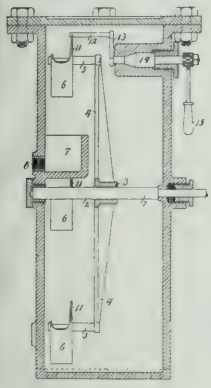
**Casein from Buttermilk. R. Eilersen, Jan. 26, 1915. U. S. Pat. 1,126,429.** Buttermilk is heated to from 40° to 65° C. to separate the whey and the curd. The curd is washed with cold water adding sufficient cold water to replace the separated whey. The casein is dissolved in an alkaline bicarbonate, separated and precipitated by a mineral acid, the precipitate being washed with cold water.

## BRITISH PATENTS

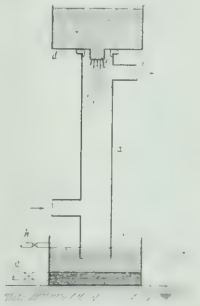
By D. Geddes Anderson
Chemical Engineer and Patent Chemist, Glasgow, Scotland

The following abstracts are taken direct from the patent specifications as soon as these are published by the British patent office. The date given at the end of the abstract is the date of acceptance.

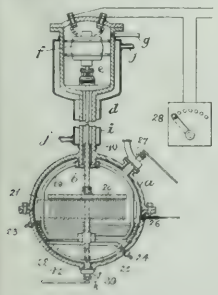
**Apparatus for Carburetting Air. H. A. Taylor, and The British and Colonial Lighting Co., Ltd., Application, Nov. 5,1913. Brit. Pat. 25,271.** This invention relates to apparatus of the type wherein travelling pivoted buckets pick up hydrocarbon and deliver it to a carburetter. The primary feature is the adjustable bucket tipping obstruction. In the sectional view shown, the bucket 6 with lug 11 travels, filled with hydrocarbon, to the top of chamber and is there tipped by adjustable post 12 into receiver 7, from which the hydrocarbon passes to the carburetting chamber through opening 8.—Accepted Feb. 25, 1915.



**Purification of Gases for Heating or Power Purposes. E. Howl and F. Perry, Feb. 26, 1914. Brit. Pat. 5,051.** Tar and tar fog are separated from industrial gases by subjecting the gases to a spray of electro-statically charged water. "*a*" is a metal tower with gas inlet "*e*," and gas outlet "*f*." "*b*" is a liquid sump for the collection of tarry deposits. The water in the receptacle "*d*" is electrified negatively and issues through suitable jets "*c*."—Feb. 26, 1915.

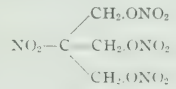


**Recovery of Sulfuric Acid from Waste Pickle. E. Howl and F. Perry, March 7, 1914. Brit. Pat. 5,830.** The acid liquor from operations in which iron and steel have been treated with sulfuric acid is run into lead-lined tanks and evaporated to a concentration of 75 per cent acid. At this concentration the ferrous sulfate in the liquor is precipitated in an anhydrous form and separated with a centrifugal separator.—March 4, 1915.



**Mixing Devices for the Hydrogenization of Oils. G. Calvert, March 9, 1914. Brit. Pat. 5,967.** Oil and catalyst are fed in through 27, and hydrogen through "*g*". The co-mingling device in the container "*a*" comprises a propeller, 39, at the base, and rotary agitators 20 in the form of a comb; 29 is a yoke to support bearing 42 for shaft "*b*."—Feb. 25, 1915.

**A New Explosive. F. E. Matthews, March 13, 1914. Brit. Pat. 6,447.** This invention relates to a new explosive substance, nitroisobutyl glycerol trinitrate, having the chemical formula



For its preparation solid nitroisobutyl glycerol is brought into contact with "mixed acids" (equal vols. concentrated sulfuric and strong nitric acids) at a low temperature. The new product separates on the surface as a yellow oil. It is insoluble in water and has great stability towards heat.—March 11, 1915.

**Metallic Paint. The British Patent Surbrite Co. Ltd., and E. G. Meadway, March 20, 1914. Brit. Pat. 7,087.** Metallic powder, 2 lbs.; gum mastic, 320 grams; India rubber dissolved in naphtha, 2 fluid ounces; celluloid dissolved in amyl acetate, 113 fluid ounces; amyl acetate, 45 fluid ounces. The gum mastic is first dissolved in the rubber solution and this mixture added to the other ingredients.—March 18, 1915.

**Accelerating the Vulcanization of Rubber. S. J. Peachey, March 24, 1914. Brit. Pat. 7,370.** Vulcanization is carried out in the presence of a compound resulting from the interaction of an amine of the cyclic (aromatic or benzenoid) series, with an aldehyde of the aliphatic or of the cyclic series; or of an aldehyde of the cyclic series with ammonia. Two examples of such compounds are formaldehyde aniline, and benzylidene aniline.—Feb. 25, 1915.

**Utilizing Waste Rubber. H. Gare, April 23, 1914. Brit. Pat. 10,030.** Old or waste vulcanized India rubber is ground with sufficient water to bring the mass to a pasty condition and this semi-fluid mass is then molded under a pressure varying from 10 to 15 tons per pound of rubber used.—March 11, 1915.

**Accelerating Vulcanization of Rubber. S. J. Peachey, May 2, 1914. Brit. Pat. 10,833.** In this process the vulcanization is carried out in the presence of a small quantity of paranitrosodiphenylamine, or of the reduction product of paranitrosodimethylaniline, namely dimethyl-paraphenylenediamine.—March 4, 1915.

**Cement. J. F. Goddard, June 3, 1914. Brit. Pat. 13,542.** Relates to a process for making Portland cement waterproof. Plaster of Paris is allowed to set with tannic acid (1 acid to 5 plaster) and is then ground to a powder and added to the cement clinker during the grinding process. About 0.8 per cent by weight of this treated plaster is added to the clinker.—March 11, 1915.

**Insecticides. Wilkie and Soames, Ltd., and W. F. Soames, July 1, 1914. Brit. Pat. 15,765.** Material consists of powdered, dried soap and sulfur. It is made up with water and sprayed, or else used in powdered form.—March 4, 1915.

**Antiseptic and Germicides. G. T. Morgan and G. E. Scharff, Aug. 31, 1914. Brit. Pat. 19,253.** Peat tar is dried at 100° C., and distilled in suitable retorts. Three fractions are made (1) 100° C. to 200° C., (2) 200° C. to 250° C.; (3) 250° C. to 360° C. This separation leads to the segregation of the cresols in the least germicidal fraction boiling at 100° C. to 200° C. The distillates are extracted with a 10 per cent caustic soda solution and the acidic oils then set free by neutralizing with sulfuric acid.—March 11, 1915.

**Improved Absorbent for Carbon Dioxide in Breathing Apparatus. E. J. Bevan and R. H. Davis, Nov. 18, 1914. Brit. Pat. 22,719.** The absorption chamber of breathing apparatus, such as is used in mine rescue work, is charged with a material made by grinding cellulose with a strong solution of caustic soda; 3 lbs. of caustic soda liquor (1 of caustic to 2 of water) are ground with 2 lbs. of ground wood pulp. The resulting material resembles bread crumbs in form, and does not deliquesce.—March 11, 1915.

# MARKET REPORT—JUNE, 1915

AVERAGE WHOLESALE PRICES IN THE NEW YORK MARKET FOR LARGE QUANTITIES OF STANDARD CHEMICALS

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lime, gray | 100 Lbs. | 3.50 | @ | 3.55 |
| Alum, lump | 100 Lbs. | 2.50 | @ | 3.00 |
| Aluminum Sulfate, high-grade | 100 Lbs. | 1.25 | @ | 1.50 |
| Ammonium Carbonate, domestic | Lb. | 8 1/2 | @ | 9 |
| Ammonium Chloride, gray | Lb. | 6 1/4 | @ | 6 1/2 |
| Aqua Ammonium, 16°, drums | Lb. | [illegible] | @ | 2 1/2 |
| Arsenic, white | Lb. | [illegible] | | |
| Barium Chloride | Ton | 80.00 | @ | 90.00 |
| Barium Nitrate | Lb. | 15 | | |
| Barytes, prime white, foreign | Ton | 19.00 | @ | 23.00 |
| Bleaching Powder, 35 per cent | 100 Lbs. | 1.40 | @ | 1.50 |
| Blue Vitriol | Lb. | 7 [illegible] | | |
| Borax, crystals, in bags | Lb. | 4 [illegible] | @ | 4 1/2 |
| Boric Acid, powdered crystals | Lb. | 7 1/2 | @ | 7 3/4 |
| Brimstone, crude, domestic | Long Ton | 22.00 | @ | 22.50 |
| Bromine, technical, bulk | Lb. | 85 | @ | 87 |
| Calcium Chloride, lump | Ton | — | @ | 11.78 |
| Calcium Chloride, granulated | Ton | — | @ | 14.78 |
| Caustic Soda, 60 per cent domestic, in drums | 100 Lbs. | 2.35 | | |
| Caustic Soda, 70 @ 76 per cent | 100 Lbs. | 2.25 | | |
| Caustic Soda, powdered or granulated, 76% | 100 Lbs. | 3.00 | | |
| Chalk, light precipitated | Lb. | 4 1/2 | @ | 4 3/4 |
| China Clay, imported | Ton | 30.00 | @ | 33.00 |
| Feldspar | Ton | 8.00 | @ | 12.00 |
| Fuller's Earth, foreign, powdered | 100 Lbs. | 80 | @ | 85 |
| Glauber's Salt, in bbls. | 100 Lbs. | 60 | | |
| Green Vitriol, bulk | 100 Lbs. | 90 | @ | 1.00 |
| Hydrochloric Acid, commercial, 18° | 100 Lbs. | 1.50 | @ | 1.75 |
| Hydrochloric Acid, C. P., conc., 22° | 100 Lbs. | 2.00 | @ | 2.25 |
| Iodine, resublimed | Lb. | 3.75 | @ | 3.80 |
| Lead Acetate, white crystals | Lb. | 11 5/8 | @ | 11 7/8 |
| Lead Nitrate | Lb. | 11 | @ | 11 1/2 |
| Litharge, American | Lb. | 8 1/4 | | |
| Lithium Carbonate | Lb. | 1.00 | @ | 1.10 |
| Magnesium Carbonate | Lb. | 5 1/2 | @ | 6 |
| Magnesite, "Calcined" | Ton | 25.00 | @ | 30.00 |
| Nitric Acid, 68 per cent, sp. gr. 1.42 | Lb. | 5 7/8 | @ | 6 1/4 |
| Nitric Acid, fuming | Lb. | 7 7/8 | @ | 8 1/4 |
| Phosphoric Acid, sp. gr. 1.750 | Lb. | 28 | @ | 31 |
| Phosphorus | Lb. | 35 | @ | 90 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate, casks | Lb. | 20 1/2 | | |
| Potassium Bromide | Lb. | 1.10 | @ | 1.11 |
| Potassium Carbonate, calcined, 80 @ 85% | 100 Lbs. | 20 | | |
| Potassium Chlorate, crystals, spot | Lb. | 34 | | |
| Potassium Cyanide, bulk, 98–99 per cent | Lb. | 25 | @ | 29 |
| Potassium Hydroxide | Lb. | 25 | @ | 30 |
| Potassium Iodide, bulk | Lb. | 3.15 | @ | 3.20 |
| Potassium Nitrate, crude | Lb. | 12 | @ | — |
| Potassium Permanganate, bulk | Lb. | 70 | @ | 72 1/2 |
| Quicksilver, flask, 75 lbs. | | 95.00 | @ | 100.00 |
| Red Lead, American | Lb. | 8 1/2 | @ | 8 3/4 |
| Salt Cake, glass makers' | 100 Lbs. | 55 | | |
| Saltpeter, crude | 100 Lbs. | 2.35 | | |
| Silver Nitrate | Oz. | 31 1/2 | @ | 33 |
| Soapstone in bags, $Na_2O$ | Ton | 10.00 | @ | 12.00 |
| Soda Ash, 48 per cent. $Na_2O$ | 100 Lbs. | 67 1/2 | @ | 72 1/2 |
| Sodium Acetate | Lb. | 4 | @ | 4 1/2 |
| Sodium Bicarbonate, domestic | 100 Lbs. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate, English | Lb. | 3 1/2 | @ | 3 3/4 |
| Sodium Bichromate | Lb. | 10 1/2 | | |
| Sodium Carbonate, dry | 100 Lbs. | 1.10 | @ | |
| Sodium Chlorate | Lb. | 15 | @ | 17 |
| Sodium Hydroxide, 60 per cent | 100 Lbs. | 2.25 | | |
| Sodium Hyposulfite | 100 Lbs. | 1.80 | @ | 2.00 |
| Sodium Nitrate, 95 per cent, spot | 100 Lbs. | 2.35 | | |
| Sodium Silicate, liquid | 100 Lbs. | 85 | @ | 1.20 |
| Sodium Sulfide, 30%, crystals, in bbls. | Lb. | 1 3/4 | @ | 2 1/4 |
| Sodium Sulfite, crystals | Lb. | 2 1/2 | @ | 2 5/8 |
| Strontium Nitrate | Lb. | 17 1/2 | @ | 18 |
| Sulfur, flowers, sublimed | 100 Lbs. | 2.20 | @ | 2.60 |
| Sulfur, roll | 100 Lbs. | 1.85 | @ | 2.15 |
| Sulfuric Acid, chamber, 60° | 100 Lbs. | 85 | | |
| Sulfuric Acid, conc., sp. gr. 1.842 | 100 Lbs. | 1.25 | @ | 2.00 |
| Sulfuric Acid, oleum (fuming) | 100 Lbs. | 1.50 | @ | 2.00 |
| Talc, American | Ton | 9.00 | @ | 13.00 |
| Terra Alba, American, No. 1 | 100 Lbs. | 75 | @ | 80 |
| Tin Bichloride, 50° | Lb. | 14 1/4 | @ | 15 |
| Tin Oxide | Lb. | 45 | @ | 47 |
| White Lead, American, dry | Lb. | [illegible] | @ | 7 3/4 |
| Zinc Carbonate | Lb. | 10 | @ | 12 |
| Zinc Chloride, granulated | Lb. | 9 | | |
| Zinc Oxide, American process | Lb. | 15 | @ | 17 |
| Zinc Sulfate | 100 Lbs. | 4 3/4 | | |

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid, C. P., in bbls. | Lb. | 65 | @ | 70 |
| Acetic Acid, 28 per cent, in bbls. | 100 Lbs. | 2.50 | @ | 2.65 |
| Acetic Acid, glacial, 99 1/2%, in carboys | Lb. | 2.50 | @ | 2.75 |
| Acetone, drums | Lb. | 28 | | |
| Alcohol, denatured, 180 proof | Gal. | [illegible] | @ | [illegible] |
| Alcohol, grain, 188 proof | Gal. | 2.54 | @ | [illegible] |
| Alcohol, wood, 95 per cent, refined | Gal. | 45 | @ | 47 |
| Amyl Acetate | Gal. | 2.60 | @ | 2.75 |
| Aniline Oil | Lb. | 1.00 | @ | 1.20 |
| Benzoic Acid, ex-toluol | Lb. | 2.75 | @ | 3.00 |
| Benzol, 90 per cent | Gal. | 90 | @ | [illegible] |
| Camphor, refined in bulk, bbls. | Lb. | 43 | @ | 45 |
| Carbolic Acid, U. S. P., crystals, drums | Lb. | 1.50 | @ | — |
| Carbon Bisulfide | Lb. | 7 1/2 | @ | 8 |
| Carbon Tetrachloride, drums, 100 gals. | Lb. | 16 | @ | 17 |
| Chloroform | Lb. | 30 | @ | 35 |
| Citric Acid, domestic, crystals | Lb. | 55 | @ | 55 1/2 |
| Cresol, U. S. P. | Gal | 1.40 | @ | 1.50 |
| Dextrine, corn (carloads, bags) | 100 Lbs. | 3.10 | @ | 3.20 |
| Dextrine, imported potato | Lb. | 10 | @ | [illegible] |
| Ether, U. S. P., 1900 | Lb. | 15 | @ | 20 |
| Formaldehyde, 40 per cent | Lb. | 8 1/2 | @ | 9 1/2 |
| Glycerine, dynamite, drums included | Lb. | 21 1/2 | @ | 22 |
| Oxalic Acid, in casks | Lb | 23 | @ | 25 |
| Pyrogallic Acid, resublimed bulk | Lb | 1.35 | @ | 1.55 |
| Salicylic Acid | Lb. | 2 | @ | 2 1/2 |
| Starch, cassava | Lb. | 3 1/4 | @ | 4 |
| Starch, corn (carloads, bags) | 100 Lbs. | 2.43 | | |
| Starch, potato | Lb. | 5 1/4 | @ | |
| Starch, rice | Lb. | 7 | @ | 8 |
| Starch, sago | Lb. | 3 3/4 | @ | 4 |
| Starch, wheat | Lb. | 7 | @ | 7 1/2 |
| Tannic Acid, commercial | Lb. | 65 | @ | 66 |
| Tartaric Acid, crystals | Lb. | 48 | @ | 50 |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax, pure, white | Lb. | 42 | @ | 45 |
| Black Mineral Oil, 29 gravity | Gal. | 12 1/2 | @ | 13 |
| Castor Oil, No. 3 | Lb. | 9 3/4 | @ | 10 1/4 |
| Ceresin, yellow | Lb. | 10 | @ | 25 |
| Corn Oil | 100 Lbs. | 6.26 | @ | — |
| Cottonseed Oil, crude, f. o. b. mill | Gal. | 38 | @ | 39 |
| Cottonseed Oil, p. s. y. | Lb. | 6.15 | | |
| Creosote, beechwood | Lb. | 90 | @ | 95 |
| Cylinder Oil, light, filtered | Gal. | 20 | @ | 25 |
| Fusel Oil, crude | Lb. | 2.40 | @ | 2.50 |
| Japan Wax | Lb. | 12 | @ | 12 1/2 |
| Lard Oil, prime winter | Gal. | 88 | @ | 90 |
| Linseed Oil, raw | Gal. | 57 | @ | — |
| Menhaden Oil, crude | Gal. | 37 | @ | — |
| Naphtha, 68 @ 72° | Gal. | — | @ | 12 |
| Neatsfoot Oil, 20° | Gal. | 93 | @ | 94 |
| Paraffine, crude, 120 & 122 m. p. | Lb. | 2 1/2 | @ | 3 |
| Paraffine Oil, high viscosity | Gal. | 22 | @ | 23 |
| Rosin, "F" Grade, 280 lbs. | Bbl. | 3.80 | | |
| Rosin Oil, first run | Gal. | — | @ | 25 |
| Shellac, T. N. | Lb. | 14 | @ | 14 1/2 |
| Spermaceti, cake | Lb. | 25 | | |
| Sperm Oil, bleached winter, 38° | Gal. | 70 | @ | — |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid, double-pressed | Lb. | 12 | @ | 12 1/2 |
| Tallow, acidless | Gal. | 62 | @ | 63 |
| Tar Oil, distilled | Gal. | 30 | @ | 31 |
| Turpentine, spirits of | Gal. | 45 | @ | 45 1/2 |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum, No. 1, ingots | Lb. | 29 | @ | 31 |
| Antimony, Hallets' | Lb. | 44 | @ | 46 |
| Bismuth, New York | Lb. | 3.00 | | |
| Bronze powder | Lb. | 45 | @ | 3.15 |
| Copper, electrolytic | Lb. | 20 | @ | 20 1/4 |
| Copper, lake | Lb. | 20 1/4 | @ | 20 3/4 |
| Lead, N. Y. | 100 Lbs. | 5.75 | | |
| Nickel | Lb. | 42 | @ | 45 |
| Platinum, refined | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | 49 [illegible] | | |
| Tin | 100 Lbs | 40.75 | | |
| Zinc, N. Y. | Lb. | 18 [illegible] | | |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | 100 Lbs. | 3.37 [illegible] | | |
| Blood, dried | Unit | 2.65 | | |
| Bone, 4 1/2 and 50, ground, raw | Ton | 30.00 | | |
| Calcium Cyanamid | Unit of Ammonia | 2.30 | | |
| Calcium Nitrate, Norwegian | 100 Lbs. | — | | |
| Castor Meal | Unit | — | | |
| Fish Scrap, domestic, dried, f. o. b. works | Unit | 2.52 1/2 | & | 10 |
| Kainit, minimum 12.4 per cent $K_2O$, bulk | Ton | 35.00 | | |
| Phosphate, acid, 16 per cent, bulk | Ton | 8.00 | @ | 9.00 |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble, 68 per cent | Ton | 2.25 | | |
| Tennessee, 70–80 per cent | Ton | 5.00 | @ | 5.50 |
| Potassium "muriate," basis 80 per cent | Ton | 200.00 | @ | 216.00 |
| Pyrites, furnace size, imported | Unit | 14 | | |
| Tankage, high grade | Unit | 2.60 | & | 10 |

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# EDITORIALS

## SEATTLE AND THE PUGET SOUND

Attendance at the Seattle meeting of the American Chemical Society means vastly more than the technical fellowship of ordinary meetings. It will be an introduction to the great undeveloped empire of the Pacific Northwest, rich in resources and abounding in latent industrial opportunities. It will be a scenic treat nowhere equalled on the continent—the everchanging vistas will form a never-to-be-forgotten series of scenes which the traveller will ever cherish.

Of foremost importance are the potentialities which arise from rapid development of natural resources. Washington is the "Evergreen State," because its hills and mountains are almost completely enveloped with great forests of fir, cedar, hemlock and spruce. It is true that the lumberman has gone into these forests and cut down large portions of them, but ten million acres are locked up in eleven national reserves and six million acres more are under private ownership. Annually four billion feet of lumber are manufactured in the state and the supply will last for a century more. The chemist will not only be charmed by the richness and sweetness of great forests but he will be interested in studying the great needs of this industry. The waste wood of Washington annually exceeds two and a half million cords, much of which is consumed in the waste wood burners of sawmills and in land-clearing operations. The lumbermen and commercial interests of the region have not been indifferent to the problem of utilization. They have invested over a million dollars in their attempts to utilize this waste and—failed. The most enduring symposium which the chemists can achieve will be one which will point the way to success in this one line of endeavor. The lumbermen are looking for a "Moses" to lead them out of the wilderness.

Other natural resources likewise command the interest and assistance of the chemist. From the waters of Puget Sound and the North Pacific more than a hundred thousand tons of fisheries products are taken each year and an equal quantity of fish offal is produced, of which only twenty per cent is utilized for the manufacture of oil and fertilizer. Floating on the same waters are the great kelps or seaweeds with their well-known potash content; from these can be extracted 750,000 tons of potassium chloride, or nearly twice the quantity annually imported by the United States. At Seattle's back door, in Idaho, are the great phosphate rock deposits in which are found over two billion tons in the areas thus far surveyed. Almost within the city limits begin the Washington coal fields which contain nearly twenty billion tons of coal, o which only four million tons are consumed annually. Of not less importance is the fact that within easy reach of the Puget Sound district lies one-fifth of the possible water power of the United States. Such is the nature of the resources of the Pacific Northwest which are awaiting rational disposal by skilled technical men and to the problems that arise from them the attention of the chemist is directed.

Seattle and the Puget Sound region are worth seeing from the standpoint of that breadth of experience which the technical man is expected to possess. This city of 300,000 population has become metropolitan far beyond its numbers. Located on rugged hills overlooking Elliott Bay, an arm of Puget Sound, it washed a portion of those hills into the sea to make way for extensive sites of commerce and manufacturing. Other portions lent their natural beauty to that of the landscape artist about the homes that crown them or in the network of parks and boulevards which, with commendable foresight, have been constructed by its citizens. Within the shadow of the Olympic mountains, beside the western sea, surrounded by lake and forest, with blossoms and greensward the year round, Seattle invites the reader to come and see her as she is.

Puget Sound has been described as

> "A land-locked sea with harbors deep and wide
> Where all the navies of the world could hide."

Upon its waters the attendants of the Seattle meeting will spend an entire day on a chartered steamer. Those fortunate enough to attend will behold a great inland sea of nearly two thousand square miles with as many lineal miles of sinuous green wooded shore lines encompassing it. Rising gently from the water's edge in many places, little farms of meadows and orchards have replaced the forest débris left by the logger, but frequently too, may be seen patches of timber of virgin growth while further back to the east and west the rugged and snow-clad mountains stand guard. So picturesque are the scenes that it seems almost an intrusion to note that even now sixty-four steamship lines ply in and out of Seattle on these waters, carrying nearly six million tons of shipping per year, valued at over one hundred and fifty million dollars. Here, then, may we expect one of the gateways to be built through which the commerce and trade of the Orient and of Alaska shall pass in ever-increasing volume.

Space does not permit speaking of those romances whereby deserts have been transformed into orchards riotous in their profusion of green leaves, blossoms and fruit, nor of the mineral wealth yet largely locked up in mountain fastnesses. Again and finally it must be urged upon each individual member of the society that if he enjoys great and beautiful scenes of nature, if he is interested in the wise use of diminishing natural resources, if he is eager to inform himself concerning the opening of the last door to the commerce of a new Orient—then he must join the throng that will gather to make the Seattle meeting a great success.

UNIVERSITY OF WASHINGTON
SEATTLE

H. K. BENSON

## FOOD FOR THOUGHT

There is much food for thought, both for our industries and for our educational institutions, in the presidential address recently given before the London Chemical Society, by Dr. William Henry Perkin, on the present position of England in the Organic Chemical Industries.[1]

Dr. Perkin has made a most frank and clear analysis of England's present predicament, has uncovered the unmistakable causes which lead to such a condition of industrial stagnation and has pointed with incisive clearness to the remedial measures which will have to be applied before recovery or substantial growth will ever be possible.

The situation as applied to the organic chemical industries in England is no worse as a result of this war than it is in America and Dr. Perkin's analysis applies with equal force to our undeveloped organic industrial problems, with the important difference that for England the analysis is after the fact—a post mortem—while for us his reasoning and suggestions come in time for guidance. Three points of particular force as applied to American conditions may be selected from Dr. Perkin's address:

(1) "In almost every direction, and to a far greater extent than has been the case in any other country, Germany has recognized the value of the closest possible contact between the industries and the universities. In Germany the majority of the professors and Privatdocenten are in close touch with the large factories, and spend part of their time in solving technical problems which they either devise themselves or which may be submitted to them by the manufacturer. I have it on the authority of several of the best known directors of German works that the atmosphere of the University laboratory is much more suitable for discovery than that of the works, and that, as a fact, many of the most valuable discoveries which subsequently proved to be of the highest technical importance have been made in university laboratories and transfe red to the works. Close association of the universities with the industries does not exist to any extent in this country, and is one of the things we have to aim at in the future. It must be of great advantage to industry and cannot fail to be of great value also to the university, for it must result in the manufacturer taking a keen interest in the welfare of the department with which he is associated. Contact with the research department of a large works must always be stimulating; problems are encountered, many of them of great scientific interest, which would never suggest themselves in strictly academic circumstances, and as one of the results, the tendency, which is always present under existing university conditions, for the professor to become an academic fossil and unproductive, is postponed. Again, contact with the research departments of a flourishing works cannot fail to suggest subjects for investigation which are eminently suitable to occupy the attention of research students, many of whom will ultimately take up technical work. I look forward to the time when the scientific staffs of our universities and technical schools will not only be available for industrial research, but will be encouraged by those in authority to undertake such work."

(2) "It is scarcely necessary to point out that, if a chemical works is to be successful, the first essential is that it must be under chemical control, and that every department must be in the hands of an expert; the board of directors may then be a mixed board, provided that steps are taken to ensure that chemical opinion is largely represented on it. The recognition of the soundness of this principle is one of the main reasons for the success of the German works."

(3) "Failure to develop on research lines is scarcely conceivable if the works is in charge of a highly trained chemical staff, but, on the other hand, if it gets into the power of the business man who wants an immediate return for his outlay, is not willing to wait for results, and fails to appreciate the importance of scientific control, then no tariff can avert disaster."

[1] Published in full in the *Journal of the Chemical Society*, **107** (1915), 557-578. Extended abstract *Jour. Soc. Chem. Ind.*, **34**, 474.

## THE SECOND PAN-AMERICAN SCIENTIFIC CONGRESS

Many matters of international character with particular significance to the college world have happened during the scholastic year now closing. The present European war has precipitated a general interest throughout the nation in foreign trade; an interest, however, that has slowly been developing for years through the vision and courage of an organization like the Pan-American Union, conferences and societies with peace and international comity propaganda, large business concerns with foreign trade connections, and various individuals who, by virtue of their position in the service of the Government of the United States or in the international and business world, have not only seen the tendency in the United States to view all things from an enlarged or international viewpoint but have materially assisted in directing, through the press and in public utterance, an ever-growing current of sentiment for a larger commerce and comity of the United States in relation with the other countries of the world. Among these none stand potentially in closer relation with us than the countries of Latin America. Linked to us by propinquity, a common origin and political destiny, Pan-Americanism is not a visionary dream, but is purposed with immediate and practicable results fraught with untold advantages to the entire world through the increase in culture and commerce among the participating countries of this new world group of nations.

During the present year two great Pan-American gatherings convene in Washington under the auspices of the Government of the United States. The first of these, the Pan-American Financial Conference, occurred the week of May the 24, 1915. In this conference delegates from the Latin American countries conferred with representative bankers and business men from our nation at the Pan-American Union, on invitation of the Secretary of the Treasury, on financial questions of pertinent interest that must have far-reaching beneficial results to Pan-American banking and commerce.

Of greater interest to the educational world, however, is the Scientific Congress that will convene in Washington beginning December 27, 1915, and concluding its sessions on January 8, 1916. Through the splendid coöperation of the Latin American countries the second Pan-American Scientific Congress, likewise held under the auspices of the United States Government through the Department of State, bids fair to be not only thus far the greatest Pan-American Congress, but the most important international scientific congress ever held in the United States. The first congress of this name was held in Santiago, Chile, in 1908. It had its origin in earlier Latin American Scientific Congresses; and

at the time of the Santiago congress was enlarged through the generous initiative of the Latin American countries to include the United States. This Congress was well attended by visiting delegates from the United States. On its adjournment, entirely unsolicited on the part of the latter, Washington was designated as the place of meeting of the Second Congress.

This honor has a singular appeal to our nation at this time. The present European war has brought the Western Hemisphere suddenly face to face with grave economic problems that invite the serious attention of scientists and experts in the various fields of applied science. The Scientific Congress will concern itself with the constructive discussion of these as well as with the contributions in the domain of pure science wherein great advance has been made since the last Congress in Santiago, Chile. Science is comprehensively defined by the Congress and includes, under nine heads, such main subjects as: Anthropology; Astronomy, Meteorology, and Seismology; Conservation of Natural Resources, Agriculture, Irrigation, and Forestry; Education; Engineering; International Law, Public Law, and Jurisprudence; Mining and Metallurgy, Economic Geology, and Applied Chemistry; Public Health and Medical Science; Transportation, Commerce, Finance and Taxation.

The significance of the Congress, through the importance of the above subjects, is greatly enhanced through the international reputation of the persons chosen to arrange for the program of the different sections of the Congress, most of whom have an intimate first-hand acquaintance as well with the local resources, development and scientific interest in the various Latin American countries.

Washington offers unusual advantages for a Congress of this nature. It enjoys an enviable distinction among the world capitals for the keen scientific interest and investigation in its various Federal Bureaus, the varied and extensive nature of its libraries and museums, the beauty of its buildings and the growing importance of detached but semi-official institutions and bureaus engaged in work of international scope. Among these none occupy a position of greater importance than the Pan-American Union, the Governing Board of which, composed of the diplomatic representatives of the participating Latin American countries with the Secretary of State of the United States as *Ex-Officio* Chairman, has signally honored the Second Pan-American Scientific Congress by authorizing the use of its beautiful building for the office and sessions of the Congress. The Board also, in response to the request of the President and Secretary of State of the United States, authorized to act as Secretary-General of the Scientific Congress, the Director-General of the Pan-American Union, the Honorable John Barrett, who has doubtless done more than any one American in the establishment of commerce and comity among the republics of the Western world; whose good fortune it has also been to see, through the seeming accident of war, the potential promise of his great work becoming realized so soon.

GLEN LEVIN SWIGGETT

# ORIGINAL PAPERS

## TOXICITY OF VARIOUS WOOD PRESERVATIVES. II

BY RUTH M. FLEMING AND C. J. HUMPHREY

Received June 21, 1915

Since February, 1914, when an article of similar nature was published by us in THIS JOURNAL, **6**, 128, the senior author has run approximately 2300 Petri dish tests upon 46 wood preservatives.[1] This paper will supplement that article by giving further results on several new preservatives and by limiting the toxic points of some of the earlier substances more closely, also by adding a few studies on accommodation to toxic media and vitality of cultures as affected by the age of the fungus transfers. For a fuller discussion of the literature upon the various phases of toxicity and for a more complete description of the effect of each preservative upon *Fomes annosus* and *Fomes pinicola*, the authors would refer those interested to United States Department of Agriculture, *Bull.* **227**, entitled "The Toxicity to Fungi of Various Oils and Salts, Particularly Those Used in Wood Preservation." Results of tests on other properties of these preservatives are reported in Department of Agriculture, *Bull.* **145**, "Tests of Wood Preservatives."

The substances reported upon in the present paper were submitted by various coöperators, the toxicity tests being carried out at the Forest Products Laboratory, Madison, Wisconsin. The tests were confined to the toxic effect of the substances when tested out in nutrient agar by the Petri dish method.

### METHOD

The method of testing is essentially the same as was quite fully explained in the earlier paper,[1] therefore only a summary of the process is necessary here.

The culture medium was prepared according to the following formula:

Extract of 1 lb. lean beef in 1000 cc. distilled water.
25 grams Lōfflund's malt extract.
20 grams agar-agar.
(Mixture carefully filtered but reaction not adjusted; slightly acid.)

In making the cultures, 17 cc. of the above medium were measured into 50 cc. glass-stoppered bottles. The oil preservatives were weighed and the salt solutions measured into similar bottles, after which the stoppers were sealed into the preservative bottles with a rubber-glycerine mixture and all were capped with muslin. If necessary, sufficient distilled water was added to the preservative to make 3 cc., the combined medium and preservative always equaling 20 cc. All the bottles were then placed in clamp frames (Page 654, Fig. 1) and sterilized with steam at

[1] Seventeen of these preservatives are coal-tar creosote and water-gas-tar distillates. Results from these will be published elsewhere in connection with another study.

[1] THIS JOURNAL, **6** (1914), 128.

100° C. for 35, 30 and 30 minutes, respectively, on three successive days.

After sterilization, both agar and preservative bottles were heated in a water bath and the contents of the former were poured into the latter, thoroughly shaken and the mixture poured into sterile Petri dishes 100 mm. in diameter. Upon cooling, each plate was inoculated at the center (Page 654, Figs. 2 and 3) with a transfer of mycelium 6 mm. square from cultures of *Fomes annosus* Fr. 2 to 3 weeks old. For each set of tests a check culture (Page 654, No. 109) of 17 cc. agar and 3 cc. water was prepared at the same time. These cultures were then placed in an incubator and held at approximately 25° C. for 6 weeks.

This method has proven quite satisfactory in testing the toxicity of most of the oils, but in case of the salt solutions, it is quite probable that some of the constituents of the culture medium combine with the preservative, thus modifying its toxicity. Many studies by various investigators have been made upon this subject which strongly indicate this possibility. For instance, Hawkins[1] found that the germination of spores of the fungus *Gloeosporium cingulatum* was influenced by changing the constituents of the medium although the amount of the toxic agent need not be altered. The toxicity of certain heavy metals, as copper, lead, and zinc was thus diminished by the addition of calcium, magnesium, and potassium nitrates to the culture solutions.

Likewise, Kunkel[2] found, from his numerous experiments upon the influence of starch, peptone, and sugars on the toxicity of various nitrates to *Monilia sitophila*, that the concentration at which various inorganic salts are toxic to this fungus depended on the kind of organic substances contained in the media to which those salts were added. For instance, his tests showed that barium nitrate was more toxic in peptone media than in starch media, while aluminum nitrate and ferric nitrate were more toxic in starch media than in peptone media.

Toxicity varies not only with the medium into which the preservative is introduced but also with the organism. In general, yeasts and molds are less sensitive to toxic substances than the wood-destroying fungi. There is also a difference between the various wood-destroying species, as shown by our former study.

In these tests *Fomes annosus* was selected because of its very destructive effect upon coniferous wood, particularly in mines, because of its wide distribution in the United States, and since it grew well on the agar culture medium used

## VARIATION IN GROWTH DUE TO AGE OF TRANSFER[3]

It was noted in the description of our method that only cultures between 2 and 3 weeks old were used for transfers. The importance of this precaution will be made evident by a study of Tables I and II, where the age of the fungus used for inoculations varies from 6 to 55 days.

The preservatives recorded in Table I apparently always greatly inhibited growth, allowing only a narrow marginal development to appear, even when lower concentrations were used. Since the older and the younger transfers were placed upon the same plate containing a certain concentration, thus being kept under the same conditions, and also since the tests were duplicated with quite similar results, it is almost certain that variation of growth is due principally to the age of the transfers. It is to be noted that in every case the younger culture had the advantage.

TABLE I—VARIATION IN GROWTH IN TOXIC CULTURES DUE TO AGE OF TRANSFER

(Most of these tests were duplicated with quite similar results)

| PRESERVATIVE SOLD AS | Per cent in medium | Marginal growth of *Fomes annosus* Fr. after 2 weeks Age of transfer (days) 15 | 28 | 4 weeks 15 | 28 | 6 weeks 15 | 28 |
|---|---|---|---|---|---|---|---|
| Coal-tar creosote, Fraction III, No. 1107 | 0.125 | * | None | 8 mm. | * | 14 mm. | 3 mm. |
| | 0.2 | None | None | * | None | 2 mm. | None |
| Coal-tar creosote, Fraction IV, No. 1108 | 2.2 | None | None | None | None | *(a) | None |
| *Age of transfer (days)* | | 16 | 37 | 16 | 37 | 16 | 37 |
| Coal-tar creosote, No 1800 | 0.15 | None | None | 3 mm | * | 7 mm. | 1 mm. |
| | 0.175 | None | None | * | None | 1 mm. | * |
| Water-gas-tar distillate, No. 2233 | 3.0 | * | None | * | * | .2 mm. | * |

* Growth on transfer only.

(a) In later tests several cultures showed marginal growth on 3 per cent concentrations.

In Table II the variation in growth from different-aged transfers on non-toxic media is still more evident than in Table I. This table shows that the three fungi tested all exhibited a marked difference (Plate I, Fig. 4) for the first ten days. After 20 days but one species showed the same growth of 40 mm. from the 6- and 48-day cultures, and here probably the size of the plate limited the growth, since the younger transfer growth reached the limit (40 mm.) in 14 days, while the older showed but a 32 mm. margin.

TABLE II—VARIATION IN GROWTH IN NON-TOXIC CULTURES DUE TO AGE OF TRANSFER

(Each culture consisted of 15 cc. of 2 per cent malt-extract agar, sterilized with 12 lbs. steam-pressure for 40 minutes and poured into sterile Petri dishes 100 mm. in diameter, one inoculation being made at the center of each plate. The cultures were then kept in an incubator held at approximately 20° C.)

| FUNGUS | Age of transfer Days | Marginal growth in mm. after 4 | 7 | 10 | 14 | 20 days |
|---|---|---|---|---|---|---|
| *Fomes annosus* | 6 | 5 | 15 | 20 | 30 | 40(a) |
| *Fomes annosus* | 53 | None | 5 | 10 | 24 | 35 |
| *Fomes pinicola* | 6 | 3 | 15 | 23 | 40 | 40 |
| *Fomes pinicola* | 48 | 1 | 8 | 17 | 32 | 40 |
| *Lentinus lepideus* | 6 | None | 8 | 20 | 30 | 40 |
| *Lentinus lepideus* | 55 | None | 3 | 12 | 24 | 35 |

(a) 40 mm. margin reached the limit of the plate, so no further growth was possible.

## ACCOMMODATION OF FUNGI TO TOXIC SUBSTANCES

Studies on the accommodation of fungi to toxic substances have yielded some interesting results. Pulst[1] found that the green mold, *Penicillium glaucum*, can gradually gain resistance to a toxic substance. He showed that an individual can gradually increase its resistance, without passing to another generation, if sufficient time be given. In his experiments with copper sulfate, he claimed that spores planted from generation to generation upon constantly increasing concentrations of this salt gradually acquired a resistance, so that the last generation endured a much stronger solution than the first.

[1] Lon A. Hawkins, "The Influence of Calcium, Magnesium, and Potassium Nitrates upon the Toxicity of Certain Heavy Metals towards Fungus Spores," *Physiol. Researches*, **1** (Aug., 1913), 57–92.

[2] Otto Kunkel, "The Influence of Starch, Peptone and Sugars on the Toxicity of Various Nitrates to *Monilia sitophila* (Mont.) Sacc.," *Bull. Torr. Bot. Club*, **40** (1913), 624.

[3] The term "transfer" throughout this paper refers to the small square of fungus mycelium, with its adhering agar, which was used for inoculating the Petri dishes.

[1] Carl Pulst, "Die Widerstandsfähigkeit einiger Schimmelpilze gegen Metalgifte," *Jahrb. wiss. Bot. von Pringsheim*, **37** (1902), 205–263.

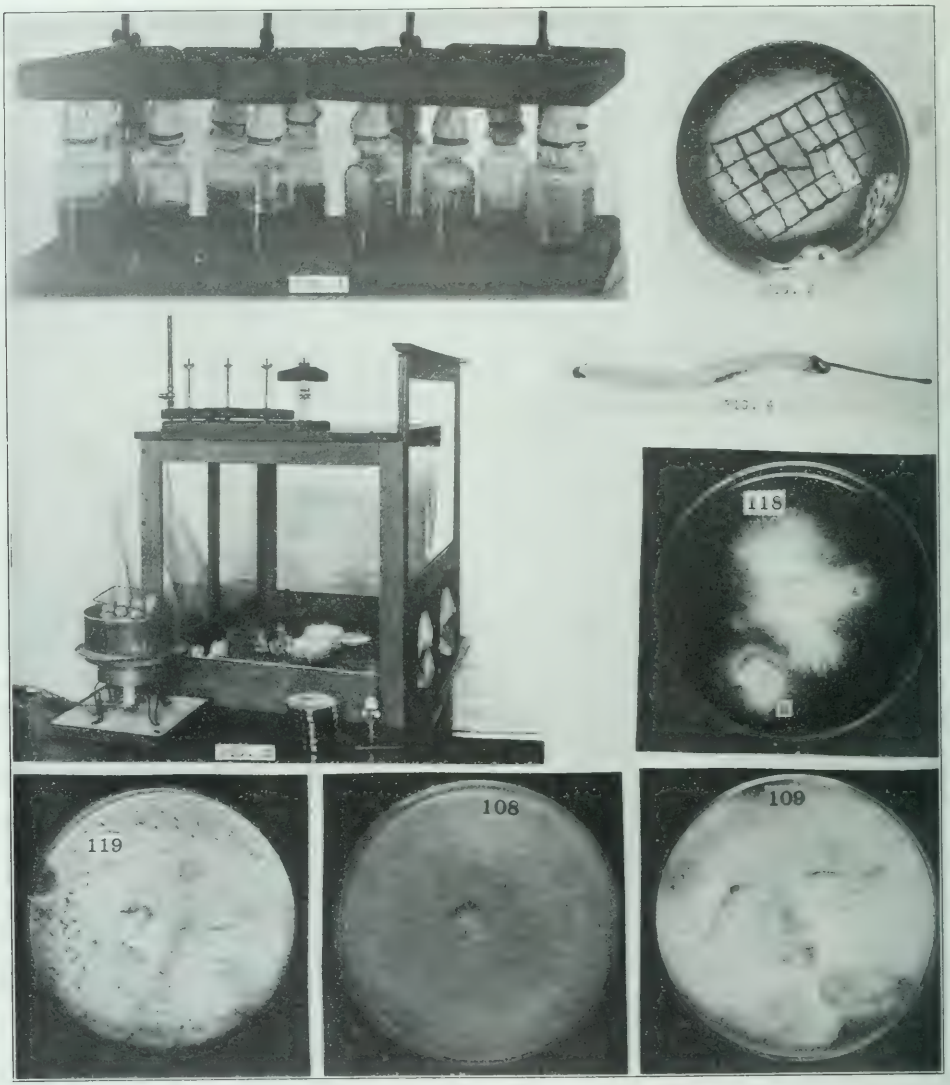



FIG. 1—PRESERVATIVE AND AGAR BOTTLES IN CLAMP FRAME READY FOR STERILIZATION

FIG. 2—INOCULATION CASE WITH HEATING APPARATUS, CLAMP FRAME, AND PILE OF INOCULATED PLATES

FIG. 3—CULTURE OF *Fomes annosus* CUT INTO TRANSFERS

FIG. 4—PLATINUM INOCULATION NEEDLE WITH FLATTENED TIP

No. 118—Non-toxic cultures of *Fomes annosus* showing the retarded growth from transfer 5 days old (B) as compared with 10-day old transfer (A)

No. 119—*Fomes annosus* growing on 40 per cent Timber asphalt, No. 1100. Age of culture, 18 days.

No. 108—*Fomes annosus* growing on 40 per cent kerosene No. 1847. Age of culture, 6 weeks.

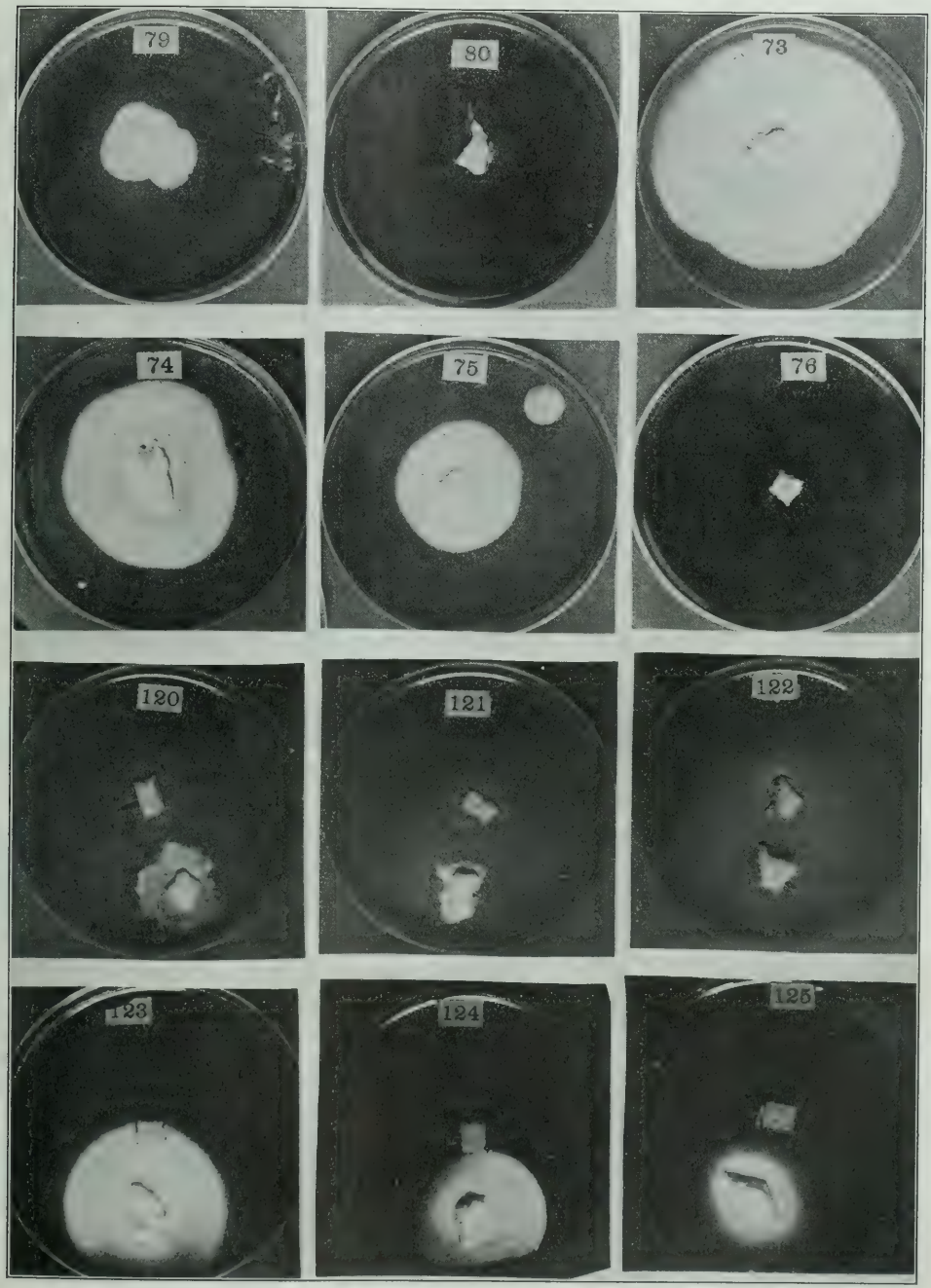
No. 109—Check culture of *Fomes annosus*. Age, 5 weeks.

Nos. 79 and 80—*Fomes annosus* on 0.75 and 1.0 per cent Spirittine, No. 1932. Age of culture, 6 weeks.

Nos. 73, 74, 75 and 76—*Fomes annosus* on 0.05, 0.375, 0.5 and 1.0 per cent C. A. Wood Preserver, No. 1931. Age of culture, 6 weeks.

Nos. 120, 121 and 122—Accommodation cultures of *Fomes annosus*. Transfers from non-toxic cultures show no growth, while transfers from 0.5 per cent Coal-tar Creosote, No. 1756, show growth on 0.4, 0.6 and 0.7 per cent, respectively, of the same preservative.

Nos. 123, 124 and 125—Accommodation cultures of *Fomes annosus*. Transfers from non-toxic cultures show no growth, while transfers from 1.2 per cent Spirittine, No. 1932, show growth on 1.3, 1.4 and 1.5 per cent, respectively, of the same preservative.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A few tests upon accommodation were made by the senior author. The method used was quite similar to the regular toxicity tests described previously, with the exception that generally two transfers were made upon each plate, one from a check culture containing no preservative and the other from a toxic[1] culture of the same preservative.

In Table III are found the results of these tests. Here the reader should note not only the source of each transfer but also the age. In all cases but two, where the transfers were taken from toxic cultures they were fully twice as old as those from the non-toxic cultures. Although the vitality of the transfers from toxic cultures was probably considerably reduced, still they equaled or surpassed the growth of those taken from a younger check culture. It is noticeable that upon the concentrations equal to and surpassing the killing point of the preservative that the growth was always greater from the "accommodated" transfer. The margins of growth from both transfers upon some of the lower concentrations were equal.

The tests on Spirittine (Page 655, Nos. 123, 124 and 125) were the only ones where the experiment was carried further than the first generation. On the 3 per cent Spirittine cultures a good margin of 10 mm. developed. This is a concentration 3 times the killing point for this preservative when inoculated with transfers from non-toxic cultures.

Although these tests showed that accommodation was possible, still it was evident, especially from experiments with the coal-tar creosotes (Page 655, Nos. 120, 121 and 122) that resistance could not be acquired easily. Only 2 of the 5 creosotes tested allowed fungus growth upon concentrations equal to or exceeding the killing point.

[1] By toxic culture is meant a culture containing preservative.

Table III—Accommodation to Toxic Medium

| Preservative Sold as: *Fomes annosus* | Transfers: Per cent in medium | Transfers: Age of transfer | Transfers: Source of culture(*a*) (Per cent preservative) | Marginal Growth after: 4 weeks | Marginal Growth after: 6 weeks | Killing Point(*b*) of preservative (derived from toxicity tests) |
|---|---|---|---|---|---|---|
| Zinc sulfate (by product), No. 1712 | 0.5 | 8 wks. | 0.4 | 6 mm. | 12 mm. | 0.6 |
| | | 19 da. | 0 (check) | 6 mm. | 12 mm. | |
| | 0.6 | 8 wks. | 0.4 | 2 mm. | 4 mm. | |
| | | 19 da. | 0 | Growth on transfer | Growth on transfer | |
| | 0.8 | 8 wks. | 0.4 | None | 1 mm. | |
| | | 19 da. | 0 | None | None | |
| Coal-tar creosote, No. 1720 | 0.1 | 7 wks. | 0.1 | 9 mm. | 13 mm. | 0.125 |
| | | 19 da. | 0 | 6 mm. | 13 mm. | |
| Coal-tar creosote, No. 1722 | 0.25 | 7 wks. | 0.25 | Growth on transfer | 6 mm. | 0.3 |
| | | 19 da. | 0 | 3 mm. | 7 mm. | |
| Coal-tar creosote, No. 1755 | 0.15 | 6 wks | 0.2 | 3 mm. | 8 mm. | |
| | | 21 da. | 0 | 3 mm. | 8 mm. | |
| | 0.2 | 6 wks. | 0.2 | 3 mm. | 20 mm. | 0.275 |
| | | 3 wks. | 0 | None | 2 mm. | |
| | 0.35 | 6 wks. | 0.5 | 8 mm. | 15 mm. | |
| | | 17 da. | 0 | Growth on transfer | 4 mm. | |
| Coal-tar creosote, No. 1756 | 0.5 | 6 wks. | 0.5 | 5 mm. | 8 mm. | 0.55 |
| | | 17 da. | 0 | Growth on transfer | Growth on transfer | |
| | 0.6 | 6 wks. | 0.5 | Growth on transfer | Growth on transfer | |
| | | 17 da. | 0 | None | None | |
| Spirittine wood preserver, No. 1932 | 1.2 | | $1.2_1$ | Growth on transfer | 15 to 20 mm. | 1.0 |
| | 1.2 | 37 da. | $1.2_2$ | 25 mm. | .... | |
| | 1.5 | 37 da. | $1.2_2$ | 20 mm. | .... | |
| | 1.5 | 17 da. | $1.2_3$ | 18 mm. | 25 mm. | |
| | 1.8 | 17 da. | $1.2_3$ | 18 mm. | 25 mm. | |
| | 2.0 | 4 wks. | $1.8_4$ | 15 mm. | 15 mm. | |
| | 3.0 | 4 wks. | $1.8_4$ | 10 mm. | 10 mm. | |
| *Fomes pinicola* | | | | | | |
| Coal-tar creosote, No. 1074 | 0.15 | $7\frac{1}{2}$ wks. | 0.15 | 20 mm. | .... | 0.225 |
| | .... | .... | 0 | 5 mm. | .... | |
| | 0.25 | $7\frac{1}{2}$ wks. | 0.15 | 3 mm. | .... | |
| | .... | .... | 0 | Growth on transfer | .... | |
| | 0.3 | $7\frac{1}{2}$ wks. | 0.15 | 1 mm. | .... | |
| | .... | .... | 0 | None | .... | |

(*a*) In this column are given the concentrations from which transfers were made to the other concentrations of the same preservative, indicated in the second column. The sub-figures following the percentages indicate the number of successive transfers from one toxic medium to another. Thus, under Spirittine, "$1.2_4$" means that in this instance the culture from which the transfer is taken has itself been derived from a toxic culture one "generation" back; the culture indicated as "$1.8_4$" means that this culture has been successively transferred through four "generations" of varying, usually increasing concentrations. Where no explanations of this sort are made it is to be understood that the transfer was taken from a toxic culture of high efficiency selected from the routine series of ordinary toxicity tests.

(*b*) The killing point is the concentration which will just prevent all marginal growth of the fungus, when the transfer is taken from a culture containing no preservative. This killing point is carried to within an accuracy of approximately 10 per cent, and has been checked at least in duplicate.

## RESULTS OF TOXICITY TESTS

In Tables IV and V will be found the results of most of our toxicity tests. In Table IV the preservatives are arranged according to their nature as follows: wood-tar products, coal-tar products, water-soluble salts, and crude and refined petroleum oils.

In Table V the list of preservatives is somewhat extended by adding those of the earlier paper.[1] These are arranged in order of their toxicity and compared to two of the standard preservatives, coal-tar creosote,[2] No. 1074, and zinc chloride, No. 2239. The killing point of the coal-tar creosote as given in our former publication was based upon a 5 per cent gum arabic emulsion of the preservative and was found to be considerably higher than that of the 100 per cent oil which was used in ascertaining the killing point used in the present paper. It is evident by comparing the killing points of the gum arabic emulsion of coal-tar creosote, No. 1074, and wood tars, Nos. 1561 and 1099, with the corresponding pure preservatives that the toxicity was considerably lessened by the addition of gum arabic. Accordingly, the opportunity is taken to make this correction in comparison.

Of the wood distillates, beechwood creosote proved highly toxic, two to three times as effective as coal-tar creosote, No. 1074, which represents an average grade. Of the remaining four representatives of the

[1] This Journal, **6** (1914), 128

[2] Some tests have been made recently on seven coal-tar creosotes distilled in this laboratory from authentic samples of coal tars. The killing points of these preservatives range from 0.125 to 0.3 per cent, all showing a higher toxicity than the coal-tar creosote here reported.

TABLE IV—LIST OF PRESERVATIVES TESTED, SHOWING ESSENTIAL PROPERTIES AND KILLING POINT

| No. | PRESERVATIVE SOLD AS: | Killing point (Per cent) | Specific gravity (60° C.) | DESCRIPTION | COÖPERATOR |
|---|---|---|---|---|---|
| 1 | Beechwood creosote, No. 3183 | Between 0.12 and 0.24 | 1.04 | Dark brown liquid; liquid at room temperature | Lake Superior Iron and Chemical Co., Manistique, Mich |
| 2 | Preservol, No. 2236 | 0.7 | 1.172 | Thick, viscous liquid; probably pyroligneous acid plus wood tar | Newbold Manufacturing Co., New York, N. Y. |
| 3 | Spirittine wood preserver, No. 1932 | 1.0 | 1.006 | Reddish brown liquid; 0.47% acid; a softwood creosote. | Spirittine Chemical Co., Wilmington, N. C. |
| 4 | Wood tar (hardwood), No. 1561(*b*) | ... | 1.195 | Black, viscous liquid with pyroligneous odor; 24% water. | Marden, Orth and Hastings, Chicago, Ill |
| | 100 per cent preservative | 0.625 | .... | | |
| | 20 per cent gum arabic emulsion | 1.25 | ... | | |
| 5 | Wood tar (Douglas fir), No. 1099(*b*) | ... | 1.052 | Black liquid with strong pyroligneous odor. | Logged off Land Utilization Co., Seattle, Wash |
| | 5 per cent gum arabic emulsion | 0.65(*a*) | ... | | |
| | 100 per cent preservative | Between 0.35 and 0.46 | ... | | |
| 6 | C. A. wood preserver, No. 1931 | 1.0 | 1.12 | Brown liquid; probably high boiling fractions of coal-tar creosote. | C. A. Wood Preserver Co., St. Louis, Mo. |
| 7 | Coal-tar creosote, No. 1074(*b*) | .... | 1.048 | Liquid; 8.4% water. | Creosote Supply Co., Chalmette, La. |
| | 5 per cent gum arabic emulsion | 0.55 | | | |
| | 100 per cent preservative | 0.35 | | | |
| 8 | Coal-tar creosote, Fraction III, No. 1107 | 0.225 | 1.045 | Liquid at room temperature. | Semet-Solvay Co., Ensley, Ala. |
| 9 | Coal-tar creosote, Fraction IV, No. 1108 | 3 | 1.088 | Liquid at room temperature | Semet-Solvay Co., Ensley, Ala. |
| 10 | Coal-tar creosote, Fraction V, No. 1109 | 33(*a*) | 1.18 | Heavy tarry liquid | Semet-Solvay Co., Ensley, Ala. |
| 11 | Water-gas tar distillate, No. 2233 | 6.5(*a*) | 1.042 | Dark brown liquid. | United Gas Improvement Co., Philadelphia, Pa. |
| 12 | Water-gas tar distillate, No. 2235 | 0.65 | 0.995 | Greenish brown liquid. | United Gas Improvement Co., Philadelphia, Pa. |
| 13 | Zinc sulfate (commercial), No. 1711 | 0.65(*a*) | | Commercial salt. | |
| 14 | Zinc sulfate (by-product), No. 1712 | 0.6 | | By-product from copper smelter. | Balaklala Cons. Copper Co., Coram, Cal. |
| 15 | Bruening and Marmetschke preservative | 0.5 | | 6²/₃% zinc chloride plus 3¹ ₃% aluminum sulfate. | Bruening and Marmetschke, Schoepfurth, Germany. |
| 16 | Holzhelfer, No. 2097 | 11 | 1.113 | Thick greenish brown liquid; partial emulsion of zinc chloride, creosote, and small amount of copper. | Vaughan Paint Co., Cleveland, Ohio. |
| 17 | Fuel oil, No. 1103 | 40+ | 0.871 | Light liquid; odor of crude oil. | U. S. War Department, Picatinny Arsenal, Dover, N. J. |
| 18 | Kerosene, No. 1847 | 40+ | 0.798 | Refined petroleum oil. | |
| 19 | Timber asphalt, No. 1100 | 40+ | 1.063 | Residue from distilling off lighter fractions from a crude oil. Very viscous. | Indian Refining Co., Cincinnati, O. |

PER CENT PRESERVATIVE DISTILLING BELOW

| No. | 180 | 215 | 245 | 275 | 305 | 320 | 360° C |
|---|---|---|---|---|---|---|---|
| 1 | .... | About 15.7 | 48.2 | 72.7 | . . | . | . |
| 2 | 13.9% Distills below 205° C. | | | | | | |
| 3 | 14.2 | 23.2 | 35.2 | 36.7 | . . | . | . |
| 4 | About 27 | About 31 | 51 | .... | .... | .... | .... |
| 5 | About 16 | About 31 | 54.7 | .... | .... | .... | .... |
| 6 | 0.5 | 2 | 4 | 8.2 | 20.6 | 28.9 | 70.1 |
| 7 | 4.8 | 17.8 | 44.4 | 54.1 | 67.2 | 74.1 | . . |

PER CENT PRESERVATIVE DISTILLING BELOW

| No. | 180 | 215 | 245 | 275 | 305 | 320 | 360° C. |
|---|---|---|---|---|---|---|---|
| 8 | | 0.9 | 16.2 | 49.2 | 77.7 | 85 | . . |
| 9 | . | | 0.9 | 4.7 | 38.5 | 54.3 | . . |
| 10 | | | . | . | 4.1 | 10.1 | 48.7 |
| 11 | 3 | 6.7 | 21.2 | 35.3 | 48.5 | 53.5 | 77.6 |
| 12 | 3.3 | 12.8 | 37.7 | 61.7 | 75.3 | 80.3 | .... |
| 16 | 7.3 | 7.8 | 9.9 | 12.8 | 23.8 | 29.6 | 58.9 |
| 17 | | About 3 | About 9 | About 20 | 40.6 | About 51 | About 75 |
| 18 | 25.1 | 65.5 | 89.7 | .... | .... | .... | .... |

(*a*) Killing point was not checked in duplicate.

(*b*) A gum-arabic emulsion was tried first. Later the regular method proved satisfactory with coal-tar creosote as the oil made a good mixture with the agar. In case the two wood tars, the drop method was tried, in which 1, 2, 3, 4, or 5 drops of pure preservative were added directly to the heated agar, shaken and poured. This made a good mixture and was approximately accurate, as the average weight of a drop of this oil from the same pipette had previously been calculated. The killing point given in the earlier publication was taken from tests upon emulsions.

TABLE V—PRESERVATIVES ARRANGED IN ORDER OF TOXICITY TO FOMES ANNOSUS AND SHOWING RATIO TO COAL-TAR CREOSOTE AND ZINC CHLORIDE

| PRESERVATIVE SOLD AS: | KILLING POINT Per cent | KILLING POINT Lbs. per cu. ft. | Ratio of killing point to Coal-tar creosote, No. 1074 (Killing point 0.35%) | Ratio of killing point to Zinc chloride, No. 2239 (Killing point 0.5%) |
|---|---|---|---|---|
| Coal-tar creosote, Fraction II, No. 1106 | 0.225 | 0.140 | 1.55 | 2.2 |
| Coal-tar creosote, Fraction III, No. 1107 | 0.225 | 0.140 | 1.55 | 2.2 |
| Beechwood creosote, No. 3183 | Between 0.12–0.24 | 0.075–0.150 | 3–1.5 | 4.2–2.1 |
| Sodium fluoride, No. 1929 | 0.25 | 0.156 | 1.4 | 2.0 |
| Cresol calcium, No. 2098 | Between 0.14–0.28 | 0.087–0.174 | 2.5–1.25 | 3.6–1.8 |
| Coal-tar creosote, Fraction I, No. 1094 | 0.30 | 0.187 | 1.17 | 1.7 |
| Coal-tar creosote, No. 1074: | | | | |
| 100 per cent preservative | 0.35 | 0.218 | 1.0 | 1.4 |
| 5 per cent gum arabic emulsion | 0.55 | 0.343 | 0.64 | 0.909 |
| Wood tar (Douglas fir), No. 1099: | | | | |
| 100 per cent preservative | Between 0.35–0.46 | 0.218–0.287 | 1.0–0.76 | 1.4–1.09 |
| 5 per cent gum arabic emulsion | 0.65(*a*) | 0.405 | 0.54 | 0.77 |
| Bruening and Marmetschke preservative | 0.5 | 0.312 | 0.7 | 1.0 |
| Zinc chloride, No. 2239 | 0.5 | 0.312 | 0.7 | 1.0 |
| Zinc sulfate (by-product), No. 1712 | 0.6 | 0.374 | 0.58 | 0.83 |
| Wood tar (hardwood), No. 1561: | | | | |
| 100 per cent preservative | 0.625 | 0.39 | 0.56 | 0.8 |
| 20 per cent gum arabic emulsion | 1.25 | 0.78 | 0.28 | 0.4 |
| Water-gas-tar distillate (sp. gr. 0.995), No. 2235 | 0.65 | 0.405 | 0.54 | 0.77 |
| Preservol, No. 2236 | 0.7 | 0.436 | 0.50* | 0.70 |
| Zinc sulfate (commercial), No. 1711 | 0.65(*a*) | 0.405 | 0.54 | 0.77 |
| C. A. Wood Preserver, No. 1931 | 1.0 | 0.624 | 0.35 | 0.5 |
| Spirittine wood preserver, No. 1932 | 1.0 | 0.624 | 0.35 | 0.5 |
| S. P. F. Carbolineum, No. 1844 | 2.25 | 1.404 | 0.155 | 0.22 |
| Coal-tar creosote, Fraction IV, No. 1108 | 3.0 | 1.872 | 0.117 | 0.17 |
| Avenarius carbolineum, No. 1843 | 5.25 | 3.28 | 0.66 | 0.095 |
| Water-gas-tar distillate (sp. gr. 1.042), No. 2233 | 6.5(*a*) | 4.05 | 0.054 | 0.077 |
| Holzhelfer, No. 2097 | 11.0 | 6.86 | 0.032 | 0.045 |
| Coal-tar creosote, Fraction V, No. 1109 | 33.0(*a*) | 20.59 | 0.0106 | 0.0151 |
| Copperized oil, No. 1095 | 40 | 25 | 0.0088 | 0.012 |
| Fuel oil, No. 1103 | 40+ | 25+ | 0.0088— | 0.012— |
| Kerosene, No. 1847 | 40+ | 25+ | 0.0088— | 0.012— |
| Timber asphalt, No. 1100 | 40+ | 25+ | 0.0088— | 0.012— |
| Water gas tar distillate (sp. gr. 1.058), No. 1101 | 40+ | 25+ | 0.0088— | 0.012— |
| None-such special, No. 2696 | 45+ | 28+ | 0.0077— | 0.011— |
| Sapwood antiseptic, No. 1611 | 75+ | 46.8+ | 0.0047— | 0.0066— |

(*a*) The killing point has not been checked in duplicate but is approximately correct.

group (Preservol, Spirittine, hardwood tar, wood tar from Douglas fir) three are about half as toxic as coal-tar creosote. The fourth, Spirittine (Page 655, Nos. 79 and 80), proved only one-third as toxic.

Further work on Fractions III, IV, and V of coal-tar creosote indicates that Fraction III is somewhat more toxic than first reported; the other two remain essentially the same as the first work demonstrated. As the results stand to date, Fractions II and III are equally highly toxic and with beechwood creosote are the three most toxic compounds reported upon. If the volatility of Fraction I could be controlled, this fraction perhaps would prove equally as toxic as II and III.

Since the greater part of Fractions II and III distils between 215 and 305° C. we may infer that, with the possible exception of phenolic bodies in Fraction I, the more highly toxic constituents of coal-tar creosote have their boiling points between these limits. Additional tests on the two water-gas-tar distillates previously reported upon indicate that the toxic point lies somewhat higher than there indicated. The distillate of low specific gravity (0.995) is somewhat less toxic than coal-tar creosote, No. 1074, while that of high specific gravity (1.042) falls comparatively low in the toxicity scale.[1]

Zinc sulfate (both by-product and commercial) compares very favorably with zinc chloride and also with coal-tar creosote.

When drawing comparisons between zinc chloride and the Bruening and Marmetschke preservative (zinc chloride + aluminium sulfate) it should be kept in mind that zinc chloride cannot be tested satisfactorily by mixing with ordinary nutrient agar, on account of its tendency to combine with the medium. With the straight zinc chloride, different tests have yielded killing points lying between 0.3 and 0.5 per cent; the Bruening and Marmetschke preservative varied between 0.4 and 0.5 per cent.

Holzhelfer, although composed of such toxic constituents as zinc chloride and creosote, must be in comparatively dilute form, since its toxicity is quite low, about 11 per cent being required to prevent the growth of *Fomes annosus*.

The three petroleum oils (Page 654, No. 108) showed but slight or no toxic qualities, in that generally 40 per cent cultures nearly equalled and sometimes even excelled the growth on the check cultures.

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INVESTIGATIONS IN FOREST PATHOLOGY, BUREAU OF PLANT INDUSTRY
IN COÖPERATION WITH THE FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

Some preliminary tests have recently been made at the Forest Products Laboratory, Madison, Wis., on the toxicity of ten authentic water-gas-tar distillates. The approximate killing point of most of these falls considerably below, or around, that of the most toxic water-gas-tar distillate here reported.

## A STUDY OF SOME RECENT METHODS FOR THE DETERMINATION OF TOTAL SULFUR IN RUBBER[1]

By J. B. Tuttle and A. Isaacs

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### PURPOSE OF INVESTIGATION

One of the most important problems in the chemical analysis of rubber compounds is the determination of total sulfur. Many investigators have worked on this subject, with the result that different laboratories have their own methods, and comparison of results obtained by these various methods is always difficult, and at times impossible.

This Bureau is now using in its routine analysis the method of Waters and Tuttle.[2] In order to learn whether or not the methods for this determination which have been recently published were an improvement, either in accuracy or time required, over the one now in use, and if not, to determine wherein these methods are faulty, this present investigation was undertaken.

### GENERAL CONSIDERATION

The determination of the total sulfur in rubber is far from being a simple problem, involving as it does the simultaneous determination of sulfur in a number of different substances. Sulfur may be found in vulcanized rubber compounds in any of the following forms:

1—Free sulfur.

2—Sulfur combined with rubber (*i. e.*, vulcanized rubber).

3—Metallic sulfates, usually lead and barium.

4—Metallic sulfides, usually lead and zinc.

5—Sulfur compounds of fatty acids (from the so-called oil substitutes, or "factis").

6—Sulfur in bituminous substances ("mineral rubbers").

The first and second of these are always present, and the others may or may not be, according to the nature of the compound. Any method which has for its purpose the determination of the total sulfur must be adequate to determine any or all of these in widely varying amounts. In our experience in testing material for use in the Government departments, the total sulfur has varied from 1.5 to 25 per cent; the free sulfur from practically nothing to 10 per cent; and sulfur in metallic sulfates from nothing up to 6 per cent. The rubber content varied from 20 to 90 per cent, and the quality of the rubber varied from the best to the poorest. We have no quantitative data on the other sulfur-bearing components of rubber goods, but we are certain that they are frequently present and carry appreciable quantities of sulfur.

The almost universal use of litharge (in amounts sometimes 15 and even 20 per cent) in rubber mixings may have considerable bearing on the determination of sulfur by some methods even though the litharge does not in itself contain sulfur. Its effect on the determination of total sulfur will be referred to later in the discussion of the results obtained by the methods investigated.

[1] Published by permission of the Director of the Bureau of Standards.

[2] Bureau of Standards, *Reprint* **174**; This Journal, **3** (1911), 734.

### REVIEW OF RECENT METHODS

In connection with the previous publication on this subject from this Bureau,[1] a number of the methods in use at that time were investigated and discussed. Since then several new methods have been proposed. Alexander's[2] method involving the oxidation of the rubber with sodium peroxide was recommended by Allen[3] as a "reliable rapid method." Spence and Young[4] worked on a variation of the electrolytic oxidation first suggested by Gasparini[5] and afterwards developed by Hinrichsen.[6] Kaye and Sharp[7] proposed fusing the rubber directly with a mixture of zinc oxide and potassium nitrate. Ernst Deussen[8] offered a new idea in an attempt to determine only the free sulfur and the sulfur combined with the rubber. After decomposition with concentrated nitric acid and evaporation, he treated the residue with sodium carbonate and water, and filtered, determining the sulfur in the filtrate colorimetrically. The Joint Rubber Insulation Committee[9] proposed a procedure for the complete analysis of rubber insulation material according to which the total sulfur is determined by fusion with a mixture of sodium peroxide and potassium carbonate. While this method was recommended for 30 per cent Para insulation compounds only, it is desirable to know whether it has a wider application. H. P. Stevens[10] suggested a method for correcting for the loss of volatile sulfur in the Henriques method, by absorbing the gases from the determination in alkali and subsequently determining the sulfur thus absorbed. Utz[11] gave a review of the subject in which the method of Kaye and Sharp was compared with that of Frank and Marckwald.[12] He considered the two methods of equal value.

There are two general methods for determining sulfur in organic compounds which have been used to determine the sulfur in rubber, *viz.*, the Carius and the bomb methods. These are so well known that description at this time is unnecessary. Both of them are considered adequate to determine the total sulfur when modified to suit the conditions peculiar to rubber. Such modifications, however, are time-consuming and render these methods undesirable for the routine analysis of rubber goods. It was therefore not considered necessary to give analytical data in this paper.

### SAMPLES

Even when the assumed total sulfur content is given, this information is not sufficient to enable one to judge the efficiency of the method, since some methods will give low results with materials containing much free sulfur. For the proper interpretation of the results by any method, the entire composition of the samples used, at least as far as the sulfur-bearing constituents are concerned, should be known and reported.

The samples used in this investigation are described in Table I. Sample A was one of the samples used

TABLE I—COMPOSITION OF SAMPLES

The figures given are approximate percentages only

| Sample | Description | Rubber content | Sulfur: Total | Sulfur: Free | Mineral fillers |
|---|---|---|---|---|---|
| A | Insulation | 30 Fine Para | 5.0 | 0.5 | 18 Barytes |
| B | Suction hose | 40 High grade | 6.0 | 0.5 | 18 Barytes |
| C | Special | 48 Fine Para | 4.25(*a*) | 0.6 | 16 Barytes<br>16 Litharge |
| D | Insulation | 28.5 Fine Para | 1.75 | 1.0 | 4 Litharge |
| E | Rubber bands | 93 High grade | 5.0 | 2.7 | 2 Litharge |
| F | Special | 42 Coarse Para | 8.1(*a*) | 4 | 30 Sublimed lead<br>5 Litharge |
| G | Gasket | 55 Poor quality | 12.0 | 8 | 2 Barytes<br>2 Litharge |
| H | White tubing | 20 Poor quality | 21.0 | 9 | 36 Barytes |

(*a*) The amount of sulfur added as such in Samples C and F was 2 per cent and 5.4 per cent, respectively

in the investigations of the Joint Rubber Insulation Committee. Samples B, E, G and H were taken from deliveries on various Government contracts.[1] Sample D was prepared especially for the investigations of the Analytical Committee of the Rubber Section of the American Chemical Society. Samples C and F were specially prepared by one of the authors (J. B. Tuttle) at the factory of the Voorhees Rubber Mfg. Co., at Jersey City, N. J., for the purpose of investigating the determination of total sulfur. Great care was taken in the weighing and mixing. The composition was chosen so as to show the effect upon the analysis of the two commonly used sulfates, barytes and sublimed lead, and the vulcanization was controlled so that one of the samples should have a rather large free sulfur content. These two samples have practically the same composition as many that are frequently met with in our routine work and may therefore be considered as representative of such materials.

### METHODS COMPARED

DIRECT SOLUTION METHODS—1. Spence and Young: conc. $HNO_3$, fuming $HNO_3$ and electrolysis.

2. Deussen: conc. $HNO_3$ and extraction with $Na_2CO_3$.

DIRECT FUSION METHODS—3. Alexander: $Na_2O_2$.

4. Joint Rubber Insulation Committee: $Na_2O_2$ and $K_2CO_3$.

5. Kaye and Sharp: ZnO and $KNO_3$.

SOLUTION AND FUSION METHODS—6. Frank and Marckwald: fuming $HNO_3$, fusion with $Na_2CO_3$ and $KNO_3$.

7. Waters and Tuttle: conc. $HNO_3$ and Br, fusion with $Na_2CO_3$ and $KNO_3$.

SPECIAL METHOD—8. Acetone extraction, and separate determination of free and residual sulfur.

The methods as originally described by the various investigators were followed as closely as possible. Whenever it was considered advisable to depart from the original method, the reasons therefor are given. Unless otherwise stated, 0.500 gram was taken for each determination. The "fusion mixture" used

[1] In this connection it will be of interest to note that G was taken from a delivery offered on a contract calling for 50 per cent fine Para rubber and not over 3 per cent sulfur other than that present as barytes.

[1] Waters and Tuttle, *Loc. cit.*

[2] *Gummi Ztg.*, **18** (1904), 729–730.

[3] Allen's "Commercial Organic Analysis," 4th Ed., Vol. IV, p. 140, 1911.

[4] THIS JOURNAL, **4** (1912), 413.

[5] *Gazz. chim. ital.*, [II] **37** (1907), 426–461.

[6] *Chem. Ztg.*, **33** (1909), 735.

[7] *India Rubber Journal*, **44** (1913), 1189.

[8] *Z. angew. Chem.*, **24** (1913), 494.

[9] THIS JOURNAL, **5** (1914), 78.

[10] *Analyst*, **39** (1914), 74, *India Rubber Journal*, **47** (1914), 785.

[11] *Gummi Ztg.*, **28** (1914), 631–632.

[12] *Ibid.*, **17** (1903), 71.

was composed of equal parts of sodium carbonate and potassium nitrate. Fusions were made with the gasoline gas generator described by Waters.[1] The barium sulfate precipitates were allowed to stand over night before filtering, and were ignited and weighed in porcelain crucibles. Insoluble residues were examined for sulfur, the amounts of which, if present in appreciable quantities, are given. The reagents used were tested and found to be practically free from sulfur, so that no corrections are necessary on their account. Methods 4, 6, 7 and 8 are intended to determine the total sulfur, while 1, 2, 3, and 5 are intended for the determination of sulfur other than that present as insoluble sulfates.

1—SPENCE AND YOUNG—The rubber was treated with 5 cc. of concentrated nitric acid, and heated gently. When the first reaction was over, about 50 cc. (exact amount was not specified by the authors) of fuming nitric acid were added and the solution electrolyzed. As a source of current, an 8-volt storage battery was used. This was connected directly to the platinum electrodes. The resistance of the electrolytic cell was such that the current was usually between 2 and 3 amperes, though at times it was as low as 1 ampere. After two or three hours, the current was discontinued, the electrodes removed, 1 gram of potassium nitrate[2] was added and the solution evaporated to dryness. The nitric acid was completely removed with hydrochloric acid by several evaporations. A few drops of hydrochloric acid were added, the residue was treated with hot water and filtered. The sulfur in the filtrate was precipitated as usual. The insoluble matter filtered off above was fused with 5 gms. of fusion mixture, extracted with hot water, filtered, and after acidification the sulfur in the filtrate was precipitated as usual.

2—DEUSSEN—The Deussen method was not followed exactly as given by the author. The rubber was treated in a porcelain crucible with concentrated nitric acid and covered. After heating for a short time, the cover was removed and the solution evaporated to dryness. The residue was treated with sodium carbonate and water, and after heating, the solution was filtered. Up to this point the original method was followed exactly. Deussen reduces the sodium sulfate to sulfide and determines the latter colorimetrically. In order to avoid any error introduced by this procedure and to obtain a better comparison with the other methods, we added potassium nitrate to the filtrate, evaporated to dryness and fused. The sulfur in the cooled melt was determined as under the Waters and Tuttle method. The insoluble residue from the sodium carbonate filtration was fused with 5 grams of fusion mixture and the sulfur determined as usual.

3—ALEXANDER—The Alexander method, as given in Allen's "Commercial Organic Analysis," is said to be rapid and reliable. The rubber is intimately mixed with 16 grams of sodium peroxide in an iron crucible provided with a lid through which a small hole has been bored. The combustion is started by introducing through this hole a red hot iron wire. No further heating is required. When the mass is cool it is dissolved in water, the crucible, lid and wire are removed, the solution is acidified with hydrochloric acid and boiled, then filtered if necessary and the sulfate precipitated by means of barium chloride.

4—JOINT RUBBER INSULATION COMMITTEE—The rubber was fused with 4 grams of sodium peroxide and 6 grams of potassium carbonate. The cooled melt was extracted with hot water to which some bromine water had been added. The solution was filtered, acidified with hydrochloric acid and evaporated to dryness to dehydrate silica. About 400 cc. of water were added, the solution made slightly acid with hydrochloric acid, filtered, and the sulfur in the filtrate determined as usual.

5—KAYE AND SHARP—The rubber was mixed with 4 grams of zinc oxide and 2 grams of potassium nitrate, placed in a crucible (both iron and porcelain were used), and covered with a layer of zinc oxide about 1 cm. deep. This was carefully heated, at first with a low, and afterwards with a full Bunsen flame. The crucible and contents were placed in a beaker, covered with water and heated; the solution was acidified with hydrochloric acid and filtered. The sulfur in the filtrate was determined as usual.

The insoluble residue filtered off from the hydrochloric solution was fused with 5 grams of fusion mixture and the sulfur determined as under the insoluble matter in the Spence and Young method.

6—FRANK AND MARCKWALD—The rubber was treated with about 20 to 25 cc. of fuming nitric acid in a porcelain crucible, the vessel covered with a watch glass and allowed to stand over night. The solution was evaporated to dryness, the residue fused with 5 grams of fusion mixture, extracted with hot water and filtered. The filtrate was acidified with hydrochloric acid and the sulfur precipitated as usual.

7—WATERS AND TUTTLE—The rubber was treated in a porcelain crucible with 25 cc. of concentrated nitric acid saturated with bromine, the vessel covered with a watch glass and allowed to stand one hour. It was heated on a steam bath for one hour and then the cover was removed and the solution evaporated to dryness. The residue was fused with 5 grams of fusion mixture, extracted with hot water, filtered, the filtrate acidified with hydrochloric acid and the sulfur precipitated as usual.

8—EXTRACTION WITH ACETONE—Some determinations were made by extracting 2 grams of rubber with freshly distilled acetone for eight hours. The acetone solution was evaporated to dryness, distilled water and bromine added, the solution heated until colorless, filtered, and the sulfur in the filtrate determined as usual. The insoluble residue was examined for sulfur by fusing with 5 grams of fusion mixture. The amount of sulfur thus found was scarcely ever more than a few tenths of a milligram.

The extracted rubber was dried at about 60° C.

[1] THIS JOURNAL, **5** (1913), 853.

[2] Spence and Young add 1 gm. of sodium carbonate, but, inasmuch as this on solution is changed to sodium nitrate, we used potassium nitrate, which serves the same purpose and obviates the spattering caused by the addition of a carbonate to the hot concentrated acid.

and the sulfur determined according to the method of Waters and Tuttle. The sum of these various determinations should be the total sulfur.

### DISCUSSION OF RESULTS

Although the method of Waters and Tuttle is No. 7, it has been considered advisable to discuss it first since it is the most reliable and accurate method we have found for the determination of total sulfur. The reaction proceeds slowly without any very great evolution of heat so that there is little or no chance of losing free sulfur. Even when the free sulfur is very high the method is adequate to determine it with accuracy. A large number of determinations were made, and the results are concordant and agree with the calculated results in samples of known composition.

The Waters and Tuttle method has been in use at the Bureau of Standards for a number of years, and during that time has frequently been used in determining the total sulfur in samples of known composition. The results have invariably been satisfactory even when obtained by comparatively inexperienced analysts.

The methods which have been compared in the course of this investigation may be divided into two classes, *viz.*, those for the determination of the total sulfur, and those for the determination of sulfur other than that present in the insoluble sulfates. They may be further classified, according to the method of attack employed, as follows: direct solution, direct fusion, and solution and fusion methods.

The methods which have for their object the determination of sulfur other than that present in the insoluble sulfates (Nos. 1, 2, 3, and 5), attempt to separate the insoluble sulfates by filtration. Spence and Young, Alexander, and Kaye and Sharp filter from an acid solution. The securing of correct results by this method is based upon the obviously incorrect assumption that the lead sulfate originally present would remain insoluble while that formed from the litharge would be completely dissolved. Deussen filters from an alkaline carbonate solution, but this procedure is open to the objection that lead sulfate will react with sodium carbonate solution with the formation of soluble sodium sulfate. It is apparent, therefore, that such methods cannot give reliable results since their basic principles are faulty.

Considering the methods as classified according to the mode of attack, we find that the direct solution methods (Nos. 1 and 2) employ concentrated nitric acid. The use of this reagent in the determination of the total sulfur in rubber was first suggested by Henriques, and many investigators have shown that its use gives low results, probably on account

RESULTS OF TESTS FOR SULFUR

| METHOD | 1—Spence and Young | | | 2—Deussen | | | 4—Joint Rubber Insulation Committee | 5—Kaye and Sharp | | | 6—Frank and Marckwald | 7—Waters and Tuttle | 8 Extraction with acetone | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Filtrate | Residue | Total | Filtrate | Residue | Total | Total | Filtrate | Residue | Total | Total | Total | Extracted | Residue | Total |
| A | .... | .... | .... | .... | .... | .... | 4.90 | .... | .... | .... | .... | 4.87 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | 4.94 | .... | .... | .... | .... | .... | .... | .... | .... |
| B | .... | .... | .... | 4.53 | 1.66 | 6.19 | 6.26 | 3.63 | 2.43 | 6.06 | 6.00 | 6.29 | 0.51 | 5.74 | 6.25 |
| | .... | .... | .... | 4.84 | 1.41 | 6.25 | 6.31 | .... | .... | .... | 6.18 | 6.30 | 0.40 | 5.90 | 6.30 |
| | .... | .... | .... | 3.84 | 2.74 | 6.58 | .... | .... | .... | .... | 6.26 | 6.33 | 0.44 | 5.85 | 6.29 |
| | .... | .... | .... | 3.89 | 2.65 | 6.54 | .... | .... | .... | .... | 6.28 | 6.35 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 6.42 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 6.42 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 6.43 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 6.44 | .... | .... | .... |
| C | .... | .... | .... | 3.19 | 0.88 | 4.07 | 4.09 | 3.38 | 0.66 | 4.04 | 4.19 | 4.17 | 0.61 | 3.59 | 4.20 |
| | .... | .... | .... | 2.55 | 1.52 | 4.07 | 4.13 | 2.45 | 1.68 | 4.13 | 4.20 | 4.18 | 0.63 | 3.60 | 4.23 |
| | .... | .... | .... | .... | .... | .... | 4.19 | 3.32 | 0.86 | 4.18 | 4.28 | 4.20 | 0.60 | 3.64 | 4.24 |
| | .... | .... | .... | .... | .... | .... | 4.31 | .... | .... | .... | .... | 4.22 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 4.23 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 4.25 | .... | .... | .... |
| D | .... | .... | .... | .... | .... | .... | 1.73 | .... | .... | .... | .... | 1.65 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | 1.76 | .... | .... | .... | .... | 1.67 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | 1.78 | .... | .... | .... | .... | 1.70 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | 1.80 | .... | .... | .... | .... | 1.73 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | 1.81 | .... | .... | .... | .... | 1.75 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | 1.83 | .... | .... | .... | .... | 1.78 | .... | .... | .... |
| E | 4.91 | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 4.95 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 5.15 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 5.22 | .... | .... | .... |
| F | 5.39 | 2.33 | 7.71 | 7.47 | 0.47 | 7.94 | 7.78 | 6.89 | 0.21 | 7.10 | 7.72 | 7.90 | 3.59(a) | 4.22 | 7.81 |
| | 6.90 | 0.88 | 7.78 | 7.74 | 0.22 | 7.96 | 7.80 | 6.81 | 0.38 | 7.19 | 7.78 | 7.96 | 3.26(a) | 4.81 | 8.07 |
| | 6.42 | 1.36 | 7.78 | .... | .... | .... | 7.83 | .... | .... | .... | 7.80 | 7.96 | 4.02 | 4.06 | 8.08 |
| | 5.04 | 2.75 | 7.79 | .... | .... | .... | 8.01 | .... | .... | .... | 7.86 | 7.96 | 4.04 | 4.04 | 8.08 |
| | 4.67 | 3.17 | 7.84 | .... | .... | .... | 8.02 | .... | .... | .... | 7.88 | 8.00 | .... | .... | .... |
| | 5.05 | 2.81 | 7.86 | .... | .... | .... | .... | .... | .... | .... | .... | 8.01 | .... | .... | .... |
| | 4.52 | 3.38 | 7.90 | .... | .... | .... | .... | .... | .... | .... | .... | 8.02 | .... | .... | .... |
| | 4.71 | 3.26 | 7.97 | .... | .... | .... | .... | .... | .... | .... | .... | 8.09 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 8.11 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 8.12 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 8.12 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 8.13 | .... | .... | .... |
| G | 11.49 | 0.35 | 11.84 | 5.52 | 4.04 | 9.56 | 10.98 | 9.89 | 0.04 | 9.93 | 11.56 | 11.96 | 8.31 | 3.69 | 12.00 |
| | 11.45 | 0.40 | 11.85 | 5.51 | 4.71 | 10.22 | 11.34 | 9.77 | 0.57 | 10.34 | 11.64 | 12.00 | 8.14 | 3.88 | 12.02 |
| | 11.46 | 0.39 | 11.85 | 8.33 | 2.81 | 11.14 | 12.04 | 9.80 | 0.55 | 10.35 | .... | 12.04 | 8.06 | 3.97 | 12.03 |
| | 11.52 | 0.34 | 11.86 | 7.96 | 3.43 | 11.39 | 12.10 | 10.74 | 0.03 | 10.77 | .... | 12.08 | .... | .... | .... |
| | 11.36 | 0.53 | 11.89 | .... | .... | .... | .... | 10.42 | 0.41 | 10.83 | .... | 12.16 | .... | .... | .... |
| | 11.57 | 0.32 | 11.89 | .... | .... | .... | .... | .... | .... | .... | .... | 12.18 | .... | .... | .... |
| | 11.43 | 0.47 | 11.90 | .... | .... | .... | .... | .... | .... | .... | .... | 12.19 | .... | .... | .... |
| | 11.56 | 0.34 | 11.90 | .... | .... | .... | .... | .... | .... | .... | .... | 12.20 | .... | .... | .... |
| | 11.47 | 0.45 | 11.92 | .... | .... | .... | .... | .... | .... | .... | .... | 12.23 | .... | .... | .... |
| | 11.44 | 0.48 | 11.92 | .... | .... | .... | .... | .... | .... | .... | .... | 12.29 | .... | .... | .... |
| H | .... | .... | .... | 15.77 | 4.94 | 20.71 | 20.52 | 15.68 | 5.20 | 20.88 | 20.71 | 21.09 | 9.60 | 11.52 | 21.12 |
| | .... | .... | .... | 15.69 | 5.16 | 20.85 | 20.68 | .... | .... | .... | .... | 21.16 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | 20.74 | .... | .... | .... | .... | 21.20 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | 20.83 | .... | .... | .... | .... | 21.30 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 21.32 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 21.36 | .... | .... | .... |
| | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | 21.40 | .... | .... | .... |

(a) These samples were not completely extracted.

of the loss of free sulfur. Even when the sulfur which is remaining in the insoluble residue is included with that in the filtrate, the sum does not equal the calculated value.

The direct fusion methods (Nos, 3, 4, and 5) give results which are satisfactory only when the free sulfur content is relatively low. In view of the results obtained by the other fusion methods, it was not considered necessary to make any determinations by the Alexander method. The reaction between rubber and sodium peroxide often proceeds with explosive violence, particularly so when, as in this method, the sodium peroxide is not diluted with some less active flux. The more important points have been demonstrated by the results on the other methods, namely, (1)—that the direct fusion may give low results, and (2)—that the filtering of the solution of the melt after the addition of acid gives results which have no relation to the sulfur it is desired to determine.

Although the reaction during the fusion in the Kaye and Sharp method is not attended by an explosion, the results show that it is open to all the other objections which have been made above; hence it cannot be relied upon to give results which have any significance.

The results obtained by the method of the Joint Rubber Insulation Committee (No. 4) are accurate when the free sulfur is low, as it is in insulation compounds, so that it may be relied upon to do all that this committee has claimed for it. This has been also substantiated by the work of the Analytical Committee of the Rubber Section of the American Chemical Society.[1] Whenever the free sulfur content is high, our results indicate that this method has the same serious defect as the other direct fusion methods.

The methods which require both solution and fusion yield the most satisfactory results. One of these (the Waters and Tuttle method) has already been referred to. The Frank and Marckwald method is at times very satisfactory, but unfortunately it does not seem reliable with large amounts of free sulfur. The reaction between the rubber and the fuming nitric acid is at times very violent and considerable heat is evolved. In fact in several cases, by adding only 1 or 2 cc. of the acid, the heat was so great as to cause the rubber to take fire. It seems probable that this heating is responsible for the loss of sulfur and the consequent low results.

In view of the fact that the free sulfur can be determined by several methods (one of which has already been described) with considerable accuracy in the acetone extract, and since this determination is usually made in analyses of vulcanized rubber goods, it is possible, and in some cases may be convenient, to determine the total sulfur by adding to the result for free sulfur, the amount found in the residue after acetone extraction. Such a method would have the advantage of first removing the free sulfur, which has been found to be one of the most disturbing factors in many of the methods for the determination of total sulfur. Our experience indicates that accurate results can be obtained by this method.

We have determined the sulfur remaining in the rubber after the acetone extraction, by the Waters and Tuttle method. It is more than possible that other methods will be equally efficient.

### OUTLINE OF THE METHOD ADOPTED BY THE BUREAU OF STANDARDS

As the result of this and other investigations and the experience of the Bureau of Standards, extending over some years, we believe that the Waters and Tuttle method is the most reliable and it has been adopted for use in the routine work there. The determination is made as follows:

Half a gram of rubber is placed in a porcelain crucible of about 100 cc. capacity, 20 to 25 cc. of concentrated nitric acid which has been saturated with bromine, are added, the crucible covered and allowed to stand for 1 hour. It is then heated gently for 1 hour; after which the cover is removed, rinsing it with a little distilled water, and the solution is evaporated to dryness.

Five grams of fusion mixture (1 potassium nitrate : 1 sodium carbonate) and 3 or 4 cc. of distilled water are added, the mixture is digested for a few moments on the steam bath and then spread halfway up the side of the crucible to facilitate drying. The drying is done on a steam bath or electric hot plate; in the latter case care is taken to avoid spattering caused by possible overheating. When dry, the mixture is fused over a sulfur-free flame until all the organic matter has been destroyed and the melt is quite soft. The crucible and contents are cooled, placed in a 600 cc. beaker, covered with distilled water and heated on the steam bath for 3 or 4 hrs. The solution is then filtered and the insoluble matter washed thoroughly. The combined filtrate and washings should amount to about 500 cc. About 7 or 8 cc. of concentrated hydrochloric acid are added, the beaker covered, and the solution heated almost to boiling. The solution is now tested and if necessary made slightly acid toward Congo paper; if the directions have been followed exactly, there should be a slight excess of acid present. Ten cc. of 10 per cent barium chloride solution are added, and the solution is allowed to stand over night. The precipitated barium sulfate is filtered off and ignited over a small Bunsen flame, care being taken to see that the filter paper does not inflame. The barium sulfate is calculated to sulfur by means of the factor 0.1374.

### SUMMARY

It is shown that the methods which have been proposed for the determination of the total sulfur other than that present as insoluble metallic sulfates, are not satisfactory.

It is shown that loss of sulfur is likely to occur in the direct fusion methods, and this loss is apt to increase with increasing free-sulfur content.

The method of Waters and Tuttle is recommended for the determination of total sulfur. This method is accurate and comparatively rapid, and has given

[1] This Journal, 6 (1914), 514-518

satisfactory results in the hands of a number of analysts over a rather extended period of time.

A new suggestion is offered, namely, to determine separately the free sulfur and the sulfur remaining after the acetone extraction, reporting the sum of the two quantities as the total sulfur. This procedure eliminates the troublesome effect of the free sulfur upon the determination of the total sulfur.

The authors wish to express their appreciation of the many suggestions made by Dr. C. E. Waters, of this Bureau, and of the assistance given by the Voorhees Rubber Mfg. Co., of Jersey City, in permitting us to make up some compounds of known composition in their factory.

Bureau of Standards, Washington, D. C.

## PRELIMINARY EXPERIMENTS ON THE EFFECT OF TEMPERATURE CONTROL ON THE YIELD OF PRODUCTS IN THE DESTRUCTIVE DISTILLATION OF HARDWOOD

By R. C. Palmer[1]

Received April 6, 1915

It is well known that in the destructive distillation of wood the products methyl alcohol and acetic acid are formed by a decomposition of the wood substance and that the reaction is accompanied by an evolution of heat. The heat supplied by the exothermic character of the decomposition when added to the heat furnished from some external source, tends to raise the temperature at which the reaction is taking place. Increasing the temperature of the wood beyond the point where spontaneous decomposition takes place will increase the speed or violence of the reaction, and this condition in turn will accelerate the rate at which the temperature is further increased.

There can be no doubt that subjecting the methyl alcohol and acetic acid to an excessive temperature at the moment of formation may result either in an immediate decomposition of some of these products or may prevent their formation from some intermediate products, and probably increases the tendency for many secondary reactions to take place.

Several facts would seem to fully substantiate this viewpoint. The yield of alcohol and acid in the destructive distillation of wood is much less than the proportion of methoxy and acetyl groupings would lead one to expect. Small scale distillations, where the opportunity for secondary decomposition and interreactions are minimized by better control, frequently yield much more acid or alcohol than the usual commercial distillations.

These fundamental considerations indicate that the speed and temperature of the destructive distillation reaction have an important effect on the formation of alcohol and acid. It would seem then that the amount of these products could be materially increased:

1—By causing the reaction to take place at as low a temperature as possible.

2—By decreasing the speed of the reaction.

These two methods may be in effect the same under certain circumstances, owing to the exothermic nature of the reaction, since low temperature distillation is a result of slowing down the reaction.

The fact that increasing the time of distillation will increase the yield of valuable products is generally known in commercial wood distillation practice. Lengthening the time of the complete process simply means slowing down the entire decomposition. In the study described in this paper, the application of temperature control to the critical stage of the decomposition has shown that a similar result may be obtained without increasing the time.[1]

### EXPERIMENTAL

In making a large number of destructive distillations[2] in laboratory apparatus as a part of studies on the relative value of different species of hardwoods, it became apparent that the temperature at which the reaction took place and the critical stage had as much influence on the yield of products as the theoretical considerations would indicate.

A more detailed laboratory study of this interpretation of temperature control was therefore made. The basic principles developed were then applied to a commercial plant in order to determine their practicability. The experiments were carried on at the Forest Products Laboratory,[3] Madison, Wis., and in the plant of the Cleveland Cliffs Chemical Company, Gladstone, Mich., as a part of a series of studies on methods of increasing the yields of valuable products in the destructive distillation of hardwoods.

This opportunity is taken to acknowledge the assistance and many helpful suggestions of Mr. H. C. Merriam, operating superintendent in the wood distillation plant of the Cleveland Cliffs Iron Company, in conducting the commercial experiment and interpreting and applying the results.

### PART I—LABORATORY DISTILLATION

APPARATUS—The retort used in the laboratory studies is shown in Fig. 1. This retort (A) held approximately 80 lbs. of wood. The oil jacket (B) completely surrounded the circumference of the retort, the ends being insulated with heavy asbestos packing. The oil was heated by means of a row of 20 Bunsen burners, the flame playing largely on the side of the oil jacket, as in this way it was found that a fairly good natural circulation of the hot oil could be obtained. By means of the Bunsen burners the temperature of the heating medium was controlled fairly easily.

The temperature within the retort was measured in three places: At (1) which is close to the inner shell of the retort, directly above the point where the flames play on the oil jacket; the temperature at this point was also approximately the highest temperature of the oil at all times; at (4) which is a point at the bottom

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[1] Attention was first called to the effect of "slow and fast" distillation on the yield of products by Sennft, but since the comparison was made between distillation from the cold and distillation beginning with red hot retorts, the results could not be interpreted to actual practice.

[2] A detailed description of methods of distilling the wood and analysis of products is given in United States Department of Agriculture, *Bull.* **129**, "Yields from the Destructive Distillation of Certain Hardwoods."

[3] Maintained by the Forest Service, U. S. Department of Agriculture, in coöperation with the University of Wisconsin.

of the retort near the inner shell corresponding to (1); and at (5), the center of the retort.

UNCONTROLLED DISTILLATION—The laboratory retort distillations were made in all cases on pieces of wood approximately 18 in. × 2½ in. × 1 in. sawed from 1 in. lumber to insure average material. The raw material consisted of maple, beech, and birch. The largest number of tests were made with maple and the best comparisons obtained with this species. The samples tested in comparative runs did not differ more than 2 or 3 per cent in moisture content, and showed from 12 to 15 per cent of the dry weight as moisture.

For the purposes of studying the effect of control it was necessary to have for comparison distillations conducted rapidly and at a comparatively high temperature. The manner of making the distillations was as follows: The burners were so regulated that the maximum temperature of the oil was not higher than 270° C. until the center of the retort reached at least 175° C., at which point it was considered that the moisture in the charge was largely distilled off. As soon as the center temperature was about 175°, the gas was so regulated that the oil was raised as quickly as possible to about 350° C.[1] and the distillation allowed to proceed to the end. The distillation practically stopped when the center reached its maximum temperature and began to fall. In all cases this maximum in the center was higher than the temperature of the oil (indicated at (1)) showing the exothermic character of the reaction. The exothermic reaction was further indicated by a rise of 30 to 50° C. in the center after the gas was turned off and the temperature at (1) was falling.

A distillation of this kind was comparable in many ways with the commercial method of distilling, especially in relation to the rise in temperature during the critical part of the distillation.

The exothermic destructive distillation of hardwood begins at approximately 275° C. and this point is indicated by the appearance of free tar in the distillate. In the laboratory, where the temperature difference between the heating medium and the wood is negligible and the variation in temperature in different parts of the retort is not great, the critical part of the distillation may be considered either as the period after the average temperature has reached 275° or after tar appears in the distillate.

CONTROLLED DISTILLATION—The control of the distillation, as interpreted in this study, required that the largest possible portion of the reaction be completed at the lowest possible temperature, or, in other words, that the rate of rise of temperature during the critical state of the reaction should be at its minimum. The control distillations were conducted by regulating the burners so that the heating medium was not higher than the critical decomposition temperature (275 to 300° C.) until the temperature in the retort and the rate of flow of distillate indicated that the reaction was being stopped. The center temperature indictaed at (5), (Fig. 1) usually passed 275° C. and reached nearly 300° C. when the temperature in (1) began to fall, indicating the checking of the reaction. The oil bath was then raised as quickly as possible to 350° C. and the distillation allowed to finish.

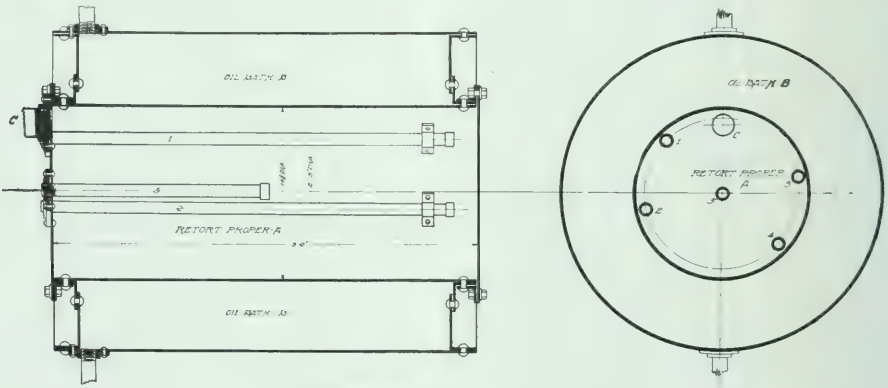


FIG. 1—EXPERIMENTAL LABORATORY RETORT

The crude pyroligneous acid liquor obtained in the distillations was analyzed for its acetic acid and alcohol content by the methods given in "Technologie der Holzverholung," by M. Klar, p. 337.

### RESULTS OF LABORATORY TESTS

The results of the laboratory tests are given in Table I. The data are given (1) in terms of percentage of wood alcohol and acetic acid per unit weight of the oven-dry wood distilled and (2) as gallons of 95 per cent alcohol and lbs. of 80 per cent acetate of lime per cord of wood. One cord is taken as 80 cu. ft. of solid wood based on actual determination of a commercial cord which equaled 3425 lbs. for maple wood containing 15 per cent of its dry weight as moisture.

From these data the effect of controlling the distillation is seen to increase the yield of alcohol 45 per cent for maple, 6 per cent for beech, and 7 per

[1] The oil used was a high flash cylinder oil, f. p. 330° C. The temperature was raised above this point by keeping the oil under 15 to 20 pounds pressure, the pressure being relieved only when the decomposition became excessive as indicated by a rapid rise in pressure.

cent for birch, while the increase in acetic acid was 2, 9, and 5 per cent, respectively.

INTERPRETATION OF RESULTS—The curves designated X in Fig. 2 show the relation between the percentage of total distillate and the average temperature of the retort (average of the temperatures indicated at (1) and (5), Fig. 1). Curve A is the average for the con-

TABLE I—RESULTS OF LABORATORY TESTS ON EFFECT OF TEMPERATURE CONTROL ON YIELDS OF DISTILLATION PRODUCTS

| | Yield of Wood Alcohol | | | | Yield of Acetic Acid | | | |
|---|---|---|---|---|---|---|---|---|
| | Uncontrolled | | Controlled | | Uncontrolled | | Controlled | |
| Species of Wood Used | % of wt. of dry wood | Gal. 95% alc. per cord | % of wt. of dry wood | Gal. 95% alc. per cord | % of wt. of dry wood | Lbs. 80% acetate of lime per cord | % of wt. of dry wood | Lbs. 80% acetate of lime per cord |
| Maple | 1.56 | 7.4 | 2.16 | 10.2 | 5.29 | 240 | 6.30 | 290 |
| | 1.59 | 7.5 | 2.36 | 11.15 | 5.74 | 267 | 5.45 | 251 |
| | 1.62 | 7.6 | 2.41 | 11.25 | 5.91 | 275 | 5.52 | 256 |
| Av. | 1.59 | 7.5(a) | 2.31 | 10.90 | 5.65 | 261(b) | 5.76 | 266 |
| Beech | 2.01 | 9.2 | 2.15 | 9.80 | 5.70 | 259 | 6 28 | 285 |
| | 2.03 | 9.28 | .. | ... | 5.78 | 262 | | ... |
| | 2.07 | 9.45 | .. | ... | 5.85 | 266 | | ... |
| Av. | 2.04 | 9.31 | 2.15 | 9.80 | 5.77 | 262 | 6.28 | 285 |
| Birch | 1.59 | 6.95 | 1.73 | 7.6 | 6.58 | 284 | 6.96 | 301 |
| | 1.67 | 7.32 | 1.76 | 7.7 | 6.50 | 281 | 6.78 | 292 |
| Av. | 1.63 | 7.15 | 1.75 | 7.65 | 6.54 | 282 | 6 87 | 296 |

(a) The average yield from a number of more normal uncontrolled laboratory distillations on maple was 9.00 gallons of alcohol and 253 pounds of acetate.

(b) In converting the acetic acid yields to acetate of lime, the results have been decreased 5 per cent in order to allow for the usual commercial sludge loss.

trolled distillations and curve B the average for the uncontrolled distillations obtained with maple wood. The tar point has been indicated on each curve and the portion of the curve above the tar point, principally that nearest to it, is considered the critical stage of the distillation.

From curves A and B, it would appear that two things might account for the marked increase in alcohol:

1—The actual temperature at which the reaction has taken place in curve A is from 20 to 50° C. lower than curve B.

2—The rate at which the distillation has taken place, indicated by the per cent distillate per degree rise, is slower for A than for B. The first 20 per cent of distillate after the tar point in curve A came off during a rise in temperature of 22° while at a corresponding period in curve B the rise was 33°.

The uncontrolled runs given for maple were pushed as fast as possible in order to give a reaction that would determine the extreme effect of this procedure as compared with especially controlled methods. A number of more normal uncontrolled distillations for this species gave 9.00 gal. of alcohol per cord and 253 lbs. of acetate. The curve is not shown for these runs; it lies very nearly between A and B but with a slope more like curve B.

Similar curves for the distillations on beech and birch have not been shown, but these were found to lie much closer together than the curves for maple and have only slight differences in rate of distillation (upward slope of curve). It may, therefore, be considered that the comparatively small increases in yields for these species are explained by relatively less actual control of the distillation as compared to the runs with maple.

In the case of the maple runs the yields of alcohol obtained in the laboratory tests, particularly those obtained in the more normal uncontrolled distillations, are very nearly the same as yields from commercial plants, but the yields of acetate are about 40 per cent higher than commercial yields. It will be noted that the small average increase in acetate in the controlled runs is due to an exceptional run while the yields from the other two are actually lower than two of the uncontrolled runs. Neither varying the temperature of the reaction within the limits of the laboratory test nor a change in the rate of distillation appears then

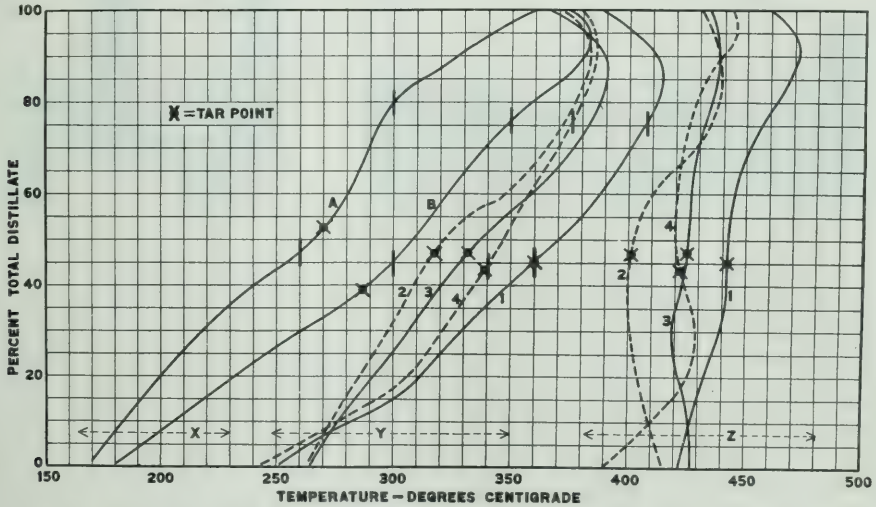


FIG. 2 RELATION BETWEEN TEMPERATURE AND DISTILLATE

X = Laboratory Retort Vapors Y = Commercial Retort Vapors Z = Commercial Retort Flues

to be the cause of the high acetate yield. However, it was known that the temperature at which the distillation reaction is carried out commercially is much higher than in the laboratory and an application of this fact seemed to be a possible method of approaching the laboratory yield.

In order to test the practical value of these results, it was, of course, necessary next to conduct distillations with a commercial retort. The commercial test was made (1) to measure the yields of alcohol and acetate produced by approaching the laboratory temperature during the critical stage, especially since the commercial acetate yield was so much lower than the laboratory results; (2) to determine if the increase in yield of alcohol produced by a control of the speed of the exothermic reaction could be duplicated on a large scale; and (3) to determine the economic application of any results obtained.

### PART II—COMMERCIAL DISTILLATION

APPARATUS—A diagrammatic sketch of a commercial retort and setting similar to the one used in the test is shown in Fig. 3. The retort held two cars,

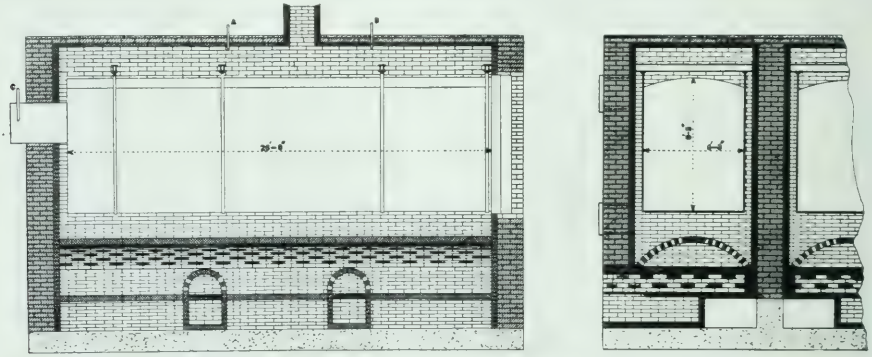

FIG. 3—EXPERIMENTAL COMMERCIAL RETORT

each having a capacity of $2^1/_4$ cords, or a total of $4^1/_2$ cords of wood. The retort was fired at two points on one side and the hot gases passed along the bottom of the retort in opposite directions, up the sides and ends before passing up the stack. A and B were pyrometers placed in the top flue gases and the average temperature at these points was taken as the average temperature of the heat being applied to the retort. The pyrometer C was located in the center of the outlet pipe as close to the retort as the outer brick casing would permit and its readings were assumed to be the average temperature to which the distillation vapors had been subjected in the retort.

The retort was fired with soft coal and at certain periods with the uncondensable gases coming from some other retort. The experimental retort was one of a battery of ten, five of which supplied fuel gas to the other five during about 7 out of 24 hours.

MANIPULATION—The experiments were made while the entire plant was in usual operation and in order to determine the yields from the single retort the distillate was caught in 50-gal. barrels. The distillate was thoroughly mixed in the barrels and samples of equal volume taken from each. The mixed sample, therefore, represented an average of the entire distillate. This sample was analyzed[1] for alcohol and acetate by commercial methods of determining the yields of products in this manner.

The total amount of wood for each charge was weighed and the relative amount of each species determined and moisture samples taken.

At the outset it was of course evident that the practical value of the test depended on introducing no procedure that would reduce the efficiency of operation. Since an increase in the time of distilling seemed the most likely drawback, it was decided to vary the method of firing or change the manner of distillation only so as to insure that the run would be finished in the usual cycle of 24 hours. Without exception the retort was "pulled" at the end of that time.

The raw material consisted of 93 per cent maple, 4 per cent birch, and 3 per cent beech, as an average. It was in all cases 4-ft. cord wood ranging from 6 to 8 in. in maximum diameter. From 35 to 45 per cent of the dry weight of the wood was water, which was 10 to 20 per cent more moisture than the average distillation wood contains. In view of the necessity of adhering to the 24 hour cycle, the high moisture content materially shortened the time available for temperature control.

DISTILLATION—Observations of the temperatures produced by the usual method of firing were first made and the yields determined for comparative purposes.

With the apparent effect of the temperature of distillation as an explanation of the high yields of acetate in the laboratory, experiments were first made in which the critical distillation point was brought as nearly as possible to the laboratory temperature.

In the commercial test, where the heating medium is necessarily at a much higher temperature than that desired in the retort because of the large diameter to be penetrated, the critical stage could not be observed, except by the indication of tar in the distillate. All distillations were, of course, made from a hot retort,

[1] The methods of analysis were the same as those used in the laboratory tests.

the previous charge being "pulled" within two hours at most after finishing.

It was at once apparent that the temperature was not the important factor since the laboratory yields were not approached.

In attempting to carry the distillation within the low temperature range of the laboratory retort, it was found that the critical stage of the distillation proceeded very rapidly for a while, but had to be pushed hard at the end, in order to complete the run in 24 hours.

A series of runs was then made in which the method of firing was varied in several ways, in order to produce differences in the temperature at which the exothermic reaction took place and also the rate of distillation during the critical state.

### RESULTS OF COMMERCIAL TESTS

The results of the different distillations on the commercial retort are given in Table II. The different runs were not made consecutively, but have been divided into groups including similar tests.

The results are given both in percentage of the unit weight of dry wood and in the commercial units, gal.

TABLE II.—RESULTS OF COMMERCIAL TESTS TO DETERMINE THE EFFECT OF TEMPERATURE CONTROL ON THE YIELDS OF DISTILLATION PRODUCTS

| Group No | Lbs. wood per cord: As used for tests | Lbs. wood per cord: Free from moisture | % moisture(a) based on dry weight | Wood alcohol: % of wt. of dry wood | Wood alcohol: Gal. 95% alc. per cord | Acetic acid: % of wt. of dry wood | Acetic acid: Lbs. of 80% acetate(b) of lime per cord | Charcoal: % of wt. of dry wood | Charcoal: Lbs. per cord (20 lbs. to bu.) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4265* | 3025 | 41.0 | 1.70 | 8.2 | 3.75 | 187 | 36.4 | 53.5(d) |
| 2 | 4250 | 3025 | 40.6 | 1.99 | 9.56 | 4.05 | 201 | 34.2 | 51.75 |
| | 4120 | 3010 | 36.9 | 2.01 | 9.63 | 3.92 | 194 | 35.5 | 53.5 |
| | 4075 | 2910 | 40.0 | 2.09 | 9.67 | 4.03 | 188 | 34.7 | 50 |
| Av. | 4160 | 2982 | 39.2 | 2.03 | 9.62 | 4.03 | 194.5 | 34.8 | 51.75 |
| 3 | 4050* | 2965 | 36.5 | 2.06 | 9.73 | 4.36 | 213 | 36.5 | 54.25 |
| | 4070* | 2970 | 37.2 | 2.07 | 9.8 | 4.34 | 212 | 37.6 | 54.75 |
| | 4325 | 3000 | 44.4 | 2.16 | 10.32 | 4.15 | 205 | 37.2 | 56.25 |
| | 4060 | 2965 | 36.9 | 2.11 | 9.95 | 4.24 | 207 | 36.0 | 53.5 |
| Av. | 4125 | 2975 | 38.75 | 2.10 | 9.93 | 4.25 | 209 | 36.9 | 55.4 |
| 4 | 4175* | 3000 | 39.2 | 2.18 | 10.42 | 4.24 | 209 | 37.8 | 56.5 |
| | 4040 | 3025 | 33.5 | 2.25 | 10.78 | 4.39 | 218 | 34.4 | 52 |
| | 4175 | 3000 | 39.2 | 2.27 | 10.80 | 4.33 | 214 | 37.4 | 56 |
| | 3860(c) | 2805 | 37.7 | 2.30 | 10.27 | 4.45 | 205 | 34.7 | 49 |
| Av. | 4130 | 3008 | 37.3 | 2.23 | 10.66 | 4.32 | 213.6 | 36.4 | 54.8 |

(a) The moisture content of runs * were not determined but were estimated from runs with corresponding weights per cord that were determined.

(b) The acetate included 15 pounds per cord obtained from the settled tar by distillation.

(c) This run was not included in the average for this group as the charge consisted of very badly decayed wood, also shown in the light weight per cord. The curves for this run were the same as the average for the group. The yields in per cent of dry wood are seen to be the highest of any run but the light weight per cord brought down the yields on the cord basis.

(d) Estimated from a number of commercial distillations.

of 95 per cent wood alcohol and lbs. of 80 per cent acetate of lime per cord.

INTERPRETATION OF RESULTS—The results have been interpreted as in the laboratory tests by drawing the curve showing the relation between the percentage of total distillate and the temperature. These curves are shown in Fig. 2 for comparison with the laboratory tests. The curves are numbered to correspond with the groups and are the average of all the runs in that group. The curves designated Y show the relation between the distillate and the temperature of the vapors (indicated by the pyrometer C, Fig. 3) while the curves Z show the relation between the distillate and the heat applied to the retort (indicated by the pyrometers A and B, Fig. 3) for the corresponding groups. The results for the different groups are summarized in Table III.

GROUP 1—This is the usual commercial method of firing and has been described as "fast drying—fast exothermic reaction."[1] The method of firing to produce this kind of distillation is clearly indicated in Fig. 2, curve Z1. The temperature of the retort is raised continually until the destructive distillation point is indicated by the flow of distillate and the appearance of tar. The fire is then held steady for a while and then pushed at the end to "make charcoal." It should be noted especially that curve Y1 is very close to the general slope of B—the uncontrolled laboratory distillation.

TABLE III.—SUMMARY OF EFFECT OF TEMPERATURE CONTROL ON THE YIELDS OF PRODUCTS

| Condition | Wood Alcohol: Gals. 95% per cord | Wood Alcohol: Increase over uncontrolled runs % | Acetate: Lbs. 80% per cord | Acetate: Increase over uncontrolled runs % | Charcoal: Bushels per cord |
|---|---|---|---|---|---|
| Laboratory uncontrolled | 7.50 | .. | 261 | .. | ... |
| Laboratory controlled | 10.90 | 45 | 266 | 2 | ... |
| Commercial Group 1—Fast drying, fast exothermic | 8.2 | .. | 187 | .. | 53.5 |
| Commercial Group 2—Slow drying, fast exothermic | 9.62 | 17.3 | 194.5 | 4 | 51.75 |
| Commercial Group 3—Faster drying, slower exothermic than Group 2 | 9.93 | 21.1 | 209 | 11.8 | 55.4 |
| Commercial Group 4—Fast drying, slow exothermic | 10.66 | 30 | 213.6 | 14.2 | 54.8 |

GROUP 2—In this group is shown the effect of bringing the distillation temperature as low as possible for as long a time as the cycle would allow. In curve Y2 it is seen that the distillation reaction went very rapidly after the tar point was indicated. These runs have been designated as "slow drying—fast exothermic." In all cases the rise in temperature is due partly to the exothermic heat and partly to the external fire but in this group much of the rapid sloping off of the curve is due to the exothermic reaction. In distillations of this kind the bottom of the retort became so hot that in practice this procedure would be impractical for continuous operation because of excessive depreciation.

Curve Z2 shows the manner of firing. It should be pointed out that the cold wood in the hot retort at the start takes up a large amount of heat and while the temperature of the fire was actually being lowered the normal quantity of fuel was consumed.

Compared with Group 1, the method of distillation showed an appreciable increase in alcohol and acid.

GROUP 3—This group is really a modification of Group 2 and is, therefore, described as "faster drying—slower exothermic reaction than Group 2." This is clearly seen in curve Y3. Curve Z3 shows that the retort was fired by allowing the temperature to fall slightly during the first part of the drying stage and then keeping the fire on a gradual rise until the last few hours when the temperature was increased more rapidly in order to insure good charcoal.

[1] Most of the curves Y up to the tar point simply indicate the removal of moisture from the charge. The moisture content of the different groups was as follows: (1), 41 per cent; (2), 39.2 per cent; (3), 38.75 per cent; (4), 37.3 per cent. These are close enough together to make the curves entirely comparable. An analysis of the distillate up to the tar point was made for one run in Group 3 and indicated 21.9 per cent of the total alcohol and 28.7 per cent of the total acetate obtained in the run.

A decided increase in yields over Group 2 is shown. In the light of the laboratory curves, this increase must be attributed to the slower exothermic reaction rather than the effect of temperature.

GROUP 4—The results obtained by the method of distilling used for this group prove conclusively the importance of the rate of distillation on the yields of alcohol and acid, since the highest yields are obtained in these runs. As shown by the curves, these runs were made by "fast drying and slow exothermic reaction."

Referring to curve $Z_4$, it is seen that the drying period was accomplished by a rapid rise in temperature (or steady firing), and in this stage the distillation curve $Y_4$ parallels curve $Y_1$ very closely.

The important procedure in achieving this manner of distillation was the anticipation of the tar point as indicated in the bending back of the Z curve before the tar appeared. In practice, if the distillate can be observed as it flows from the end of the condenser, the time to lower the temperature of the fire would be noted by the first appearance of particles of tar, which precedes the true tar point by from one to two hours. When wood of a uniform moisture content was being used, this method might, however, be replaced by firing at a definite time period.

A comparison of curve $Y_4$ with curve A of the laboratory-controlled runs indicates the similarity of the slopes of these curves, especially after the tar point.

FUEL—The fuel required in the different groups is given in Table IV.

TABLE IV—FUEL USED IN COMMERCIAL TEST PER CORD OF WOOD DISTILLED

| Group No. | Coal Pounds | Gas Hours | Total fuel as coal Pounds |
|---|---|---|---|
| 1 | 240 | 10 | 412 |
| 2 | 352 | 4 | 412 |
| 3 | 250 | 10 | 407 |
| 4 | 275 | 12 | 463 |

Owing to the variation in the length of time gas was used, the results, as actually measured, are not comparable. On the basis of one run made without gas, which required 412 lbs. of coal per cord, compared with Group 1, in which 240 lbs. of coal and 10 "hrs." of gas were used, 1 hr. of gas was taken as equivalent to 15 lbs. of coal per cord. Then on calculating the "hrs." of gas into coal for the different groups, the results are shown in the last column of Table IV under "total fuel as coal." On this basis, Group 4, which gives the highest yields of alcohol and acetate, would require the equivalent of about 50 lbs. more coal per cord. This would be practically negligible where waste wood was used as fuel, but with coal at $3.50 per ton it would amount to about 10 cents per cord additional fuel cost.

## COMMERCIAL APPLICATION

In the commercial application of temperature control as developed in this preliminary study, an accurate method of measuring temperature would be required, and probably for successful operation also the employment of a head fireman. Economically the balance is apparently drawn between the cost of installing pyrometers, the employ of a day and night head fireman for at least each 50 cords per day distilled, and the additional small fuel cost per cord, as compared with a possible increase in yield of 25 lbs. of acetate and $2^1/_2$ gals. of alcohol per cord. Also the control distillations were shown to be possible within the time required for the usual cycle of operation.

## CONCLUSIONS

It was shown in the small scale distillations that a lowering of the temperature of the process and decreasing the speed with which it took place gave marked increases in the yields of alcohol. Also the laboratory methods gave much higher yields of acetic acid than those obtained commercially but this yield was not greatly affected by varying the laboratory methods.

It is now seen in applying these variations in methods of distilling on a much larger scale that a change in the rate of distillation produces practically the same results on the yield of alcohol while the actual temperature of the reaction is not shown to be of as great importance. If it could be shown that the formation of alcohol in the destructive distillation reaction and its probable secondary decomposition into methane and carbon monoxide in the presence of the hot charcoal is reversible, the increase in alcohol by control of the reaction, allowing an accumulation of the end products, would be easily explained.

If the products after formation are lost by decomposition, the greater stability of alcohol after formation as compared to acetic acid seems evident since the large retort which probably involves many interreactions gives practically the same yields of alcohol as the small apparatus while the acid yield is much less than the laboratory yield.

Any process of approaching the high laboratory production of acetic acid will probably have to involve some method of preventing the interreactions in the large apparatus.

It is not improbable that still higher yields than those given can be obtained in the commercial plant with the application of temperature control alone. Thoroughly air-seasoned wood would require appreciably less time to enter into the destructive distillation stage, thus giving a better opportunity to lengthen the period of slow reaction. The drying stage would also not require so high a temperature at the end, thus bringing all but the last portion of the reaction into a lower range of temperature.

These tests are considered as a preliminary indication of the results that may be obtained from this interpretation of temperature control. The study of this phase is being continued by longer runs comprising an entire plant. Other phases of directing the destructive distillation reaction of wood to produce maximum yields of products are also being made by the United States Forest Products Laboratory.

## SUMMARY

I—Destructive distillations of hardwood in the laboratory on 70-lb. samples indicated that lowering the temperature of the reaction and decreasing the speed of the distillation at the critical stage increased the yield of methyl alcohol 45 per cent.

II—The laboratory distillations gave 40 per cent more acetate of lime than commercial yields, but the acetic acid was not greatly influenced by variations in the method of distilling.

III—The application of the laboratory methods to a commercial retort holding $4^1/_2$ cords of wood indicated possible yields of alcohol 30 per cent higher than by the usual methods of firing and an increase of 15 per cent in yields of acetate of lime.

IV—The best results were obtained by slow distillation during the critical stage rather than by lowering the temperature at which the reaction took place. This was accomplished by rapidly removing the moisture content of the wood in the first stages, and then anticipating the period when destructive distillation or critical stage began. At this point the temperature of the fire was decreased.

V—This method of temperature control gave promise of being entirely applicable in the commercial plant. The fuel requirements were only slightly higher than the usual methods of firing and the cycle of operation was not changed.

VI—The studies of temperature control have shown that wood alcohol either exhibits sufficient stability in the retort or its formation is of a simple enough character to allow it to be easily effected and the amount recovered greatly increased. Acetic acid, however, is apparently much more subject to variations in the original wood decomposition and methods of preventing the many interreactions going on in the complex vapors of a large retort will be required to secure yields of this product that will more nearly approach the theoretically possible yields.

FOREST PRODUCTS LABORATORY, MADISON, WISCONSIN

## THE DETERMINATION OF BENZOL IN GAS MIXTURES[1]

By G. A. BURRELL AND I. W. ROBERTSON

Received April 29, 1915

With the present great demand for benzol and the installation of plants at different places for obtaining this constituent, there has arisen a demand for a rapid method of determining the benzol content of gas mixtures. Hence a scheme follows which the authors have used in determining it in the carbureted mixed coal and water gas of Pittsburgh. Fig. 1 illustrates the apparatus. The bulb contains phosphorus pentoxide for removing water vapor. To start a determination the apparatus is connected to a vacuum pump and exhausted of its air: a Gerky pump will do. The gas mixture is then introduced at atmospheric pressure, the barometer read, and the two bulbs immersed in a mixture[2] of solid carbon dioxide and acetone or alcohol. After waiting about 10 minutes, as much gas as possible is withdrawn from the bulbs by means of the vacuum pump. The gases removed will be those of high vapor pressure at —78° C. In the case of the mixed coal and water gas the authors worked with, they are $CO_2$, $O_2$, CO, $H_2$, $CH_4$, $N_2$, $C_2H_4$, $C_2H_6$, $C_3H_6$, $C_3H_8$ and $C_4H_8$; in fact, practically all the gases except the benzol. Next the stopcock on the apparatus is closed, the cooling mixture removed, and the benzol allowed to vaporize at room temperature. Its pressure is then read on the side-arm mercury manometer attached to the apparatus. This pressure compared with the atmospheric pressure gives the percentage of benzol in the gas mixture. The results of two determinations are shown in Table I.

TABLE I—BENZOL DETERMINATION IN PITTSBURGH GAS

| SAMPLE NO. | 1 | 2 |
|---|---|---|
| Original pressure of gas | 744 mm. | 744 mm. |
| Partial pressure of benzol vapor | 10 mm. | 9 mm |
| PERCENTAGE OF BENZOL | $\frac{10 \times 100}{744} = 1.34$ | $\frac{9 \times 100}{744} = 1.31$ |

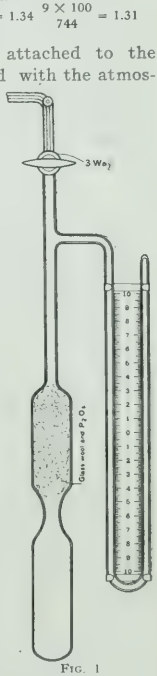


FIG. 1

To obtain other data on this method of separation, the distillate from the above freezing process was next passed into fuming sulfuric acid. In the case of Sample No. 1 there was obtained 7.32 per cent of illuminants, and in the case of Sample No. 2, 7.39 per cent. The total illuminants in the Pittsburgh gas, as found by absorption in fuming sulfuric acid, is 8.67 per cent. In other words, the benzol percentages as found when added to 7.32 and 7.39, respectively, equal 8.66 and 8.70 per cent, or almost identically the same quantities as the total illuminants in the coal gas.

Benzene reacts with oxygen as follows:

$$C_6H_6 + 7.5O_2 = 6CO_2 + 3H_2O.$$

The contraction is 2.5 volumes and the carbon dioxide is 6 volumes. Table II shows the results of analysis of the residual vapor that was held in the liquefaction bulb (Fig. 1) when the coal gas was cooled at a temperature of —78° C. Before analysis the benzol was diluted with air.

TABLE II—ANALYSIS OF BENZOL VAPOR

| | Cc. |
|---|---|
| Volume taken for analysis | 28.29 |
| Oxygen added | 51.94 |
| Total volume | 80.23 |
| Volume after burning | 75.47 |
| Contraction due to burning | 4.76 |
| Volume after KOH absorption | 64.25 |
| Carbon dioxide produced by burning | 11.42 |

It will be observed that the ratio of the carbon dioxide to the contraction is almost exactly 6 : 2.5, showing that the vapor obtained in the benzol determination was principally benzol. Traces of other easily condensible vapors may have been present but apparently in such small quantities as to be negligible.

The authors were unable to find, in the literature, the vapor pressure of benzol at —78° C., but apparently it is very small. Benzol boils at 80.12° C.: at —20° the vapor pressure is 5.76 mm.[1] The authors prepared saturated vapors of benzol by shaking the pure liquid with air. It was a simple matter to pre-

[1] Published with the permission of the Director of the Bureau of Mines.

[2] This mixture gives a temperature of about —78° C. The solid carbon dioxide, obtained by releasing the gas from a commercial cylinder, through a cloth towel, is mixed with acetone or alcohol to the consistency of slush.

[1] Landolt and Börnstein Tables, **1905**, p. 143; according to Regnault.

pare unsaturated vapor by merely diluting the saturated vapor with air. The percentage of benzol was checked by combustion analysis. It was found that all of the benzol could be separated at —78° C.

The above tests show that as far as the Pittsburgh gas is concerned the method is satisfactory.

In extracting benzol from coke-oven gases (large-scale operations for this purpose are in progress), the gas is washed with a petroleum distillate, in which the benzol is dissolved, also toluol and other products. As a check on the efficiency of the scrubbing apparatus there is needed a rapid test for the benzol, etc. In this case, toluol or other easily condensible hydrocarbons would interfere with the test, as the vapor pressure of toluol is only 0.0058 mm. at —78° C.[1] The best one could do would be to estimate them together, along with any other vapors that might also be retained, so that the test would give the efficiency of absorption of all the easily condensible vapors in the scrubbing oil. The authors have made no experiments with coke-oven gas.

Acknowledgment is made to Dr. G. A. Hulett, consulting chemist to the Bureau of Mines, for suggesting this scheme of analysis.

LABORATORY OF GAS INVESTIGATIONS
BUREAU OF MINES, PITTSBURGH

## THE POTASH SITUATION[2]

By Edward Hart

The files of the Patent Office show that the question of supplying our own potash has greatly exercised the brains of inventors. Among the sources of supply so far proposed two have seemed to me of special interest. With the termination of the present highly artificial situation, German competition of the old-fashioned Standard Oil brand must again be encountered. It seems highly improbable that most of the processes which must depend for revenue upon the price of potash alone can be successful because the nature of the German source of supply is such as to give them an immense initial advantage.

A considerable amount of potash must in the near future come from cement fume. This appears to exist chiefly as sulfate. A sample, which I obtained from this source, contained 94 per cent sulfate and 5 per cent carbonate. The sulfur probably comes from the coal. The total amount obtainable from this source is problematical, of course, and it is questionable whether all the potash can be extracted, but if we place the amount recoverable as 0.4 per cent sulfate, the total amount obtainable would be in the neighborhood of 60,000 tons annually.

This cement dust has caused much annoyance and even serious loss in Northampton Co., Pa., and the adjacent districts and cement manufacturers recognize that condensation of this fume is one of the problems that must soon be solved. They also seem to be of the opinion that so far no practical solution has been offered. That this fume must be condensed is quite independent of any revenue to be derived from the material recovered. The dust recovered, only partly converted into cement, is worth, as cement material, but 75 cents per ton.

Another source that has attracted much attention is the potash of feldspar.

Arthur S. Watts has enumerated the feldspar supplies of the Eastern United States.[1] He has, however, omitted to mention the fact that a considerable amount of very fine potash feldspar is imported from Canada where it occurs in a great lens deposit, unlike any other deposit I have seen, about thirty miles north of Kingston. This deposit is not a pegmatite in the ordinary sense of that term. The spar occurs as a mass of uniform composition in a deposit which has been mined as an open cut, 40 feet in width, together with lump quartz of apparently good quality in a deposit of less width alongside of and partly surrounded by the spar. This deposit contains no mica. The mining cost of this material is very low, as very little cobbing is needed, but the cost of transportation to our markets is very high.

A study of the analyses quoted by Watts shows that very few orthoclase deposits run above 12 per cent $K_2O$, and as a matter of fact, I think 11 per cent is a much safer basis for such calculations. This corresponds to 220 pounds $K_2O$, 350 pounds KCl or 422 pounds $K_2SO_4$ per short ton of spar. Lump spar of this quality cannot be obtained at the mine at less than $3.00 to $3.50 per ton, f. o. b. car.

Many of the processes proposed contemplate the extraction as chloride by some modification of the J. Lawrence Smith method, using calcium chloride as the material for supplying chlorine. If we allow two cents per pound as the value of potassium chloride, a figure above the truth for normal conditions, and 2¼ cents for potassium sulfate (which may be produced in my own process) this would yield:

| | |
|---|---|
| 350 lbs. KCl at 2 cents | $7 00 |
| 422 lbs. $K_2SO_4$ at 2¼ cents | 9 49 |

It is at once evident that the probability of profit from any process which contemplates only the extraction of potash from this material is very small.

In mining feldspar in most localities, only a small proportion of the material taken out can be classed as No. 1 spar, and very large refuse heaps accumulate which may contain as much as 9 per cent potash and 15 per cent alumina. In addition to this, not a few of the openings yield quantities of material so mixed with mica and still high in potash, as to be available for potash extraction, while quite useless as feldspar. It is from these materials, quite low in first cost, that our potash must be derived. Such material exists in quantity in the district near Erwin, Tenn., on the Carolina, Clinchfield and Ohio Railroad, where a plant is to be erected by the Clinchfield Products Company in the near future. This location has the advantage of proximity to supplies of cheap coal and barytes, both of which are needed in the exploitation of the process to be used.

Briefly, the process consists in heating a mixture of feldspar refuse and barytes in proper proportion in a

Landolt and Bornstein Tables, **1912**, p. 894, according to Barker.

[2] Presented at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

[1] *Trans. Am. Ceramic Soc.*, **16** (1914), 80.

reducing atmosphere where a barium aluminum potassium silicate results containing about 36 per cent silica. This is run into water while molten and the granulated material ground and floated. The settled material is then treated as a paste with the proper quantity of sulfuric acid which decomposes it perfectly, giving a solution of alum and aluminum sulfate and a solid residue consisting of nearly equal parts of very finely divided barium sulfate and silica. It might be supposed that the silica would be so gelatinous as to be unwashable, but this has not been found true. On the contrary, where properly manipulated, the precipitate is somewhat granular, but entirely free from grit, and forms an excellent material, after ignition, for use as a pigment in printing ink, rubber incorporation and as a coating for paper. In value we believe this material will be found to be superior to very pure china clay. As you will see[1] from the sample submitted, it has a beautiful white color.

The solution, when evaporated, yields the potash as potash alum, and if the little iron present be kept in the ferrous condition, this alum, after washing with a little water and whizzing, is entirely free from iron and well suited for the preparation of pure potassium sulfate and iron-free alumina or aluminum sulfate, as desired. We expect to sell our alum as such so far as the market will take it and decompose only so much of it as may be necessary. This process may, therefore, furnish no potash at all. But inasmuch as potash for alum production now comes from over seas, this method is an indirect contribution to the supply.

The solution never contains enough potash to precipitate all the aluminum as alum. An excess of aluminum sulfate remains in the mother liquor together with the sodium and a little iron. This is allowed to cool and is broken up, furnishing a material equal in value to that now made from bauxite.

LAFAYETTE COLLEGE, EASTON, PA.

## AVAILABILITY OF ORGANIC NITROGEN[2]

By J. E. BRECKENRIDGE

Received April 12, 1915

In the last few years this subject has been coming to the front very rapidly. In some of the northern states more unscrupulous manufacturers secured all their nitrogen in their 1 per cent nitrogen brands from garbage tankage and peat. The state control officials soon became aware of the practice and argued that the farmer was paying for first-quality readily active nitrogen and received an inert and less expensive nitrogen; in other words, the farmer was not receiving full value for his money. This fact led to a thorough investigation as to the methods by which the control people could identify the activity of organic nitrogen. Much criticism was made as to the rendering available of inert organic nitrogen such as horns, hoofs, hair, leather, feathers, fur waste, etc., by digesting in sulfuric acid. While it was believed possible, it was considered that manufacturers were not doing it.

This led to the appointing of a committee to arrange, if possible, for a visit to some factory to watch the process. Such arrangements were made. Samples of all materials which went into the mixing were drawn as they entered the mixer. One hundred and fifty tons were mixed, the den sealed by officials and allowed to stand 48 hours. Then the seal was broken, and in the presence of the state committee, the den was discharged and samples drawn. This sample was used to further investigate the methods for active organic nitrogen.

From this investigation came the publication of a pamphlet dated March 4, 1911, entitled "A Method for Examining the Activity of Organic Forms of Nitrogen," signed by the directors of the New York, New Jersey, and New England States Experiment Stations.

This pamphlet included instructions for carrying out the Alkaline Permanganate Method and results obtained by seven Experiment Stations' Laboratories on the three samples.

SAMPLE NO. 1 was base goods made from hair waste, treated sole leather, garbage tankage and sulfuric acid. The average test on this was:

| | Per cent | | Per cent |
|---|---|---|---|
| Total nitrogen | 1.75 | Water-soluble organic | 1.01 |
| Nitrogen as ammonium salts | 0.25 | Water-insoluble organic | 0.49 |
| Total organic | 1.50 | Active insoluble | 0.21 |
| | | Inactive insoluble | 0.28 |

The percentage availability of the insoluble by this method on this sample varied from 39.21 to 47.36 per cent, a difference of 8.15 per cent.

SAMPLE NO. 2 was made from blood (100 parts), cottonseed-meal (50 parts), acid phosphate (500 parts) and muriate of potash (75 parts). Average total nitrogen, 2.50 per cent. The percentage of available insoluble nitrogen varied from 61.11 to 77.97 per cent.

SAMPLE NO. 3 was made from treated sole leather (200 parts), garbage tankage (150 parts), peat (100 parts), acid phosphate (500 parts), and muriate of potash (50 parts). The average total nitrogen was 2.09 per cent. The percentage availability of insoluble nitrogen varied from 37.06 to 53.03 per cent.

The following forms for expressing results were suggested:

LONG FORM, to be used where nitrates and ammonia are present and determined:

| | |
|---|---|
| Nitrogen as nitrates | Active insoluble organic |
| Nitrogen as ammonium salts | Inactive insoluble organic |
| Water-soluble organic nitrogen | Total nitrogen |

SHORT FORM (where it is desired to shorten the above procedure):

| | |
|---|---|
| Water-soluble nitrogen | Inactive insoluble organic |
| Active insoluble organic | Total nitrogen |

We also have in this pamphlet a chart showing the comparison as to availability of insoluble nitrogen, of the results by the Alkaline Method and pot experiments.

This was the first instance of grading of quality of organic nitrogen by chemical methods. Jones of the Vermont Station had done much work on this and was the first to report this kind of work; he reported according to the long form, giving the water-soluble organic nitrogen, as well as the nitrates, ammoniacal,

[1] Samples of all materials were furnished for inspection

[2] Chairman's Address, Fertilizer Division, 51st Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

FIG. I—BLANK NO FERTILIZER

FIG. II—NITROGEN AS SODIUM NITRATE

and insoluble nitrogen. His classification of the quality of the organic nitrogen was based on the water-soluble organic, plus the active insoluble, a reasonable and perfectly just and fair basis for classification.

Street, of Connecticut, carried on further experiments with the Neutral Permanganate Method and found that mixtures of acid phosphate and so-called high-grade ammoniates such as blood and tankage caused the neutral method to give lower results in such mixtures than in the materials themselves. On suggestion of the writer, sodium carbonate was added to the neutral permanganate solution just before adding the material to be analyzed, and the results on mixtures of acid phosphate and high-grade ammoniates were much more satisfactory. From this work came the so-called Modified Neutral Permanganate Method.

Both the Alkaline and Modified Neutral have been tried out by the A. O. A. C. and have been adopted, the Alkaline being adopted by the northern and middle western states and the Neutral being preferred by the southern states. Other methods have been suggested for determining the availability of organic nitrogen, such as "A Bacteriological Method for Determining Availability of Organic Nitrogen" by McCandless and Atkinson"[1] and "Bacteriological Method for Determining the Availability of Nitrogen in Fertilizers" by Dr. Lipman.[2] Neither of these methods have had any wide application because the Alkaline and Modified Neutral were much simpler and easier to manipulate.

From Vermont the use of the Alkaline Method has spread to Massachusetts, Maine, Rhode Island, New Jersey, Pennsylvania, Michigan and Indiana, with the probability of other states doing this line of work.

The Fertilizer Industry welcomes anything that will drive the unscrupulous manufacturers from the business, but does not welcome anything that causes unjust discriminations.

The interpretation of the results from any of these methods must be with a view to give justice to all classes of ammoniates. During the first of this work credit was given to the water-soluble organic nitrogen and the availability of the organic nitrogen was considered to be the water-soluble organic plus the active insoluble, which was a reasonable, just and fair ruling.

As an illustration of this, I quote the experiments of Hartwell and Pember[1] "average relative increase in yield (blood at 80 per cent) Base Goods nitrogen 84 per cent." This was on pot experiments where all the nitrogen of base was used. Another result was on the soluble part of Base, page 443 of above article—"soluble part of Base seems to have had an availability higher than blood, the insoluble part useless."

Taken as a whole, we have a material in the wet mixed base goods testing total nitrogen 1.68 per cent, soluble nitrogen 1.28 per cent, and insoluble nitrogen 0.40 per cent, which is rated by the above pot experiments as 84 per cent of the nitrogen available, but if rated on the insoluble portion, it is useless. The consumer in buying this quality of nitrogen is getting as much, if not more, for his money than he would if he bought blood nitrogen.

Again some pot experiments were carried out on millet and the accompanying cuts illustrate well the value of base goods nitrogen in comparison with no fertilizer, cottonseed meal and nitrate of soda, the amounts of fertilizer used representing the same amount of nitrogen ($1^1/_4$ lbs. per $^1/_{20}$ acre) in each case.

This subject is not one to be considered lightly whether or not it is believed that the methods employed are accurate. The facts are, these methods are being used and the fertilizer manufacturers should live up to these requirements as specified by the various states.

We have as the latest comments on this subject, the following:[2] "the use of low-grade and, therefore, cheap nitrogen supplies whose nitrogen by chemical treatment has been made useful for plant food, is laudable, provided the materials are sold for what they are, instead of being sold at the prices of nitrogen in high-grade nitrogenous ingredients."

According to this, the manufacturer is given no credit for gathering waste products and spending time and money in perfecting process and machinery which will handle such materials, but should sell such nitrogen at a cheap price because the crude materials from which he has obtained his nitrogen are cheaper than so-called high-grade nitrogen. It would be as reasonable to

[1] THIS JOURNAL, **3**, 174.
[2] *Ibid.*, **2**, 146.

[1] THIS JOURNAL, **4**, 442.
[2] Pennsylvania Bulletin No. 259, page 20.

FIG. III—NITROGEN AS COTTONSEED MEAL

FIG. IV—NITROGEN AS BASE GOODS

say that sulfate of ammonia should be sold cheaper than so-called high-grade nitrogen, because it comes from coal and that is cheap.

I believe the Fertilizer Industry has been, and is willing, to coöperate along any lines which will promote progress, and it seems to me that the Fertilizer Division of the American Chemical Society has a work along the line of availability of nitrogen which is well worth serious thought.

CARTERET, NEW JERSEY

## THE DESTRUCTIVE DISTILLATION OF PACIFIC COAST KELPS

By D R. HOAGLAND

Received April 6, 1915

The giant kelps of the Pacific Coast have received considerable attention in recent years, because of their high content of potash and iodine. The production of these substances from kelp on a commercial scale was first suggested by Balch[1] and the studies were later continued by the Bureau of Soils.[2] A more extended chemical investigation, however, seemed essential, and was undertaken by this laboratory. The principal results and conclusions of this work are reported elsewhere.[3]

In order to increase the margin of profit in the kelp industry, attempts have been made to find some method of utilizing the organic matter in addition to the potash and iodine. Among the suggestions, destructive distillation was considered. It is the purpose of this paper to report experiments dealing with this particular phase of our investigations.

Balch compared the distillation of kelp with that of beech wood and states that the volatile products from kelp—acetic acid, methyl alcohol and tar—"may be regarded as approximating in value those of beech wood." He assumes a value of $6.00 per ton of dry material for the volatile products of distillation. Green and Johnson[4] afterward made two distillations of 3-lb. samples of nereocystis and expressed the opinion that the distillates were worthless, but no analyses or details were given. Turrentine[1] distilled a 3-kg. sample of *Macrocystis pyrifera* in a Hornsy rotary still. An analysis of the gas evolved is given, but no data regarding the distillates. Further experimentation seemed necessary in order to make a more definite valuation of the volatile products.

The distillations in this laboratory were conducted in an iron retort of about 1.5 gallons capacity. This was provided with a pyrometer and a suitable condenser. It is realized that distillation experiments on a small scale are not comparable with commercial practice, except to a limited extent. As a control, therefore, samples of oak and Douglas fir were distilled under identical conditions. It was hoped in this way to obtain a fair idea of the comparative value of the kelp. We believe such a comparison is permissible, especially since the yields of acid and alcohol for the oak and Douglas fir approximate those obtained in larger experiments on similar materials.[2] The methods of analysis were similar to those described by the U. S. Forest Products Laboratory.[3] The acetic acid was distilled with steam from a phosphoric acid solution.

Table I shows that the average yield of acetic acid was scarcely 0.2 that of Douglas fir and only 0.1 that of oak. The alcohol yields were in the same proportions. Tar oils to the extent of 4 to 7 per cent of the dry weight of the kelp separated out in the distillate. Most of the tarry material floats on the watery distillate. The tar oil analyzed as follows:

| Sp. gr. at 17° C. | Distillation Fractions—Percentages 0 to 125° C. | 125 to 250° C. | 250 to 300° C. | Tar residue |
|---|---|---|---|---|
| 0.984 | 11 | 27 | 23 | 39 |

The residue solidified to a hard, black, lustrous mass.

The kelp distillates were very slightly acid to litmus, but contained considerable amounts of basic substances. By the Kjeldahl method 3.2 g. of nitrogen were found in the total distillate from 1 kg. of dried kelp, approximately $1/4$ to $1/5$ of the total nitrogen contained in the material. It does not appear that ammonium compounds could be recovered from the liquors in commercially important quantities.

The gases evolved were not combustible during any of the early stages of the distillation, differing therein

[1] Balch, THIS JOURNAL, **1** (1909), 777.

[2] U. S. Senate Document, No. **190**

[3] Burd-Calif. Exp. Station, *Bull* **248**, and manuscripts in press by D R. Hoagland and G. R. Stewart

[4] Green and Johnson, *Chem. Eng.*, **16** (1912), 55.

[1] Turrentine, *Proc. Eighth Internat. Cong. Applied Chem.*, **15**, 313.

[2] Hawley and Palmer, *Proc. Eighth Internat. Cong Applied Chem.*, **6**, 138; Benson, *Ibid.*, **25**, 331.

[3] Hawley and Palmer, *loc. cit.*

TABLE I.—COMPARATIVE DISTILLATIONS OF KELP, DOUGLAS FIR AND OAK

| No. of run | Grams of Materials Obtained: Moisture | Distillate: Total | Less moisture | Settled tar | Charcoal | Gas by diff. | Total time of distillation Hrs. | % of dry wt of material: Acid as acetic | Alcohol 100% | Settled tar |
|---|---|---|---|---|---|---|---|---|---|---|
| ON 1 KG. OF KELP (*Macrocystis pyrifera*) | | | | | | | | | | |
| 3 | 116 | 290 | 174 | .. | 465 | 245 | 3 | .. | .. | .. |
| 6 | 116 | 255 | 139 | .. | 465 | 280 | 2 5 | | | |
| 9 | 116 | 265 | 149 | .. | 500 | 235 | 12 | | | |
| 11 | 116 | 262 | 146 | 48 | 485 | 253 | 3 | 0.34 | Av | 5.4 |
| 12 | 116 | 283 | 167 | 41 | 512 | 205 | 3 75 | 0 49 | Av | 4 6 |
| 13 | 116 | 277 | 161 | 60 | 472 | 251 | 4 | 0 28 | 0 14 | 6 8 |
| 14 | 116 | 242 | 126 | 37 | 487 | 271 | 4 | 0 28 | | 4 2 |
| 18 | 116 | 217 | 101 | 30 | 515 | 268 | 8 | | | 3 4 |
| 23 | 116 | 277 | 161 | 60 | 485 | 238 | 4 | 0 49 | 0 20 | 6 8 |
| 24 | 116 | 305 | 189 | 55 | 460 | 235 | 8 | 0 58 | 0 18 | 6 2 |
| ON 1 KG. OF DOUGLAS FIR | | | | | | | | | | |
| 16 | 190 | 414 | 224 | 60 | 260 | 326 | 3 | 1 5 | 0 7 | 7 0 |
| 17 | 190 | 424 | 234 | 80 | 276 | 300 | 2.5 | .. | 0.7 | 10.0 |
| 25 | 190 | 450 | 260 | 100 | 300 | 250 | 4 | 1 6 | | 12 0 |
| ON 1 KG. OF OAK SAWDUST | | | | | | | | | | |
| 18 | 366 | 550 | 184 | 45 | 200 | 250 | 4 | 2.9 | 1.1 | 7.0 |
| 19 | 313 | 424 | 111 | 60 | 230 | 346 | 3 5 | 2 6 | 1 3 | 9 0 |
| 20 | 313 | 412 | 99 | 37 | 215 | 373 | 4 5 | 2 5 | 1.2 | 6 0 |

REMARKS ON DETAILS OF DISTILLATIONS

RUN NO. 3—Retort at red heat 1.5 hrs.
RUN NO. 6—Heated rapidly to red heat
RUN NO. 9—Very slow, low heat, 12 hrs

RUN NO. 13
Started at 1.20 P.M.
Pyrometer readings
1.45 P.M. 120° C.
2.00 160
2.30 200
3.10 220
4.05 240
gases slightly combustible
4.30 360
gases burned steadily
4.50 420
5.10 500
no more distillate

RUN NO. 14—8.30 A.M.
9.15 A.M. 160° C. large watery distillate
9.30 200
10.35 220
11.15 280
gases slightly combustible
11.30 310
distillate oily
gas burns
12.25 P.M. 500

RUN NO. 15—9.00 A.M.
9.30 A.M. 140° C.
9.50 170
10.45 190
12.00 M. 200
2.00 P.M. 220
2.15 290
3.20 390
4.30 400

RUN NO. 18—8.35 A.M.
Pyrometer readings
9.05 A.M. 170° C. gases burn
9.15 200
10.05 270
11.50 290
12.30 P.M. 530

RUN NO. 20—1.05 P.M.
Pyrometer readings
1.40 P.M. 160° C.
2.40 200
3.20 250
5.25 500

RUN NO. 24—8.35 A.M.
Pyrometer readings
9.10 A.M. 160° C.
11.00 230
12.45 250
1.00 P.M. 300
2.45 440
4.45 530

from the gases produced by the oak and fir. Turrentine gives the following data regarding the gases evolved in his experiment:

ANALYSES OF GAS SAMPLES FROM DESTRUCTIVE DISTILLATION OF KELP (MACROCYSTIS)—(TURRENTINE)

| Sample No. / Pyrometer | 1 320° F. | 3 480° F. | 5 590° F. | 7 900° F. |
|---|---|---|---|---|
| $CO_2$ | 80.0 | 70.0 | 44.0 | 20.2 |
| Illuminants | 2 0 | 4.0 | 10.0 | 3.3 |
| $O_2$ | 0.5 | 1.5 | 0.8 | 0.5 |
| CO | 10.5 | 8.5 | 6.7 | 4.0 |
| $H_2$ | .... | 10.6 | 23.5 | 32.0 |
| Methane | 2.88 | 4.8 | 4.4 | 7.6 |
| Nitrogen (by diff.) | 4.12 | 0.6 | 10.6 | 32.4 |
| Total per cent | 100.00 | 100.00 | 100.00 | 100.00 |
| Wt per cu ft | 0 106040 | 0 094 | 0 074150 | 0 057600 |
| Cal. value | 107.45 | 196.70 | 352.05 | 282.54 |

The charcoal residue was very soft and had a dull luster. A leaching experiment was made, using 2860 g. of charcoal, with an excess of distilled water. The solution was evaporated and three fractions crystallized out as is shown in Table II.

TABLE II—LEACHING AND FRACTIONATION

| Fraction No. | Vol. of mother liquor | Wt. of dry salts Grams | Per cent of $K_2O$ in salts | Per cent of I in salts | Remarks |
|---|---|---|---|---|---|
| 1 | 2600 cc | 480 | 58 0 | 0 03 | Pure white crystals |
| 2 | 1600 cc. | 283 | 55.6 | 0.08 | Nearly pure |
| 3 | 860 cc | 252 | 47.3 | 0.17 | white crystals |
| Mother liquor | ... | 368 | 19.1 | 1.46 | |

Per cent $K_2O$ in 3 fractions combined = 54.6 = 86.8 per cent KCl.
Per cent of total $K_2O$ recovered in 3 crystallizations = 88
Per cent of total I in mother liquor = 87

By passing the weak liquors over fresh portions of charcoal repeatedly it was found possible to leach out practically all of the potash and iodine with minimum quantities of water.

SUMMARY

1—Comparative laboratory distillations of kelp (*Macrocystis pyrifera*) with oak and fir were made. The data obtained did not indicate that the kelp distillates would have a commercial value.

2—Most of the potash may easily be recovered from the charcoal as a high-grade product.

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CALIFORNIA AGRICULTURAL EXPERIMENT STATION, BERKELEY

## NOTE ON IDENTIFYING AMIDO-H-ACIDS

By BERNHARD C. HESSE

Received June 24, 1915

There are no published methods of identifying the 2-amido-H-acid, the 7-amido-H-acid and the 2,7-diamido-H-acid. H-acid is 1.8-amido-naphthol-3,6-disulfo acid. Ability to detect and differentiate these acids is frequently necessary for industrial purposes in obtaining light on the mode of making and the composition of certain coal-tar dyes.

The methods of identification described below were worked out with known H-acid and other materials and were successfully applied to disputed dyes; they are offered with confidence as to accuracy and conclusiveness so far as these three sulfo-acids are concerned. Corresponding mono- and di-amido derivatives of acids isomeric with, or analogous to, H-acid have *not* been similarly examined. Whether conflict exists in that regard has not been determined; this will call for further work by others. This note is not at all a notice of pre-emption but an invitation to others to enter this field. An analysis of the products worked on was not made; reliance for the constitution of these substances is placed solely upon the history and behavior of the materials employed.

The 2-amido-H-acid was made from H-acid by coupling it in hydrochloric solution with diazotized paranitranilin (one molecule), reducing and separating the acid product from the para-phenylene diamine; the 2,7-diamido-H-acid was made from the foregoing coupling product and a further molecule of diazotized paranitranilin, coupling in alkaline (carbonate), solution and treating this result as outlined above; 7-amido-H-acid was made from the coupling product of H-acid and diazotized paranitranilin (one molecule), coupled alkaline (carbonate); this product was reduced and separated as outlined above.

There is nothing new in the coupling methods used. The reducing and separation methods may be new. The general procedure was as follows:

Mix one gram of each of these coupling products with 10 cc. water, heat to 60° C., add one gram zinc dust thoroughly suspended in 5 cc. water, shake thoroughly, add 5 cc. of a 36° Bé. sodium bisulfite solution, shake thoroughly, gradually raise to a boil and maintain at boiling until further color-change does not take place; filter rapidly, cool, add 6 cc. hydrochloric acid (sp. gr. 1.16) to cooled filtrate; cool in a freezing mixture to 0° C. or below and maintain at that temperature until solid no longer separates out (this may take from half hour to 2 or 3 hours); filter upon paper through a Gooch; drain thoroughly; wash carefully with small amounts of saturated salt solution until drip is colorless

or almost so; wash with as little 95 per cent ethyl alcohol as possible (3 to 4 cc.), and follow with a wash of 1 or 2 cc. of ether; remove the solid from the filter paper and dry on a watch-glass at 90° C. The solid obtained is the amido-H-acid of the coupling product used. The same procedure applies to dyes from H-acid; if the dye-amount taken be less than one gram the proportion of reagents used should be altered to correspond.

The three identification tests used were as follows:

I—Boil a fraction of a milligram of the free acid with a few drops of 40 per cent caustic soda solution, dilute with 1 cc. water and note color produced; boiling the diluted solution may at times be necessary.

II—Place a fraction of a milligram of the free acid into 2 or 3 drops conc. $H_2SO_4$ (sp. gr. 1.84) and warm until it *begins* to turn violet; add one or two drops 0.5 per cent sodium nitrite solution; cool; dilute with 0.5 cc. water; cool (if a brown opalescence or turbidity appears here start all over again and do not heat quite so high); neutralize largely with 40 per cent caustic soda, finish neutralizing and make alkaline with slight excess saturated carbonate of soda solution; note color change.

III—Dissolve a fraction of a milligram of the free acid in one drop of saturated carbonate of soda solution, using heat if need be; add one drop concentrated hydrochloric acid, dilute with water to 0.5 cc., heat to boiling and cool; place a drop of this on good white filter paper; add right on top of it a drop or two of good hydrogen peroxide solution; when the color-development has reached its maximum, add a drop of 40 per cent caustic soda solution, preferably right on top of the other drops. Note color changes.

The behavior of these acids is tabulated as follows:

| Test | 2 Acid | 7-Acid | 2,7-Acid |
|---|---|---|---|
| I | Yellow or brown | Green | Violet going to blue |
| II | Blue-red | Blue-red | Yellow or brown |
| III $H_2O_2$ | Brown or yellow | Violet to red | Blue |
| NaOH | Red | White or cream colored | Red to violet |

By suitably combining these tests it is possible to detect all three of these acids in mixtures of 90 : 5 : 5 of any combination; with care, 200 mg. of H-acid-dye will answer to carry out this separation and all three of these tests. The colors produced by Test III can be photographed, *e. g.*, on a Lumière plate and the colors so preserved for reference; they are not stable, as such.

Condensation with phenanthrene-quinone is not satisfactory, calling for much time and care, and frequently failing where it should succeed; moreover, the amounts needed are very much larger than in the tests described; 2-amido-H-acid gives such a condensation product which is yellow, soluble in carbonate of soda and is precipitated therefrom by common salt and dissolves in concentrated sulfuric acid with a cornflower-blue color; the 2,7-diamido-H-acid does not yield such a condensation product under any practicable condition nor does the 7-amido-H-acid.

Acknowledgments are herewith made to Messrs. Read Holliday and Sons, of Huddersfield, England, for permission to publish this note.

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## INDIGOTIN CONTENT OF SOME JAPANESE INDIGOES[1]

By Shinjiro Sato

Received April 8, 1915

The analyses given below were made on commercial samples from the Province of Awa, where nearly all the Japanese indigo is produced. The remarkable features of the results are the low indigotin content and high ash. These are not surprising, however, when considered in relation to the methods of production, which have been modified but little since the introduction of indigo culture into Japan over two hundred years ago.[2]

In the native process the dried leaves of the *Polygonum tinctoria* are heaped on dirt floors, then thoroughly moistened with water and allowed to ferment. The piles are turned over from time to time, the whole process requiring about three months. The fermented mass, called "sukumo," is pounded up in large wooden mortars with mallets, then mixed with water and left to harden. The resulting cake is pressed and cut into cubes, called "tamas" ("Tama," Japanese word for "gem") in which form it is put on the market.

The above method requires much time and labor and yields a product of low indigotin content, since there is no extraction to separate the dye from the fiber of the plant. An extraction method applicable to Japanese conditions has been perfected by Dr. N. Nagai.[3] Although the method requires less time and labor than the older process and produces a superior indigo, it has not yet been generally adopted.

### METHOD OF ANALYSIS

To test out the methods of analysis pure indigotin was first prepared, starting with Indigo S Pdr. furnished by the Badische Co. This was purified according to the method of Mönlau and Zimmermann,[4] by dissolving in 100 parts glacial acetic acid and 4 parts sulfuric acid, then hydrolyzing by diluting with water. The precipitated indigotin was washed, dried at 110°, and nitrogen determined by the Kjeldahl method.

| | Found | Theoretical | |
|---|---|---|---|
| N | 10.62 per cent | 10.69 per cent | Indigotin 99.35 per cent |

The method adopted for extracting and estimating indigotin is a modification of Rawson's procedure[5] in which he extracted indigotin by sulfonation and titrated with $N/50$ permanganate. The original method was modified by its author[6] and later by Bergtheil and Briggs,[7] whose procedure was adhered to exactly in the following analyses. The above methods for preparation of pure indigotin and for analysis of commercial indigos have been alternately criticized and defended.[8]

### RESULTS OF ANALYSIS

Ash and indigotin are calculated on weight of dry

[1] Partial abstract of a thesis presented to the Faculty of the State College of Washington in part fulfillment of the requirements for the B.S. degree.

[2] History of Awa Indigo. (Published in Japanese.)

[3] Nagai, Lectures on Awa Indigo. (Published in Japanese.)

[4] *Zeits. Farb. Text. Chem.*, **10** (1903), 189.

[5] *J. Soc. Dyers and Col.*, **1** (1885), 74.

[6] *J. Soc. Chem. Ind.*, **35** (1906), 730.

[7] *Ibid.*, **18** (1899), 251; **25** (1906), 734.

[8] *Ibid.*, **26** (1907), 4, 182, 1172, 1174.

sample. In all cases duplicates represent separate extractions.

| Sample | Per cent moisture | Per cent ash | Per cent indigotin |
|---|---|---|---|
| Purified synthetic indigo | .... | .... | 99.71 |
| | .... | .... | 100.59 |
| Awa indigo No. 1 | 9.71 | 27.75 | 6.78 |
| | 9.41 | 27.41 | 6.86 |
| Awa indigo No. 2 | 9.18 | 27.28 | 5.05 |
| | 9.30 | 27.17 | 5.15 |
| Awa indigo No. 3 | 10.08 | 30.56 | 4.23 |
| | 10.10 | 30.47 | 4.32 |
| Awa indigo No. 4 | 12.44 | 32.39 | 1.94 |
| | 12.44 | 32.48 | 2.02 |
| Awa indigo No. 5 | 9.24 | 33.89 | 1.26 |
| | 9.21 | 33.77 | 1.34 |
| Awa indigo No. 6 | 11.56 | 34.50 | 2.46 |
| | 11.56 | 34.55 | 2.47 |
| Awa indigo No. 7 | 9.92 | 34.34 | 3.17 |
| | 9.95 | 34.32 | 3.23 |
| Awa indigo No. 8 | 9.46 | 35.26 | 3.59 |
| | 9.38 | 35.08 | 3.72 |
| Indigo by Nagai process | 3.18 | 33.25 | 31.45 |
| | 3.28 | 33.25 | 31.53 |

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## EXPERIMENTAL DATA COMPARING THE DELICACY OF DIFFERENT TESTS FOR HYDROGEN PEROXIDE IN MILK

By Irwin T. Darlington

Received April 12, 1915

From references on the detection of hydrogen peroxide, the reagents listed in Table I were found to be in most general use and appear to give the most delicate tests for the detection of hydrogen peroxide in milk.

A stock solution of hydrogen peroxide was made from a commercial sample containing 3.2 per cent of

Table I

| Reagent | Solution | Color in presence of $H_2O_2$ |
|---|---|---|
| Starch | Dilute (water) + KI | Bluish green |
| Paraphenylene diamine | 2 per cent (water) | Blue |
| Benzidine | 4 per cent (alcoholic) + 10 cc. milk (+ 2 or 3 drops acetic acid) | Blue |
| Titanic acid | 2 per cent solution titanium hydrate in dilute $H_2SO_4$ | Yellow |
| Vanadic acid | 2 per cent in dilute $H_2SO_4$ | Faint orange-red |

hydrogen peroxide by analysis with potassium permanganate. This stock solution was made so that each cc. contained 0.01 g. of hydrogen peroxide.

The milk to which the hydrogen peroxide was added was received from the city inspectors and was proven free from hydrogen peroxide by each of the above reagents.

Hydrogen peroxide was added to each 100 cc. of milk in separate bottles to the amounts ndicated in Table II, and tests made on 10 cc. of each sample

Table II

| | Results of tests made immediately after samples were made up | | | | | | | | | | | | | | | After standing 18 hrs. in a warm room | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Grams per 100 cc | 15.0 | 9.0 | 3.0 | 1.5 | 0.75 | 0.6 | 0.3 | 0.15 | 0.03 | 0.015 | 0.006 | 0.003 | 0.006 | 0.003 | 0.00105 | 0.00075 | 0.00037 | 1.5.0 | 9.0 | 3.0 |
| Starch | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | — | — | + | — | — |
| Paraphenylene | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | — | + | + | — |
| Benzidine | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | — | — | + | — | — |
| Titanic acid | + | + | + | + | + | + | + | + | + | + | + | + | — | — | — | — | — | + | — | — |
| Vanadic acid | + | + | + | + | + | + | + | + | + | + | + | — | — | — | — | — | — | + | — | — |

with each of the above reagents. Tests were made immediately after the samples were made up and again after standing 18 hours in a warm room.

It will be seen from Table II that paraphenylene diamine and benzidine proved to give the most delicate tests for hydrogen peroxide in raw milk. The limits of these two reagents proved to be 0.00075 g. of hydrogen peroxide in 100 cc. of raw milk. No experiments were made with milk that had been previously heated to destroy bacterial action.

Practically all the hydrogen peroxide was reduced after standing 18 hours in a warm room. This confirmed previous results obtained in this laboratory when it was found that after 18 hours' standing at room temperature no reaction could be obtained from the addition of 1 g. of magnesium peroxide to 100 cc. of raw milk. Positive tests were given only when the milk contained 9 per cent and 15 per cent of hydrogen peroxide.

The samples containing 9 per cent and 15 per cent of hydrogen peroxide failed to give a positive test with any of the above reagents, except paraphenylene diamine, which gave a delicate positive test with 15 per cent of hydrogen peroxide after standing in a warm room for 24 hours. Tests on distillates of milk treated with peroxide were negative.

A few tests were made with magnesium dioxide added as a preservative. The experiments made with this material were insufficient to afford any positive conclusions, but it appears that magnesium dioxide does not lend itself to as delicate tests as does hydrogen peroxide.

From the foregoing it is seen that paraphenylene diamine is the test of the reagents tested for the detection of small quantities of hydrogen peroxide in raw milk, and that it is probable that peroxide in amounts that would be added to milk as a preservative cannot be detected after 18 hours by these reagents.

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## THE OFFICIAL METHOD FOR DETERMINING CRUDE FIBER AS APPLIED TO COTTONSEED MEAL

By C. K. Francis

Received April 7, 1915

The well known Weende method[1] for determining crude fiber has been subjected to criticism by many chemists. The chief trouble seems to be with the filtering materials, linen, asbestos, or glasswool, which vary in their physical characteristics and, necessarily, in filtering efficiency. In a number of laboratories it has been the practice to use linen cloth for filtering. The cloth has been used in the same manner as filter paper, with and without suction, in plain and in ribbed funnels. It has been difficult to duplicate linen of a selected pick, so that the fineness of the filter has been liable to vary from time to time. However, the method seemed to be satisfactory when working with such substances as corn, but when one endeavored to filter the alkaline mixture of certain seeds like flaxseed and cottonseed it became necessary to devise some scheme to hasten the process.

A novel arrangement for filtering the mixture through cloth by upward suction has been suggested by Pickel.[2] The cloth stretched over a funnel or thistle-tube furnishes a flat surface and the liquid passes rapidly,

[1] "Official Methods of Analysis," U. S. Bureau of Chemistry, *Bull.* **107** (Rev.), 65.

[2] This Journal, **2** (1910), 280; see MacNider, *Ibid.*, 281.

but the method appears to give results which are too low. Forbes and Menching[1] have proposed a method in which fine sand is used as a filter. but our tests with this material gave no results because the cottonseed meal mixture did not pass through even after 24 hours' continuous suction. Sweeney[2] has proposed to omit the first filtration and neutralize the acid with a known amount of sodium hydroxide, then to proceed with the alkaline treatment in the same vessel, and filter through asbestos. The method has been modified in a slight detail by Kennedy[3] and the procedure has been tested by several chemists in this laboratory. The results obtained for cottonseed meal were somewhat higher than when two filtrations were made.

While studying the methods for determining crude fiber our attention has been centered upon the filtering materials, and we have endeavored to select a filter which would be uniform. Slight modifications are suggested, and the work of several investigators, especially that of Sweeney, is taken into consideration in the directions given below. The specific details mentioned, it is believed, do not alter the principles involved in the official method, but on the other hand, suggest a procedure which permits a greater accuracy than the directions usually followed.

EXTRACTION OF FAT—Two grams of the meal are weighed into a glass extraction tube provided with a plug (about an inch square) of fat-free absorbent cotton in the bottom. More cotton is placed above the sample and a small copper wire spring inserted to hold the charge in place. After drying six hours at 105°, the meal is placed in the extractor[4] and extracted with dry ether for 16 hours. The excess ether is removed by suction, the tube and contents dried in the electric oven at 105°. The loss in weight is calculated to per cent of crude fat or oil.

CRUDE FIBER METHOD—The dry fat-free residue is carefully brushed, over white glazed paper, from the glass extraction tube into an 800 cc. lipless beaker, care being taken to remove any particles of the meal that may cling to the cotton plugs. Two hundred cc. of boiling 1.25 per cent $H_2SO_4$ are added and the mixture boiled for 30 minutes, using as condensers round bottom flasks filled with cold water on top of the beakers as shown in Fig. 1: the flasks will fit closely if the beakers are round and have well-formed rims. A blast of air should be directed into the beaker when the foaming becomes serious. At the end of 30 minutes, 200 cc. of boiling 3.52 per cent NaOH are added and the boiling continued another 30 minutes.

Sweeney and others have proposed a sodium hydroxide solution of another strength but have included a separate neutralization, in the presence of an indicator, with a 10 per cent NaOH solution. A number of tests have indicated that a 3.52 per cent solution will neutralize the acid and leave a 1.25 per cent sodium hydroxide solution. Numerous titrations of this liquid were made showing the strength to vary from 1.25 to 1.27 per cent NaOH. According to the procedure outlined, one filtration is saved and there is no need to add an indicator and carefully neutralize.

A Buchner funnel, outside diameter 10.5 cm., is prepared with a 9 cm. S & S 575 filter paper. The paper should be moistened with water and pressed well into place, so that there are no holes uncovered and no open channels left about the edges. It is advisable to place a glass filter plate over the paper, to protect it and to prevent excessive packing of the fiber.

After the 30 minutes' boiling, the fiber should be filtered off rapidly with the aid of suction, washing with boiling water and then with a 1.25 per cent solution of HCl[1] (HCl 14 cc. made up to 500 cc.) until the washings are acid. Much time may be saved if the liquid is set aside for about five minutes to allow the fine material to settle so that the clear liquid may be decanted. When this has been done it has not, so far as we were able to determine, influenced the final results. The fiber should be washed with hot water until free from chlorides, and finally the filter should be washed several times with alcohol. The residue on the paper will be almost free from water and may be transferred to a prepared[2] Gooch crucible

FIG. 1—CRUDE FIBER APPARATUS

with the aid of a spatula and a small amount of 80 per cent alcohol.

The crucible is placed in an oven heated to 105–110° C. for 2 to 6 hours, cooled and weighed. Materials containing much fiber may require heating for the longer period, and a second drying and weighing may be necessary in order to get the weight constant, but many determinations show a constant weight after heating for 2 hours. When dry the crucible is partially covered and incinerated at a low red heat for 15 minutes or until a white or light gray ash is obtained; it is then cooled and weighed. The loss in weight may be calculated as crude fiber.

## EXPERIMENTAL

The tests described in the first part of this paper were made on the same sample of cottonseed meal. The quantity weighed for analysis was two grams, unless otherwise stated. All results are in terms of

[1] THIS JOURNAL, **5** (1913), 258, Ohio Agricultural Experiment Station, *Bull.* **255** (1913).

[2] U. S. Bureau of Chemistry, *Bull.* **137** (1910), 157.

[3] THIS JOURNAL, **4** (1912), 600.

[4] Francis, *Ibid.*, **3** (1911), 673.

[1] C. Kennedy, *Loc. cit.*, uses $H_2SO_4$ here but we prefer HCl, because the chlorides are easily detected and removed; moreover, dilute solutions of HCl may be quickly prepared

[2] A porcelain or platinum Gooch crucible may be used. The crucible is prepared with a pad of asbestos, about 1 mm. thick, and heated to redness for fifteen minutes. When cool, fit the crucible into a suction filtering tube and transfer the material to it.

crude fiber calculated to per cent of the original material. The composition (except fiber) of the meal used in the experiments is shown in Table I.

TABLE I—PERCENTAGE COMPOSITION OF MEAL

| Moisture | Ash | Crude protein | Crude fat |
|---|---|---|---|
| 9.32 | 5.00 | 45.44 | 7.07 |

TESTING THE ASBESTOS—A test was made to determine the effect of digesting the asbestos, used for filtering, in acid and alkali and igniting before use. Portions of the same sample were treated alike with the exception that one lot was filtered through prepared asbestos[1] while the untreated asbestos was used for the second lot. The results with the untreated asbestos were 1.3 per cent higher than those obtained with the prepared asbestos.

It appeared that the crude fiber should be completely burned at comparatively low temperatures, and that extra heating in the flame of the blast burner should not be necessary. In Table II the results of a test

TABLE II—LOSS DUE TO EXCESSIVE HEATING OF THE ASBESTOS

| Crucible No. | Wt. cr. + asbestos ignited over Bunsen flame for 3 hrs. | 5 hrs. | Loss Gram | Ignited 3 min. in blast flame | Loss Gram |
|---|---|---|---|---|---|
| 22 | 17.8641 | 17.8616 | 0.0035 | 17.8553 | 0.0063 |
| 21 | 17.6653 | 17.6645 | 0.0008 | 17.6575 | 0.0070 |
| 24 | 17.1209 | 17.1191 | 0.0018 | 17.1098 | 0.0094 |
| 19 | 18.0400 | 18.0395 | 0.0005 | 18.0310 | 0.0085 |
| 10 | 17.8555 | 17.8548 | 0.0007 | 17.8479 | 0.0069 |
| 16 | 17.7493 | 17.7487 | 0.0008 | 17.7400 | 0.0087 |

are shown in which quantities, 1.3 grams to 2.4 grams, of prepared asbestos were ignited to a constant weight and then placed in the blast flame for 3 minutes. This asbestos was used in blank determinations and consequently, subjected to action of the acid and alkali.

A separate test of the prepared asbestos was made to determine the loss due to heat alone, that is, without having to consider any influence the reagents might have on the final loss. For this purpose portions weighing from 0.5 to 2.2 grams were dried to constant weight and then placed in the blast flame for 3 minutes.

TABLE III—CRUDE FIBER IN COTTONSEED MEAL AS DETERMINED BY THE ONE FILTRATION METHOD AND DIFFERENT FILTERS

| Kind of filter | Per Cent Crude Fiber Determinations | | | Av. | Remarks |
|---|---|---|---|---|---|
| Linen | 8.57 | 8.58 | 8.54 | 8.56 | No suction; res. washed into a Gooch. |
| Hard paper | 9.54 | 9.53 | 9.37 | 9.48 | S & S 575, 9 cm. in Buchner funnel. |
| Asbestos | 10.87 | 10.81 | | 10.84 | Filter in a Hirsch funnel. |

The loss was from 8.8 to 33.2 mg., respectively, or a percentage loss of 1.85, 1.64 and 1.49 when calculated on a basis of the weight of the asbestos. When calculated as crude fiber, this loss represents 0.44, 0.76 and 1.66 per cent.

The fibrous material present in feeds is of such a nature that it should be completely incinerated after a few minutes (say 15) in the flame of a good burner, and ignition at high temperatures will tend to increase the loss which is calculated as crude fiber. In the fourth column of Table II, the weights are shown to be constant, excepting the material in crucible No. 22. Further loss, shown in the last column, obtained in the blast flame is probably due to some action on the asbestos or volatile salts present and certainly not anything closely related to cellulose or fiber.

FILTERING MATERIALS—The data presented in Table III show, to some extent, the loss that may take place with different kinds of filters when but one filtration is made.

Every precaution was taken in each test to wash free from alkali, acid and chlorides. The linen used was of good grade, having 38 threads to the sq. cm. The paper was hard filter paper, S & S No. 575, diameter 9 cm.

In Table IV are shown results obtained with the same sample of cottonseed meal, when two filtrations were made. For this experiment the regular 1.25 per cent acid and alkaline solutions were used according to the official methods.

It will be observed from a study of the data in Tables III and IV, that the determinations with a given filter appear, when considered alone, to be satisfactory. When comparisons of the groups are made, it will be seen that the results do not agree.

Determinations in addition to those reported here have shown that the loss with linen depends upon the number of times the mixture is filtered through it, thus demonstrating that there is a loss of crude fiber. The high results in Table III with asbestos have been explained under Table II, as being caused by the asbestos losing weight during the ignition process, and that the loss fluctuates with the quantity of asbestos used.

The crude fiber determinations in which filter papers were used appear to be the most uniform for both methods as indicated in Tables III and IV. The paper filters certainly do not permit any solid matter to pass into the filtrate, and they offer a uniform filter which may be easily obtained and from which the residue can be readily transferred.

Some determinations were made in which asbestos was used for both filtrations according to the official method, but the large quantity of material added to the second filter in this way caused the filtration to proceed very slowly, and introduced an additional error which may have resulted from any loss of weight of the asbestos.

PROTEIN REMOVED—An analysis of the residue remaining on the filter paper after the acid digestion, showed a protein content of 5.75 per cent. The final residue, chiefly crude fiber, contained 0.38 per cent protein. The crude fiber extracted from another meal was found to contain 0.35 per cent protein. This amount confirms the results obtained by Cross and Bevan, Tollens and others,[1] when working with the

TABLE IV—CRUDE FIBER IN COTTONSEED MEAL AS DETERMINED BY THE TWO FILTRATION METHOD AND DIFFERENT FILTERS

| Kind of filter 1 – After acid digestion | 2 – After alkali digestion | Per Cent Crude Fiber Determinations | | | Av. | Remarks |
|---|---|---|---|---|---|---|
| Linen | Linen | 8.44 | 8.16 | 7.96 | 8.19 | No suction; residue washed into a Gooch crucible. |
| Linen | Asbestos | 8.56 | 8.82 | | 8.69 | Asbestos filter in a Gooch crucible, *i. e.*, small amount asbestos used |
| Linen | Asbestos | 8.96 | 8.79 | 9.02 | 8.92 | Asbestos filter in a Hirsch funnel, *i. e.*, large amount asbestos. |
| Paper | Paper | 9.63 | 9.53 | 9.51 | 9.56 | S & S 575 paper in a Buchner funnel |

[1] Asbestos which had been digested in $HNO_3$, NaOH and $H_2O$; also ignited in a furnace. This asbestos was used wherever asbestos is mentioned

[1] *Cellulose*, **1** (1895), 101

ordinary methods for determining crude fiber. No doubt any good filter will retain approximately the same quantity of protein, pentosans and volatile ash known to be present in crude fiber.

TESTS ON CELLULOSE—Two samples of filter paper were prepared from S & S paper No. *597*. One sample, designated *coarse paper*, consisted of large pieces, each about the size of one-quarter of a 9 cm. paper. All samples for the coarse paper work were dried at 105° C. until the weight became constant. The second sample, here called *fine paper*, was made from the same kind of paper ground so as to pass a 40-mesh sieve. Both samples were boiled in the acid and alkaline solutions so as to determine the action of the reagents. In Tables V and VI the procedure is indicated. The words, *acid only*, serve to show that the portions were boiled in 1.25 per cent sulfuric acid for one-half hour, then filtered through paper, washed, dried, weighed, ignited and weighed. The treatment with alkali was similar except that 1.25 sodium hydroxide was used. The digestions in both reagents were made as outlined in the method suggested when but one filtration is to be used, and, also, according to the directions of the official methods, which require two filtrations.

TABLE V—ACTION OF CRUDE FIBER REAGENTS ON PURE FILTER PAPER
Coarse Paper, Not Pulverized

| On Paper Filters | | | | On Asbestos Filters | | | |
|---|---|---|---|---|---|---|---|
| | Fiber Recovered | | | | Fiber Recovered | | |
| Weight of sample Gram | Wt. in gram | Per cent on Sample basis | Per cent on Ash + $H_2O$ free basis | Weight of sample Gram | Wt. in gram | Per cent on Sample basis | Per cent on Ash + $H_2O$ free basis |
| Acid Digestion Only | | | | Acid Digestion Only | | | |
| 0.6333 | 0.6230 | 98.37 | | 0.5766 | 0.5705 | 98.94 | |
| 0.5551 | 0.5496 | 99.01 | | 0.6229 | 0.6315 | 101.38 | |
| 0.6084 | 0.5967 | 98.08 | | 0.5506 | 0.5589 | 101.51 | |
| Average, | | 98.49 | 99.31 | Average, | | 100.61 | 101.44 |
| Alkali Digestion Only | | | | Alkali Digestion Only | | | |
| 0.6250 | 0.6018 | 96.29 | | 0.5579 | 0.5531 | 99.13 | |
| 0.5903 | 0.5664 | 95.95 | | 0.5456 | 0.5386 | 98.72 | |
| 0.5829 | 0.5558 | 95.35 | | 0.5390 | 0.5304 | 98.40 | |
| Average, | | 95.86 | 96.66 | Average, | | 98.75 | 99.58 |
| Acid and Alkali | | | | Acid and Alkali | | | |
| 0.5227 | 0.4595 | 87.95 | | 0.5493 | 0.4863 | 88.53 | |
| 0.5657 | 0.4955 | 87.59 | | 0.5271 | 0.4667 | 88.54 | |
| 0.5569 | 0.4867 | 87.39 | | 0.5535 | 0.4902 | 88.56 | |
| Average, | | 87.64 | 88.36 | Average, | | 88.54 | 89.28 |

TABLE VI—ACTION OF CRUDE FIBER REAGENTS ON PURE FILTER PAPER
Fine Paper, Pulverized to Pass 40-Mesh Sieve

| On Paper Filters | | | | On Asbestos Filters | | | |
|---|---|---|---|---|---|---|---|
| | Fiber Recovered | | | | Fiber Recovered | | |
| Weight of sample Gram | Wt. in gram | Per cent on Sample basis | Per cent on Ash + $H_2O$ free basis | Weight of sample Gram | Wt. in gram | Per cent on Sample basis | Per cent on Ash + $H_2O$ free basis |
| (1) Acid Digestion Only | | | | (*a*) Acid Digestion Only | | | |
| 0.3130 | 0.2939 | 93.90 | 99.42 | 0.2166 | 0.2191 | 101.15 | 107.14 |
| 0.1528 | 0.1452 | 95.03 | 100.62 | 0.2091 | 0.2144 | 102.53 | 108.56 |
| 0.1821 | 0.1722 | 94.56 | 100.11 | 0.2288 | 0.2228 | 97.38 | 103.10 |
| Average, | | 94.49 | 100.05 | Average, | | 100.35 | 106.27 |
| (2) Alkali Digestion Only | | | | 2(*a*) Alkali Digestion Only | | | |
| 0.2180 | 0.1991 | 91.33 | 96.70 | 0.2112 | 0.2071 | 98.06 | 103.86 |
| 0.1630 | 0.1504 | 92.27 | 97.72 | 0.1955 | 0.1927 | 98.52 | 104.38 |
| 0.1388 | 0.1274 | 91.78 | 97.17 | 0.2145 | 0.2118 | 98.74 | 104.59 |
| Average, | | 91.79 | 97.20 | Average, | | 98.44 | 104.28 |
| (3) Acid and Alkali: 1 Filtration | | | | 3(*a*) Acid and Alkali: 1 Filtration | | | |
| 0.1485 | 0.0964 | 64.91 | 68.75 | 0.1993 | 0.1425 | 71.50 | 75.71 |
| 0.2321 | 0.1501 | 64.67 | 68.47 | 0.1934 | 0.1445 | 74.71 | 79.13 |
| Average, | | 64.79 | 68.61 | 0.2193 | 0.1601 | 73.00 | 77.30 |
| | | | | Average, | | 73.07 | 77.38 |
| (4) Acid and Alkali: 2 Filtration | | | | | | | |
| 0.4437 | 0.2885 | 65.02 | 68.85 | | | | |
| 0.4082 | 0.2667 | 65.58 | 69.18 | | | | |
| 0.4432 | 0.2848 | 64.26 | 68.05 | | | | |
| Average, | | 64.95 | 68.69 | | | | |

When considered alone, the action of the acid on the coarse paper is very slight and the alkali does not seem to dissolve a very large quantity, but when the acid digestion is followed by an alkaline digestion the loss is very material. The total loss, shown in Table V, through the paper filter is 11.64 per cent; the loss through asbestos is not so large, 10.72 per cent. In each test with asbestos filters the amount of fiber recovered appeared to be larger than with the paper filters, but it has been demonstrated that there is a compensating error here on account of the asbestos losing weight.

The results with tests on fine paper are given in Table VI.

Digestions of the fine paper in alkali, and in both acid and alkali resulted in greater losses than those of coarse paper. These experiments confirm the results shown in Table V regarding the influence of the treatment in acid (1) on the subsequent action of the alkali (3). There is practically no loss in acid, but a small loss in alkali (2), yet a large loss when the material is acted on by both acid and alkali, (3) and (4).

The quantity of fine paper recovered after digestion in alkali only, or in acid and alkali was much less than when the coarse paper was used. This indicates that samples should always be reduced to a fair degree of fineness.

Tests (3), (4) and 3(*a*), Table VI, are supposed to give the same results. The good checks obtained for (3) and (4) show that the one-filtration method will give equally as good results as the regular two-filtration method.

As cottonseed meal contains a quantity of lint, corresponding to fine paper, it may be fair to assume that the actual amount of crude fiber in the ordinary meal is much larger than will be found by the official crude fiber method. Suppose the results with paper filters in Table III and those in Table IV are correct, giving about 9.5 per cent crude fiber, then this amount represents 68.6 per cent of the total quantity of fiber present—see Table VI, (3) and (4). By simple calculation the total fiber becomes 13.8 per cent, and, therefore, 4.3 per cent is soluble or digestible.

## SUMMARY AND CONCLUSIONS

1—A method is proposed for determining crude fiber in feedstuffs in which filter paper is to be used as the filtering medium, and which requires but one filtration.

2—Loss of crude fiber may occur when linen is used as a filter.

3—Asbestos may lose weight and thus introduce errors, causing the results to be too high. The error depends upon the weight of asbestos used.

4—The solvent action of 1.25 per cent sulfuric acid on practically pure fiber (filter paper) is negligible.

5—The treatment in sulfuric acid has an influence on the subsequent action of the alkali.

6—Coarse paper dissolves to the extent of 3.44 per cent during the 30 minutes' boiling in 1.25 NaOH, while fine paper dissolves to the extent of 2.8 per cent.

7—When filter paper is boiled in both acid and alkali, the loss with coarse paper is 11.64 per cent and with fine paper 31.4 per cent.

8—The proposed one-filtration method, with hard filter paper, gives more reliable results than those commonly obtained by the present official method for crude fiber

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## THE APPARENT EFFECT OF ACETIC ACID UPON THE CONSTANTS OF BUTTER FAT

By CLARENCE BAHLMAN

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During the course of a chemical and bacteriological examination of Cincinnati's ice cream supply carried on by the laboratory of the Cincinnati Department of Health,[1] it became necessary to examine each sample for percentage of milk fat as well as to determine the presence or absence of foreign fats and oils.

The careful attention required for the estimation of fat by the laborious Roese-Gottlieb method would have made it impossible to examine more than a few samples each day. By the use of a simpler method, the laboratory helper was enabled to arrive at the fat content of 20 or 30 samples within one hour's time.

By this method,[2] 9 grams of the melted ice cream are weighed into the ordinary 10 per cent Babcock milk bottle, 20 cc. of glacial acetic acid added, and the mixture thoroughly shaken: 10 cc. of Babcock sulfuric acid are then added and the bottle again shaken. From this point the sample is treated by the ordinary Babcock method for the estimation of fat in milk. The reading of the fat column in the neck of the bottle, multiplied by two, gives the percentage of butter fat.

With this technique, the charring effect of the sulfuric acid upon the sugar is eliminated. The separated fat has a clear, pale yellow color, is free from sediment and foam, and distinctly separated from the lower acid layer.

As a test for foreign fats and oils, a few drops of the clear fat from the Babcock bottles were placed in the Zeiss butyro-refractometer and the refractive index determined at 40° C. With this instrument, pure fat from cows' milk will give, at 40° C., a reading falling between 40.5 and 44.5 scale divisions.

Practically all of the readings upon the samples, however, were well below the minimum figures for pure butter fat. As a general rule, the readings varied from 38.0 to 41.0, with a few running as low as 36.5 scale divisions.

Since it appeared highly improbable that all of our ice cream manufacturers were practicing adulteration, and in view of the fact that the food chemist places such great reliance upon the refractometer, the abnormal results shown by the samples were the subject of further study.

### EXPERIMENTAL

One of the most suspicious samples was selected and about 15 grams of fat isolated, both by ether extraction and by the acetic acid Babcock method. The fat obtained by the latter method was taken from the necks of the bottles with a pipette and filtered through paper.

The fat separated by ether extraction gave results for refractive index and other constants which agreed with those for a pure butter fat. The fat obtained by the acetic acid method, however, gave low readings for refraction value and decidedly high Koettstorfer and Reichert-Meissl numbers, although a normal Hanus iodine figure was obtained.

It would appear from the above that when butter fat is separated from dairy products in the presence of acetic acid, the constants are materially altered. The following experiments were undertaken to determine whether such abnormalities were to be attributed to complex changes or merely to mechanical retention of the acid.

EXPERIMENT I—Nine grams of rich cream of known purity were placed into each of 15 Babcock bottles and 20 cc. of glacial acetic acid added. After mixing, 10 cc. of Babcock sulfuric acid were added and the bottles centrifuged as usual. The separated fats were drawn off, combined, and filtered through paper.

Fat was also separated from the same cream by the usual Babcock method of adding 17.5 cc. of sulfuric acid to 18 grams of cream.

After standing in the refrigerator over night, the well-known constants for butter fat were determined, with results shown in Table I.

TABLE I

| Fat obtained by | Babcock method | Acetic acid method | |
|---|---|---|---|
| Refractometer reading, 40° C. | 41.8 | 39.4 | |
| Hanus iodine number | 28.9 | 29.1 | |
| Koettstorfer number | 227.0 | 242.0 | [226.0] |
| Reichert-Meissl number | 28.3 | 44.4 | [ 27.2] |
| Soluble acids | 6.0 | 8.9 | [ 5.6] |
| Insoluble acids | 86.9 | 85.6 | |

It was found that 5 grams of the fat obtained by the acetic acid method retained acetic acid equivalent to 1.9 cc. *N* NaOH. Such acidity would have no effect upon iodine absorption nor upon the weight of insoluble acids, and consequently the two samples gave practically identical results for these determinations. The other constants, however, are based upon alkalimetrical principles and acid held by the fat would naturally affect the results. The figures shown in Table I were obtained by correcting for the amount of acid retained by the fat.

It will be seen that the corrected results vary from those given by the fat separated by the Babcock method only by amounts that can be attributed to experimental error.

It appears, then, that butter fat obtained by the ordinary Babcock method will give normal results for all of the usual determinations, while fat separated in the presence of strong acetic acid gives results apparently abnormal which, however, become normal when we take into account the acidity due to retained acetic acid.

EXPERIMENT II—Hydrochloric acid is also used for the separation of fat from dairy products. Like acetic acid, this also is a volatile acid and might be expected to be retained by the fat, affecting the results as in the case where acetic acid is used.

Eighteen-gram portions of cream were mixed with

[1] See *Amer. Jour. of Public Health*, **4** (1914), 1009-1015.

[2] Lichtenburg, THIS JOURNAL, **5** (1913), 786.

20 cc. of concentrated hydrochloric acid in Babcock cream bottles. The bottles were immersed in boiling water for 5 minutes, after which the fat was separated

TABLE II

| Fat obtained by | Babcock method | Hydrochloric acid method |
|---|---|---|
| Refractometer reading, 40° C | 41.8 | 41.8 |
| Koettstorfer number | 227.0 | 228.0 |
| Reichert-Meissl number | 28.3 | 29.0 |

by the Babcock centrifuge, filtered, and compared with the fat obtained upon the same cream as in the regular Babcock method. The results are shown in Table II.

Hydrochloric acid, therefore, was not retained by the fat to any appreciable extent, 5 grams having an acidity equivalent to only 0.5 cc. of 0.1 *N* NaOH. The Koettstorfer and Reichert-Meissl figures were practically identical with those obtained when using sulfuric acid for the decomposition.

EXPERIMENT III—In order to further show that acetic acid is the only acid retained to a sufficient extent to affect the refractive index and other constants of butter fat, three samples of pure butter were melted and the filtered fat treated by shaking in a separatory funnel with such volumes of water and acid as approach the proportions of each present in the analysis as ordinarily carried on. The quantities used were as follows:

*a—Babcock Method:* 15 cc. melted fat, 30 cc. water, 40 cc. concentrated sulfuric acid.

*b—Hydrochloric Acid Method:* 15 cc. melted fat, 90 cc. hot water, 100 cc. concentrated hydrochloric acid.

*c—Acetic Sulfuric Acid Method:* 15 cc. melted fat, 30 cc. water, 100 cc. glacial acetic acid, 50 cc. concentrated sulfuric acid.

After shaking thoroughly for 3 minutes, the fat was allowed to come to the top, filtered, and cooled in the refrigerator. The refractometer readings were then taken upon all, and the Koettstorfer and Reichert-Meissl numbers upon a few, of the samples. The results were compared with the constants obtained upon the untreated fats, as shown in Table III. The refractometer readings were also taken upon the fat treated with acetic acid, after standing for certain time intervals in an air oven at 90–95° C.

This table indicates that abnormal results are obtained only in the case of fats separated in the presence of acetic acid. Such results are due to acetic acid being mechanically held by the fat. There is no acetylization. The fat obtained by the acetic acid method after thorough washing to remove acidity and treating as in the determination of the acetyl value, but without acetylating with acetic anhydride, gives results which do not differ from those upon the untreated fat.

The refraction reading and other constants are the most erratic when the greatest amount of acetic acid is present, but approach nearer to the correct results as the acid is gradually volatilized. One hour's heating at 90–95° C. is necessary to drive off all of the acetic acid, after which normal figures for all of the determinations may be obtained.

TABLE III – RESULTS FROM TREATMENTS OF PURE BUTTER

| Sample No. | Determination | Untreated | Treated as in Babcock method | Treated as in HCl method | Treated as in Acetic Acid Method Heated at 90–95° C. Not Heated | ¼ hour | ½ hour | 1 hour | 2 hours |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Refractometer | 40.7 | 40.6 | 40.6 | 36.9 | 38.7 | 39.7 | 40.6 | 40.6 |
| | Koettstorfer | 226.0 | .. | 227.0 | .. | .. | .. | 226.0 | .. |
| | Reichert-Meissl | 29.7 | .. | 29.4 | 39.5 | .. | .. | 29.3 | .. |
| 2 | Refractometer | 42.0 | 42.0 | 42.0 | 38.8 | 40.2 | 41.0 | 42.0 | .. |
| | Reichert-Meissl | ... | ... | ... | 41.6 | ... | ... | 28.2 | .. |
| 3 | Refractometer | 42.9 | 43.0 | 42.9 | 39.8 | 41.6 | 42.8 | 42.9 | .. |

acid is retained mechanically and must be entirely removed by drying for one hour at 90–95° C. before proceeding to determine the constants.

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## CONCLUSIONS

I—Fats separated from dairy products by decomposition with sulfuric or hydrochloric acid will give the correct results for all of the usual determinations without any further treatment.

II—Fats separated in the presence of acetic acid will retain this acid and cause erroneous results. The

## STUDIES IN SYNTHETIC DRUG ANALYSIS
## IV—ESTIMATION OF PHENACETIN AND SALOL IN ADMIXTURE

By W. O. EMERY, G. C. SPENCER AND C. C. LEFEBVRE

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### INTRODUCTION

In the course of certain analytical work on medicinal tablets, we were considerably handicapped for a time through lack of a quantitative method for estimating phenacetin and salol in admixture. Accordingly, efforts were directed first to their separation and second to their individual determination. It was found that a satisfactory separation could be effected by treatment either with dilute sulfuric acid or with sodium hydroxide of definite concentration, followed by extraction with chloroform.

The separation proper, therefore, follows two distinct lines of procedure, involving on the one hand the acid hydrolysis of phenacetin, on the other the alkaline hydrolysis of salol. In the first instance, the direct estimation of phenacetin only is contemplated, the salol being determined by difference in all cases where the combined weight of both constituents is known or can be conveniently ascertained. In this procedure, the phenacetin is temporarily converted into phenetidine sulfate and acetic acid, while in the case of salol partial volatilization results during the process of digestion. The phenetidine salt, by virtue of its insolubility in chloroform, is readily freed from further contaminating salol by treatment with that solvent, then by means of acetic anhydride and sodium bicarbonate reconverted into phenacetin, the latter being subsequently isolated and weighed.

In the case of alkaline hydrolysis, the salol is first converted into sodium salicylate and phenolate,

from which the phenacetin is easily separated and subsequently recovered by extraction with chloroform. The salol is thereupon treated in rotation with standard bromine solution in excess, hydrochloric acid, potassium iodide and sodium thiosulfate. The principal reactions involved in the process and which serve as the basis for the calculation of results are:

$$HOC_6H_4CO.OC_6H_5 + 3NaOH = NaOC_6H_4CO_2Na + C_6H_5ONa + 2H_2O$$

$$C_6H_5OH + 4Br_2 = C_6H_2Br_3OBr + 4HBr$$

$$HOC_6H_4CO.OH + 4Br_2 = C_6H_2Br_3OBr + 4HBr + CO_2$$

$$C_6H_2Br_3OBr + 2HI = C_6H_2Br_3OH + HBr + I_2$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

from which it follows that 12 atoms of bromine are expended on every atom of salol and that titration of the iodine liberated by the unexpended bromine affords sufficient data for the estimation of salol.

### FIRST METHOD—ACID HYDROLYSIS

PHENACETIN—If the sample is in pill or tablet form, ascertain the weight of 20 or more, reduce to a fine powder and transfer to a small tube or specimen bottle which can be kept tightly closed with a cork or glass stopper. Weigh out on a small (5.5 cm.) tared filter an amount of the sample equal to, or a convenient multiple of, the average weight of such pill or tablet, wash with successive small portions of chloroform, in quantity about 40 cc., sufficient at least to insure the complete extraction of all the phenacetin and salol present in the mixture. Collect the solvent in a tared 100 cc. beaker, evaporating by means of a blast to apparent dryness. During this operation, the beaker may, with advantage, be allowed to stand on a warm plate (50–60°) without danger of undue loss of solid substance. Permit the beaker to remain 24 hours in the open at the ordinary temperature, weigh several times until practically constant, then transfer the crystalline residue, by dissolving in and washing with sufficient chloroform, to a 50 cc. lipped Erlenmeyer, evaporate solvent by means of a blast and gentle heat, add 10 cc. dilute sulfuric acid (1 : 10) and digest at full steam-bath heat until the liquid is reduced one-half. Add 10 cc. of water, continue the digestion as before, add a second 10 cc. of water and evaporate to 5 cc. Transfer the residual liquid by pouring and washing with about 20 cc. of water to a small separatory funnel of the Squibb type and extract in rotation with 15, 10 and 5 cc. chloroform, washing each portion as obtained with 5 cc. water in a second separator, in order to recover traces of phenetidine sulfate possibly taken up by the chloroform, finally rejecting the latter, since it contains all the salol not previously eliminated during the process of digestion.

To the aqueous acid solution of phenetidine sulfate in the first separatory funnel, into which also the wash water from the second separator has been drawn, add sodium bicarbonate in small portions until an excess of this reagent persists at the bottom of separator after complete neutralization of the sulfuric acid. Now add 25 cc. chloroform and for every 100 mg. acetphenetidine or phenacetin known or believed to be present 5 drops of acetic anhydride, shake for some time vigorously, then pass the nearly clarified solvent into a second separator containing 5 cc. water, shake and receive the chloroform in a 200 cc. Erlenmeyer, first passing it through a small (5.5 cm.) dry filter. Distil at gentle heat about 20 cc. returning the latter to the first separator. Augment with 5 cc. fresh chloroform and repeat the extraction, washing and filtering as before, then collecting the solvent in the Erlenmeyer and again distilling until 25 cc. chloroform are obtained. With this portion make a third and final extraction, repeating the operations of washing, filtering and distilling to the point where about 5 cc. chloroform remain in the Erlenmeyer. Transfer this chloroformic residue by pouring and washing with sufficient fresh chloroform to a tared 50 cc. beaker or crystallizing dish, evaporate on a steam or vapor bath to apparent dryness, finally removing any pronounced excess of acetic anhydride by repeated addition of 1 cc. portions of fresh chloroform (to which a drop of alcohol has been added) and subsequent evaporation. Allow the nearly colorless crystalline residue of acetphenetidine or phenacetin to stand some time in the open, or better in a vacuum desiccator over lime, in order to eliminate the last traces of acetic anhydride. Weigh at intervals until constant.

SALOL—To ascertain the quantity of salol present in the sample, subtract the weight of phenacetin as found above from the combined weight of the two ingredients determined in the preliminary separation.

### SECOND METHOD—ALKALINE HYDROLYSIS

PHENACETIN—On a small tared filter weigh out an amount of the sample containing not more than 100 mg. salol, exhaust with chloroform as in acid hydrolysis, collecting the solvent in a small lipped Erlenmeyer. Evaporate the chloroform by means of a blast and without applying heat. Add 10 cc. 2.5 per cent sodium hydroxide solution and heat 5 minutes on a steam or vapor bath at the temperature of boiling water. At the end of this period remove from bath and cool quickly to room temperature in running water in order to reduce to a minimum any tendency of the phenacetin to undergo partial hydrolysis. Transfer the liquid to a separatory funnel by pouring and washing with a minimum of water, finally rinsing out the flask with the first 20 cc. portion of chloroform used in extraction. Extract the aqueous alkaline solution with three 20 cc. portions of chloroform, washing each portion as obtained consecutively in a second separator with 5 cc. water, prior to passing the solvent through a small, dry filter into a 200 cc. Erlenmeyer, from which the combined chloroformic portions are distilled down to a residue of about 5 cc. Transfer the latter by pouring and washing with sufficient fresh chloroform to a small tared beaker or crystallizing dish, evaporate the solvent on the steam bath by the aid of a blast, cool and weigh the phenacetin at intervals until constant.

SALOL—Transfer both aqueous alkaline solutions from the separatory funnels to a suitable (500 cc.) glass-stoppered bottle, dilute with water to about 200 cc., run in from a burette an excess (about 45 cc.) of $N/7$ potassium bromide bromate, follow with 10 cc. concentrated hydrochloric acid, close flask and shake 1 minute, then at intervals over a period of one-half hour. At the end of this time add 10 cc. 15 per cent potassium iodide solution, agitating the closed flask at intervals for 15 minutes. Titrate the free iodine with standard thiosulfate (preferably $N/7$), previously adjusted to the standard bromine solution, 1 cc. of which is equivalent to 0.002548 g. salol. From the number of cubic centimeters standard bromine solution expended, calculate the salol on the basis of 12 atoms of bromine to 1 molecule of salol.

## COMMENTS AND SUGGESTIONS

Tared filters for use in this and similar work may be conveniently prepared as follows: Fold, adjust in a small short-stemmed funnel, moisten and press carefully so that the entire rim of filter fits snugly to the glass. After drying, keep in balance case or other suitable dust-proof container, and when needed weigh on a small metal support or glass tripod. It is self-evident that all weighings with tared filters should be made as nearly as possible under comparable conditions. If, for example, the first weight is taken under a hygrometric reading of 50 per cent, the second weighing should be made under approximately similar conditions. This is indispensable when it is desired to estimate the quantity of chloroform-insoluble residue in phenacetin-salol tablets or other preparations likely to contain sodium bicarbonate, sugar, starch, talc or other more or less inert excipients. Experience has shown, however, that a variation in humidity up to 5 per cent at the time of the two weighings would not be productive of material error.

Before carrying out extractions in separatory funnels or introducing liquids therein, the valves should first be "locked" with a drop of water, otherwise losses from capillarity may result.

All distillations of chloroform should be carried out over a wire gauze or asbestos provided with a small opening and heated by a very small flame, the flask being connected with the condenser by means of a small spray trap, if available, similar to the type used in Kjeldahl work.

Phenacetin, being only moderately soluble in hot aqueous media, is accordingly somewhat difficult of hydrolysis. In order, therefore, to insure its complete conversion to phenetidine sulfate, special attention should be directed to the end that any visible particles of crystalline substance on the sides of flask during the early part of digestion should be gradually brought into solution by gently rotating the flask and, if necessary, by the occasional addition of a few drops of chloroform.

In order to facilitate the work and minimize errors due to recharging burettes, $N/7$ solutions are advocated in order that the volume of the thiosulfate required may not exceed the capacity of a 50 cc. burette. The thiosulfate solution is standardized against pure iodine. The strength of the bromine solution may also be determined by the aid of pure acetanilide.[1]

## EXPERIMENTAL

The tabulated data given below are representative of results obtained by the authors in operations carried out on control and commercial mixtures substantially in accordance with the methods outlined above. A slight variation from the prescribed procedure should, however, be noted in the second series,

### ACID HYDROLYSIS

SERIES 1

| Phenacetin Gram | Salol Gram | Phenacetin recovery Gram | Phenacetin recovery Per cent | Salol recovery Gram | Salol recovery Per cent |
|---|---|---|---|---|---|
| 0.1028 | 0.1159 | 0.1028 | 100.00 | 0.1159 | 100.00 |
| 0.1021 | 0.0996 | 0.1021 | 100.00 | 0.0996 | 100.00 |
| 0.1006 | 0.1048 | 0.1009 | 100.39 | 0.1045 | 99.71 |
| 0.1015 | 0.1015 | 0.1010 | 99.50 | 0.1020 | 100.49 |
| 0.1010 | 0.1044 | 0.1008 | 99.80 | 0.1046 | 100.19 |
| 0.1042 | 0.1004 | 0.1043 | 100.09 | 0.1003 | 99.92 |
| 0.1015 | 0.1001 | 0.1016 | 100.09 | 0.1000 | 99.90 |
| 0.1069 | 0.1186 | 0.1071 | 100.18 | 0.1184 | 99.83 |
| 0.1010 | 0.1174 | 0.1009 | 99.89 | 0.1175 | 100.09 |
| 0.0996 | 0.1014 | 0.0998 | 100.20 | 0.1012 | 99.79 |
| 0.1103 | 0.1036 | 0.1101 | 99.82 | 0.1038 | 100.19 |
| 0.2000 | 0.2000 | 0.1999 | 99.95 | 0.2001 | 100.05 |
| 0.1000 | 0.2000 | 0.0995 | 99.50 | 0.2005 | 100.25 |
| 0.2000 | 0.1000 | 0.2004 | 100.20 | 0.0996 | 99.60 |

SERIES 5

| Sample(a) Gram | Phenacetin + Salol recovery Gram | Phenacetin recovery Gram | Phenacetin recovery Grains | Salol recovery Gram | Salol recovery Grains |
|---|---|---|---|---|---|
| 0.4316 | 0.3256 | 0.1621 | 2.50 | 0.1635 | 2.52 |
| 0.4316 | 0.3253 | 0.1622 | 2.50 | 0.1631 | 2.52 |
| 0.4316 | 0.3257 | 0.1616 | 2.49 | 0.1641 | 2.53 |
| 0.4316 | 0.3273 | 0.1626 | 2.51 | 0.1647 | 2.54 |
| 0.4316 | 0.3276 | 0.1607 | 2.48 | 0.1669 | 2.58 |
| 0.4316 | 0.3268 | 0.1611 | 2.49 | 0.1657 | 2.56 |
| 0.4316 | 0.3268 | 0.1637 | 2.53 | 0.1631 | 2.52 |

### ALKALINE HYDROLYSIS

SERIES 2

| Phenacetin Gram | Salol Gram | Phenacetin recovery Gram | Phenacetin recovery Per cent | N/7 Koppeschaar solution Cc. expended | Salol recovery Gram | Salol recovery Per cent |
|---|---|---|---|---|---|---|
| . . | 0.0892 | . . | . . | 33.99 | 0.0882 | 98.88 |
| . . | 0.0895 | . . | . . | 35.06 | 0.0891 | 99.64 |
| . . | 0.0900 | . . | . . | 35.17 | 0.0894 | 99.37 |
| . . | 0.0903 | . . | . . | 35.20 | 0.0893 | 99.12 |
| 0.0125 | 0.0914 | 0.0123 | 98.40 | 35.27 | 0.0897 | 98.13 |
| 0.0141 | 0.0915 | 0.0142 | 100.70 | 35.54 | 0.0904 | 98.77 |
| 0.0516 | 0.0513 | 0.0516 | 100.00 | 20.39 | 0.0518 | 101.10 |
| 0.0516 | 0.0512 | 0.0511 | 99.04 | 20.59 | 0.0523 | 102.30 |
| 0.0503 | 0.0499 | 0.0509 | 101.20 | 19.92 | 0.0506 | 101.50 |
| 0.0504 | 0.0508 | 0.0513 | 101.70 | 20.35 | 0.0517 | 101.77 |
| 0.0495 | 0.0499 | 0.0486 | 98.18 | 19.69 | 0.0501 | 100.40 |
| 0.0522 | 0.0516 | 0.0503 | 97.32 | 20.52 | 0.0521 | 100.97 |
| 0.0891 | 0.0884 | 0.0867 | 97.30 | 34.92 | 0.0890 | 100.67 |
| 0.1020 | 0.1020 | 0.1002 | 98.22 | 39.37 | 0.1003 | 98.33 |
| 0.1000 | 0.1003 | 0.0983 | 98.30 | 38.82 | 0.0989 | 98.63 |
| | 0.0880 | . . | . . | 34.67 | 0.0883 | 100.30 |
| | 0.0896 | . . | . . | 35.23 | 0.0898 | 100.20 |
| 0.0897 | 0.0892 | 0.0880 | 98.11 | 35.47 | 0.0904 | 101.30 |
| | 0.1020 | . . | . . | 39.35 | 0.1002 | 98.32 |
| 0.0977 | 0.0999 | 0.0974 | 99.70 | 38.63 | 0.0984 | 98.55 |
| 0.1005 | 0.1008 | 0.0999 | 99.42 | 39.71 | 0.1012 | 100.39 |
| 0.0989 | 0.1012 | 0.0982 | 99.28 | 40.11 | 0.1022 | 101.00 |
| 0.1011 | 0.1009 | 0.1000 | 98.91 | 40.00 | 0.1019 | 101.00 |
| SERIES 3 | | | | | | |
| 0.1006 | 0.1000 | 0.1002 | 99.60 | 39.48 | 0.1006 | 100.60 |
| 0.1039 | 0.1017 | 0.1011 | 97.31 | 40.00 | 0.1019 | 100.20 |
| 0.1015 | 0.1014 | 0.0987 | 97.25 | 39.69 | 0.1011 | 99.75 |
| 0.0995 | 0.1200 | 0.0981 | 98.60 | 47.11 | 0.1200 | 100.00 |
| 0.1012 | 0.1010 | 0.0995 | 98.33 | 39.64 | 0.1010 | 100.00 |
| 0.0982 | 0.0991 | 0.0966 | 98.37 | 38.76 | 0.0987 | 99.58 |
| 0.1023 | 0.1000 | 0.0998 | 97.57 | 39.12 | 0.0997 | 99.70 |
| 0.0996 | 0.1016 | 0.0972 | 97.59 | 39.86 | 0.1016 | 100.00 |
| 0.1037 | 0.0988 | 0.1013 | 97.68 | 38.78 | 0.0988 | 100.00 |
| SERIES 4 | | | | | | |
| 0.1032 | 0.1014 | 0.1035 | 100.20 | 39.60 | 0.1009 | 99.54 |
| 0.1043 | 0.0978 | 0.1045 | 100.20 | 38.22 | 0.0974 | 99.58 |
| 0.1003 | 0.1011 | 0.0990 | 98.70 | 39.83 | 0.1015 | 100.40 |
| 0.0911 | 0.1012 | 0.0894 | 98.13 | 39.93 | 0.1017 | 100.49 |
| 0.0723 | 0.1013 | 0.0710 | 98.20 | 40.08 | 0.1021 | 100.59 |
| 0.0569 | 0.1020 | 0.0569 | 100.00 | 39.87 | 0.1016 | 99.61 |
| 0.0799 | 0.1002 | 0.0787 | 98.49 | 39.47 | 0.1006 | 100.30 |
| 0.0553 | 0.1092 | 0.0550 | 99.45 | 42.71 | 0.1088 | 99.68 |

SERIES 6

| Sample(a) Gram | Phenacetin recovery Gram | Phenacetin recovery Grains | N/7 Koppeschaar solution Cc. expended | Salol recovery Gram | Salol recovery Grains |
|---|---|---|---|---|---|
| 0.2700 | 0.1005 | 2.48 | 40.06 | 0.1022 | 2.52 |
| 0.2700 | 0.1002 | 2.47 | 40.15 | 0.1023 | 2.52 |
| 0.2700 | 0.1003 | 2.47 | 40.04 | 0.1021 | 2.52 |
| 0.2641 | 0.0982 | 2.48 | 39.08 | 0.0996 | 2.51 |
| 0.2641 | 0.0985 | 2.48 | 38.82 | 0.0989 | 2.49 |

(a) Average weight of single tablet 0.4316 g.

[1] *Bull.* **132**, Bureau of Chemistry, U. S. Dept. Agr.; *Proc. A. O. A. C.*, p. 198, footnote *b*.

namely, that a 5 per cent sodium hydroxide solution was employed in effecting hydrolysis; likewise, in the fourth series, where two 30-cc. and one 20-cc. portions of chloroform were used in the recovery of phenacetin.

Series 5 and 6 involve a commercial preparation in tablet form alleged to contain 2.5 grains (0.1620 g.) each of phenacetin and salol.

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## THE PRODUCTION, BOTANICAL COMPOSITION AND VOLATILE OIL STRENGTH OF AMERICAN WILD MUSTARD SEED

By A. L. WINTON AND J. H. BORNMANN

Received March 8, 1915

The term "Wild Mustard," although regarded by botanists as being synonymous with charlock (*Brassica arvensis*), is applied by the trade to variable mixtures of charlock with brown mustard (*Brassica juncea*). Charlock is one of the most troublesome weeds in the grain and flax fields of the Northwest. Notwithstanding the means employed for its eradication by both state authorities and farmers, many of the fields of the Dakotas, Minnesota and adjoining states are masses of yellow during the flowering season and the threshed grain and flaxseed are contaminated with wild mustard seed. Other plants belonging to the mustard family occur with the charlock but most of these, such as pepper grass (*Lepidium virginicum*), shepherd's purse (*Capsella bursa-pastoris*) and false flax (*Camelina sativa*), do not have globular seeds. The notable exception is brown mustard, the seeds of which resemble those of charlock in size and almost invariably occur in greater or less amount mixed with the latter in the so-called "Wild Mustard" separated at the elevators, flour mills, malt houses, seed warehouses, and linseed works.

The total production of so-called wild mustard is very large. Samples of wheat examined in a single day under the direction of Mr. G. H. Tunnell, Chief State Grain Inspector, Minneapolis, in the presence of one of the writers, contained as high as 2.15 per cent of wild mustard and much larger amounts were stated to be not uncommon. A sample representing the total screenings output of one of the large Minneapolis mills contained 11.04 per cent of wild mustard of which 10.74 per cent was charlock and 0.30 per cent brown mustard.

Assuming an average of only 0.1 per cent for the entire spring wheat crop of 1913, the grand total would be about 180 carloads of 40 tons each. This estimate, which is doubtless much too low for the wheat crop, does not include the wild mustard separated from barley, rye and linseed, and that produced in adjoining provinces of Canada.

A grain merchant thoroughly acquainted with the situation reported that upward of 100 carloads annually were separated from grain in Minneapolis alone and another trade authority stated that this estimate was much too low. Large quantities are said to be shipped to Europe.

### SEPARATION OF WILD MUSTARD FROM GRAIN AND OTHER SEEDS

Screenings consisting of foreign seeds, chaff and other impurities are first separated into different grades by means of sieves and air currents. The grade containing the wild mustard seed includes other seeds, notably green fox tail (*Chaetochloa viridis*), and seed fragments of about the same size which are removed by ingenious machines, depending on the fact that these impurities do not roll with as great ease on an inclined surface as the round seed of wild mustard.

Two types of power separators, namely, the belt and the disk machines, are in common use and recently a spiral "extractor" containing no moving parts has been placed on the market.

THE BELT MACHINE consists of a broad belt running on two horizontal pulleys, one of which is higher than the other so that the upper surface of the belt forms an inclined plane moving slowly forward toward the higher pulley. A broad but thin stream of screenings is continually delivered on the belt from a hopper. The round seeds of the wild mustard roll down the belt into a suitable receptacle while the other seeds, because of their irregular form, do not roll but are carried by the belt in the opposite direction and discharged at the upper end.

THE DISK MACHINE employs several metal disks sloping slightly toward the center and revolving on the same vertical shaft. The screenings are delivered at a point near the edge of each disk. As the disk turns, the wild mustard seeds roll toward the center where they enter a chute, while the other seeds are carried around and are brushed off near the feeding point.

THE SPIRAL "EXTRACTOR" consists of a stationary spiral with several turns made up of three chutes into which the screenings are fed through a hopper. In their passage downward, the wild mustard seeds acquire sufficient velocity to jump outward into the middle and finally the outer chute from which in turn they pass into a hopper outlet, while the other seeds and impurities remain in either the middle or inner chute and emerge through two other outlets.

### DISTINCTION BETWEEN CHARLOCK AND BROWN MUSTARD

The important distinctions between the two seeds which make up the wild mustard of commerce are as follows:

1—Brown mustard is an escaped plant which in Russia is cultivated for its seed; charlock is an introduced weed regarded everywhere as a pest.

2—Brown mustard is dark brown and under a lens shows distinct reticulations; charlock varies from dark brown to nearly black and under a lens is finely granular but not reticulated.

3—The hulls of brown mustard do not respond to the chloral hydrate test; the hulls of charlock gently heated with this reagent become carmine-red.[1]

4—Brown mustard, like black mustard (*Brassica nigra*), contains potassium myronate, which on treatment with water, owing to the action of the myrosin, splits up with the formation of volatile mustard oil;

[1] Waage, *Ber. Pharm. Ges.*, **1893**, p. 153; Winton, *Orig. Com. 8th Intern. Cong. Appl. Chem.*, **26** (1912), 409.

charlock, as shown by Dircks,[1] Jorgensen[2] and ourselves, does not contain substances which yield any considerable amount of volatile oil by this treatment.

In addition there are histological differences which need not be considered here.

The distinction based on the formation of volatile oil is of great practical importance as it affects not only the flavor but the value of the seed for plasters and other medicinal preparations. White mustard (*Brassica alba*) does not yield volatile oil with water, but it does contain sinalbin and possibly other substances to which indirectly it owes its agreeable pungency, whereas charlock, although somewhat pungent, is recognized by the trade to be of inferior flavor. Cognizance of the inferiority of charlock has been taken by authorities on both foods and drugs. It is not recognized by the U. S. Pharmacopoeia or in the food standards; furthermore, the U. S. Government has issued a decision[3] requiring that it and its products be designated as charlock and not as mustard.

## UTILIZATION OF WILD MUSTARD

The removal of foreign seeds from grain is obviously necessary in order to secure a high-grade product. The further separation of wild mustard from the screenings is also desirable as it is distasteful to farm animals. Commercial wild mustard thus obtained is properly utilized for the production of oil which is valuable for technical use if not for human food. It remains to be determined what shall be done with the oil cake. Hitherto this has been added to mustard flour and prepared mustard, but for reasons already stated, such products are considered adulterated if not properly labeled as to the presence of charlock.

A rational use for cake containing a considerable amount of charlock would appear to be as a nitrogenous fertilizer for tobacco. Castor pomace, the residue from the manufacture of castor oil, which, owing to its poisonous nature cannot be fed to cattle, is used as a fertilizer, but the supply is limited and large quantities of cottonseed meal make up the deficiency. If charlock cake were found suitable for this purpose, a corresponding amount of cottonseed meal could be released for feeding, for which purpose it is well adapted.

[1] *Landw. Versuchs.*, **28** (1883), 179.

[2] *Nyt Tidskrift for Fysik ok Kemi*, **3**, 91

[3] Food Inspection Decision No. **137**.

The percentage composition of a sample of wild mustard cake consisting largely of charlock follows:

| Moisture | Ash | Protein (N × 6.25) | Crude fiber | N-free extract | Fat | Total |
|---|---|---|---|---|---|---|
| 9.20 | 5.42 | 31.19 | 10.44 | 26.93 | 16.82 | 100.00 |

| Nitrogen | Phosphoric acid | Potash | Volatile mustard oil |
|---|---|---|---|
| 4.99 | 1.54 | 1.02 | 0.23 |

This analysis shows the product to be nearly equal in fertilizing value to castor pomace of average quality.

## EXAMINATION OF SAMPLES OF COMMERCIAL WILD MUSTARD SEED

Early in the winter of 1913 one of the writers visited a number of mills, elevators, malt houses and seed warehouses in Minnesota, Wisconsin and Illinois, where wild mustard is separated from grain and other seed, and took samples for examination. Samples of pure seed of the four common species, namely, white, black, and brown mustard, and charlock, were kindly furnished for comparison by Professors Freeman and Oswald, of The Farm School, University of Minnesota.

Determinations of the percentages of charlock, brown mustard and foreign seeds were made on the commercial samples by picking out the different seeds under a lens and weighing. The results were corrected for the foreign seeds, and determinations of volatile oil were made by Roeser's method[1] on the mixture of charlock and brown mustard obtained in the separations. The results appear in Table I. It appears from these data that while brown mustard yields a good amount of volatile oil, charlock, like white mustard, is practically valueless in this respect. Samples of brown mustard and charlock grown at the Minnesota Farm School gave 2.89 and 0.25 per cent and others picked out from commercial wild mustard, 2.42 and 0.15 per cent of volatile oil respectively. The somewhat lower amounts in the latter case are possibly due to the conditions of growth in the grain fields as compared with those on the experimental farms where the plants had undisputed claim on the soil and light and the seed was harvested when ripe. The high percentage of volatile oil in the black mustard should be noted.

The relative amount of brown mustard and charlock in the samples of commercial wild mustard was ex-

[1] *Jour. Pharm. Chim.*, [6] **16** (1902), 361; Leach, "Food Inspection and Analysis," New York, 1914, p. 457.

TABLE I—BOTANICAL COMPOSITION AND VOLATILE OIL STRENGTH OF CHARLOCK, MUSTARDS, AND COMMERCIAL WILD MUSTARD

| KIND OF SAMPLE | SOURCE OF SAMPLE | Kind of separator | Per cent analysis of samples as separated: Charlock | Brown mustard | Foreign seeds | Per cent analysis calculated free of foreign seeds: Charlock | Brown mustard | Volatile mustard oil | Per cent volatile oil calculated from botanical analysis |
|---|---|---|---|---|---|---|---|---|---|
| Pure charlock (*B. arvensis*) | Commercial wild mustard | ..... | 100 | 0 | 0 | 100 | 0 | 0.15 | .... |
| Pure charlock (*B. arvensis*) | Grown at the Farm School, University of Minnesota | ..... | 100 | 0 | 0 | 100 | 0 | 0.25 | .... |
| Pure brown mustard (*B. juncea*) | | | 0 | 100 | 0 | 0 | 100 | 2.89 | .... |
| Pure black mustard (*B. nigra*) | | | .... | .... | ... | .... | .... | 4.62 | .... |
| Pure white mustard (*B. alba*) | | | .... | .... | ... | .... | .... | 0.16 | .... |
| COMMERCIAL WILD MUSTARD: | | | | | | | | | |
| Elevator, Devil's Lake, N. D. | Flax | .... | 0.5 | 99.5 | 0 | 0.5 | 99.5 | 2.42 | .... |
| Elevator, Milwaukee, Wis. | Barley | Disk | 90.5 | 4.7 | 4.8 | 95.1 | 4.9 | 0.24 | 0.26 |
| Malt house, Minneapolis | Barley | Disk | 88.0 | 10.7 | 1.3 | 89.1 | 10.9 | 0.38 | 0.40 |
| Flour mill, Minneapolis | Wheat | Belt | 85.2 | 9.0 | 5.8 | 90.4 | 9.6 | 0.36 | 0.38 |
| Flour mill, Minneapolis | Wheat | Belt | 82.1 | 12.9 | 5.0 | 86.4 | 13.6 | 0.41 | 0.46 |
| Flour mill, Minneapolis | Wheat | Belt | 87.5 | 8.5 | 4.0 | 91.2 | 8.8 | 0.33 | 0.35 |
| Flour mill, Minneapolis | Wheat | Belt | 75.7 | 18.2 | 6.1 | 80.6 | 19.4 | 0.57 | 0.60 |
| Flour mill, Minneapolis | Wheat | Belt | 47.8 | 35.8 | 16.4 | 57.3 | 42.7 | 1.14 | 1.13 |
| Flour mill, Minneapolis | Wheat | Belt | 57.3 | 27.6 | 15.1 | 67.5 | 32.5 | 0.94 | 0.89 |
| Flour mill, Minneapolis | Wheat | Disk | 73.5 | 24.5 | 2.0 | 75.0 | 25.0 | 0.91 | 0.72 |
| Flour mill, Chicago | Wheat | Disk | 86.6 | 2.5 | 10.9 | 97.2 | 2.8 | 0.19 | 0.21 |
| Seed house, Minneapolis | .... | .. | 89.0 | 9.0 | 2.0 | 90.8 | 9.2 | 0.43 | 0.36 |
| Seed house, Chicago | .. | ... | 66.2 | 28.5 | 5.3 | 69.9 | 30.1 | 0.91 | 0.83 |
| Seed house, Chicago | ... . | ..... | 87.4 | 11.8 | 0.8 | 88.1 | 11.9 | 0.47 | 0.42 |

ceedingly variable. In all the samples from grain the amount of charlock was invariably greater than that of brown mustard, ranging from 95.1 to 57.3 per cent as calculated to the pure wild mustard after correcting for foreign seed and impurities. A single sample of wild mustard from flax seed was almost absolutely pure brown mustard.

It should further be noted that the volatile oil obtained in the commercial samples was approximately proportional to the percentage of brown mustard present. This relation is so uniform that the volatile oil can be calculated from the botanical analysis with practically as great accuracy as by direct determination. For this purpose, the following formula based on the determinations made on the samples of the seeds separated from commercial wild mustard may be used:

$$V = 2.42\,B + 0.15\,C$$

in which V is the percentage of volatile oil, B is the percentage of brown mustard and C is the percentage of charlock. A comparison of the percentages of volatile oil found by analysis and as calculated by this formula in the samples of commercial wild mustard seed cleaned free of foreign seeds is given in the last column of Table I.

It can hardly be expected that a formula based on determinations made on only one sample each of brown mustard and charlock will give strictly accurate results in all cases, but the figures obtained on the samples examined by us show remarkable agreement and suggest further work both on wild mustard seed and the cake.

Determinations of volatile mustard oil in mustard flour may prove useful in estimating the approximate amount of charlock present as an adulterant provided this determination is supplemented by careful microscopic examination. It should not be forgotten, however, that in the presence of white mustard, which, like charlock, yields practically no volatile oil, or of black mustard, which may contain more than the brown, it would be impossible to arrive at a correct estimate from the volatile oil alone. Of special value in the case of such mixtures is an estimate based on the amount of hulls reacting with acid chloral hydrate solution.

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## THE DETERMINATION OF SULFATES IN SOILS

By P. E. Brown and E. H. Kellogg

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In undertaking a study of the process of sulfofication or sulfur oxidation in soils, the first problem which arose was the selection of an accurate method for the determination of the sulfates. Wiley gives directions for the determination without comment as to any difficulties to be met with. As he describes it, the method merely calls for treatment of the soil with cold, dilute hydrochloric acid, filtration and precipitation with barium chloride and weighing the sulfate formed. In the work of the few investigators who have made observations on the formation of sulfates in soils, the method of extraction of the sulfates is usually not mentioned and when the point is considered worthy of notice, the rather indefinite statement is made that the soil is treated with dilute hydrochloric acid. Is it important that a certain strength of acid should be employed in order to accomplish complete extraction? What should be the length of time of contact with the acid? These are questions which immediately arise and the experiments reported here were carried out to answer them and to develop a method which would permit of an accurate estimation of sulfates as such in the soil.

### EXPERIMENTAL

In the first experiments, therefore, 100-gram quantities of soil were shaken in the shaking machine for two hours with 200 cc. of 0.5, 1.0, 2.0, 5.0 and 10.0 per cent hydrochloric acid and with 200 cc. of water. A comparative series was run under exactly the same conditions except that 2 cc. of a 5 per cent solution of magnesium sulfate were added to each 100-gram quantity of soil. The amount of sulfate extracted in each case from the soil itself was thus determined and subtracting this figure from the total amount of sulfate obtained, the extraction from the magnesium sulfate added was found. The sulfates were determined in these cases by the usual gravimetric method using barium chloride. The results of these tests appear in Table I.

Table I Concentrations of Acid Varied

| Lab. No. | Per cent HCl used | Grams $MgSO_4$ added | Milligrams S extracted as Sulfates Duplicates | | Av. | Milligrams sulfur as $SO_4$ from $MgSO_4$ added | Not extr from $MgSO_4$ added |
|---|---|---|---|---|---|---|---|
| 1, 2 ... | 0.5 | None | 1.18 | 0.77 | 0.97 | | |
| 3, 4 ... | 0.5 | 0.1 | 24.19 | 26.04 | 25.11 | 24.14 | 26.63 2.49 |
| 5, 6 ... | 1.0 | None | 1.10 | 1.76 | 1.43 | | |
| 7, 8 ... | 1.0 | 0.1 | 23.94 | 26.38 | 25.16 | 23.73 | 26.63 2.90 |
| 9, 10 ... | 2.0 | None | 1.74 | 0.91 | 1.32 | | |
| 11, 12 ... | 2.0 | 0.1 | 24.47 | 24.47 | 24.47 | 23.15 | 26.63 3.48 |
| 13, 14 ... | 5.0 | None | 2.04 | 1.44 | 1.74 | | |
| 15, 16 ... | 5.0 | 0.1 | 30.92 | 31.46 | 31.19 | 29.45 | 26.63 Excess |
| 17, 18 ... | 10.0 | None | 1.10 | 1.40 | 1.25 | | |
| 19, 20 ... | 10.0 | 0.1 | 36.52 | 45.38 | 40.95 | 39.70 | 26.63 Excess |
| 21, 22 ... | Water | None | 4.00 | 4.12 | 4.06 | | |
| 23, 24 .... | Water | 0.1 | 30.70 | 30.34 | 30.52 | 26.46 | 26.63 0.17 |

Upon examination of these results it is found that treating a soil with hydrochloric acid in any of the strengths used did not permit of the determination of sulfates known to be contained in the soil. The weakest acid used allowed only a partial recovery of the sulfate added and as the concentration was increased up to 2.0 per cent acid the recovery became gradually smaller. With 5 and 10 per cent acid, however, the recovery was entirely too high, that with the 10 per cent acid being greater than that with the 5 per cent.

It is evident from these tests that there are some disturbing factors which prevent the extraction of sulfates from soils by hydrochloric acid. Van Bemmelen[1] observed that with hydrochloric acid much humus substance and iron oxide were dissolved and that these interfered with the determination of sulfates, causing low results. He found further that it was impossible to remove these substances without obtaining high results because of the oxidation of the sulfur in the dissolved organic matter.

Furthermore, with 5 or 10 per cent acid there is undoubtedly some solution of silica and this would make the results too high, as they have been shown to be.

It may be concluded, therefore, from these results

[1] *Landw. Vers. Sta.*, **37**, 284.

that dilute hydrochloric acid is quite unsatisfactory for the extraction of sulfates from the soil because of the ferric oxide and organic matter dissolved by the acid and because increasing the concentration of the acid makes the results too high on account of the interference of silica.

Examining the results where the soil was treated with water, it is found that rather complete extraction of the sulfates present in the soil was secured. Almost four times as much was extracted from the soil itself as with any of the hydrochloric acid solutions and the magnesium sulfate added to the soil was practically entirely recovered. Further tests to ascertain the efficiency of water for extracting sulfates were, therefore, planned.

In the first place it was deemed advisable to determine whether the amount of sulfates extracted from soil with water could be increased by longer periods of shaking. The same soil used in the preceding tests was, therefore, shaken for 2, 4, and 6 hours in the shaking machine and the results secured, which are given in Table II, show that just as much sulfate was extracted in two hours as in the longer periods.

TABLE II.—EFFECT OF TIME OF SHAKING ON EXTRACTIONS

| Lab. No. | Hours shaken | Milligrams sulfur as $SO_4$ in soil Duplicates | | Av. |
|---|---|---|---|---|
| 1, 2 | 2 | 3.42 | 3.51 | 3.46 |
| 3, 4 | 4 | 3.54 | 3.62 | 3.58 |
| 5, 6 | 6 | 3.04 | 3.64 | 3.34 |

It would seem, therefore, that the conclusion might be drawn that complete extraction of sulfates may be accomplished by shaking with water for two hours. It was felt, however, that in some cases quite considerable amounts of sulfates might be present in soils and in the sulfofication tests which it was purposed to carry out there was no doubt but that it would be necessary to encourage a rather large accumulation of sulfates to permit of the securing of definite data. Furthermore, magnesium sulfate, which was used in the previous series, is readily soluble, much more so than sulfates, such as calcium sulfate, more likely to be present in the soil. Consequently experiments were arranged to determine the ability of water to extract calcium sulfate from soils.

In the first tests, dehydrated gypsum was employed and the extraction with water was found to be quite incomplete, the discrepancies being rather large when the larger amounts of gypsum were used but still appreciable with the smaller amounts.

Gradually increasing the time of shaking with water permitted an increasing extraction of the sulfate, the largest proportion of that added being obtained when the period of shaking was eight hours. Still, however, the recovery was incomplete.

The same amounts of gypsum as were used mixed with the soil were shaken alone with water for varying lengths of time and the results showed that while mixing with soil retarded quite considerably the rate at which the sulfate went into solution in the water, the extraction was incomplete in the absence of soil even where only very small amounts of the gypsum were used. The pure, dehydrated gypsum used in this work has been found to be very much more difficultly soluble than the hydrated calcium sulfate and hence the tests were continued using chemically pure calcium sulfate containing two molecules of water. This compound is not only more readily soluble but it is believed to be more nearly like the compounds present in the soil than the dehydrated gypsum.

Tests of the solubility of the hydrated sulfate unmixed with soil showed complete solution in two hours' shaking. Varying amounts of the material were then added to the soil and the mixture shaken for varying lengths of time with water. The results given in Table III show that the extraction was complete in six hours. Other results using ground and unground soil showed that while the extraction was somewhat quicker in the ground than in the unground samples, shaking with water for 6–8 hours accomplished in all cases the complete extraction of the sulfate added. The amounts of sulfate added were much greater than would ordinarily occur in soils, and calcium sulfate is probably the most difficultly soluble of any sulfate which might occur in the soil. Hence the solution of this material in the amounts tested may be regarded as indicating that sulfates in the soil may be estimated readily by shaking with water for a period of six to eight hours.

TABLE III—EXTRACTIONS WITH WATER

| Lab. No. | Grams $CaSO_4$ added | Hrs. shaken | Milligrams S extracted: As sulfates Duplicates | | Av. | From $SO_4$ added | Mg. Sulfur Added as $SO_4$ | Not extr. from sulfate added |
|---|---|---|---|---|---|---|---|---|
| 1, 2 | 0.25 | 4 | 50.00 | 50.00 | 50.00 | 46.00 | 46.50 | 0.50 |
| 3, 4 | 0.25 | 6 | 50.72 | 50.46 | 50.59 | 46.59 | 46.50 | .... |
| 5, 6 | 0.25 | 8 | 50.38 | 50.12 | 50.25 | 46.25 | 46.50 | 0.25 |
| 7, 8 | 0.05 | 6 | 13.36 | 13.12 | 13.24 | 9.24 | 9.30 | 0.06 |
| 9, 10 | None | 8 | 4.00 | 4.00 | 4.00 | .... | .... | .... |

One point further was tested in this work and that was the use of the sulfur photometer. Gravimetric determinations of sulfates are very tedious and it was almost essential that a more expeditious method be employed if large numbers of determinations were to be made such as are necessary in studies of sulfofication. The photometric method was tested and compared with the gravimetric and it was found to be quite as accurate and much quicker. Its use for the determination of sulfates in soils should be strongly advised.

CONCLUSIONS

I—Sulfates cannot be extracted from soils by treatment with dilute hydrochloric acid because of the interference of organic substances and iron compounds.

II—Shaking soil with twice its weight of water in the shaking machine for six to eight hours extracts sulfates completely.

III—The sulfur photometer is a rapid and accurate means of determining sulfates.

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## COMPOSITION OF THE SALINES OF THE UNITED STATES. IV—A CORRECTION

By J. W. Turrentine[1]

Received January 28, 1915

Occasion having arisen for recalculating to the conventional combination the results in the analysis, in

[1] Scientist in Soil Laboratory Investigations, Bureau of Soils, U. S. Dept. Agriculture.

CORRECTIONS

Original analyses made by R. F. Gardiner except where otherwise noted

| Bulletin No. | J. I. E. C. No. | Ions | | Conventional Combinations | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Pp. No. | B. S. Pp. No. | Na | Cl | NaCl | $CaCl_2$ | $MgCl_2$ | $Na_2SO_4$ | $CaSO_4$ | $MgBr_2$ | $MgSO_4$ |
| | | **BRINES** | | | | | | | | |
| 53[a] | 4 831 | 13 | 100.8 | . | 258.0 | | | | | |
| | 5 | 14 | | | | 5.5 | | | 1.2 | |
| | 6 | 15 | | | | 4.7 | | | 1.3 | |
| | 7 | 16 | 104.0 | 171.6 | 264.3 | 5.9 | | | 0.9 | |
| | | | | | NaBr | | | | | |
| | 8 | 17 | | | 0.0 | | 0.4 | | 0.8 | |
| | 9 | 18 | | | 0.0 | 0.0 | | 3.5 | 1.4 | 0.7 0.5 |
| | 10 | 19 | | | | 0.0 | | 0.6 | 3.4 | |
| | 11 | 20 | | | | 0.0 | | 7.2 | 2.7 | |
| | 12 | 21 | | | | 0.0 | 0.0 | 0.0 | 1.4 | 4.5 |
| | 13 | 22 | | | | 0.0 | | 7.4 | 2.0 | |
| 54 | 51 | | | | | | | | 3.1 | tr |
| [b] | 61a | | | | | | | | 3.2 | tr. |
| | 23 | 832 | 32 | | | 0.0 | | 3.7 | 2.7 | |
| | 24 | | 33 | | | 44.3 | 49.0 | | 2.0 | |
| | 25 | | 34 | | | 0.0 | | 3.1 | 2.7 | |
| | 26 | | 35 | SO4 | 0.0 | 0.0 | | 3.0 | 2.0 | |
| | 27 | | 36 | 0.6 | | | | | | |
| 55 | 138 | | | | NaCl | | 0.0 | 8.6 | | 2.0 |
| | 142 | | 133.4 | | 303.5 | 0.0 | 0.0 | 43.3 | 7.5 | 4.0 |
| [c] | 149 | | | | NaBr | | 2.0 | 0.0 | | 1.6 |
| | 30 | 887 | 73 | | 0.0 | | 2.7 | | 2.0 | |
| | | | | | NaCl | | | | | |
| | 31 | | 74 | 92.2 | 234.3 | 5.5 | 12.9 | 0.0 | 36.8 | 2.3 |
| | 32 | | 75 | Fe NH4 | NH4Cl | FeCl3 | 12.1 | | | 0.6 |
| | 34 | | 77 | 0.8 0.3 | 0.9 | 2.3 | | | | |
| | 35 | | 78 | 0.8 | | 2.3 | | | | tr |
| | 36 | | 79 | | | | 14.5 | | | 2.3 |
| | 37 | | 80 | SO4 | | | 50.1 | | | 3.2 |
| 56 | 39 | | 82 | 8.6 | NaCl | | | | 12.2 | 0.2 |
| | 40 | | 83 | | 146.4 | | 23.9 | | | 2.3 |
| | 43 | | 86 | | NaBr | | 22.3 | | | 0.7 |
| | 44 | | 87 | Na | 0.0 | | 3.1 | | | 1.8 |
| [d] | 45 | | 88 | 117.7 | NaCl 299.2 | $CaCl_2$ 0.0 | 0.8 | 0.0 | 3.4 | 7.0 |
| | | | | | NaBr | | | | | |
| | 46 | | 89 | K | 0.6 | | 0.0 | | | 1.5 |
| [e] | 204 | | | 0.3 | | | | | | |
| 57 | 48 | | 91 | Br | | | 5.1 | | | 0.8 |
| | 60a | | | Na | 0.1 | NaCl | | | | |
| | 60b | | | 53.3 | | 135.5 | 47.4 | 10.2 | | 0.3 |
| [e] | 82 | | | 185.0 | | | 6.0 | | | |
| 58 | 156 | | | | 9.9 | | 0.0 | 0.0 | 0.1 | 2.0 |
| 60 | 53 | | 96 | | | | 0.0 | 0.0 | 0.0 | 4.1 1.6 |
| | 173 | | | 2.3 | | | 0.0 | | | |
| | 63 | | | | | | 0.0 | | 1.8 | 1.4 |
| | 171 | | | | | 254.5 | | 0.0 | 0.0 | 5.8 |
| | MOTHER LIQUORS, ROCK SALT AND SCREENED SALT | | | | | | | | | |
| 61 | 57 | 832 | 48 | 56.8 | | | | | | |
| | 61 | | 38 | | Cl | | | 7.8 | | 1.3 NaBr |
| | 62 | | 39 | 120.0 | 190.6 | 305.0 | 5.8 | 2.7 | 6.5 | 1.0 0.0 |
| | 65 | | 42 | | | | 1.2 | | | 2.3 0.0 |
| 62 | 72 | | 56 | | | | 0.0 | | 0.6 | 2.0 |
| | 74 | | 58 | | | 300.7 | 0.0 | | 2.5 | 4.1 |
| 63 | 80 | 833 | 64 | | | | 9.1 | 9.4 | | MgSO4 |
| | 86 | | 70 | | | | 0.0 | 5.9 | 0.0 | 2.7 4.4 |
| | 87 | | 71 | | | 256.5 | 0.0 | 35.2 | 0.0 | 1.4 12.8 |
| 64 | 89 | 888 | 98 | 75.2 | 200.8 | 191.2 | | 34.9 | | 2.1 |
| | 90 | | 99 | 64.7 | 204.1 | 170.5 | | 41.1 | | 3.8 |
| | 91 | | 100 | | CO3 | | | 36.4 | | 2.5 |
| | 92 | | 101 | 0.0 | 0.6 | 0.0 | | 17.2 | | 1.3 |
| | | | | | Cl | | | | | |
| | 93 | | 102 | 0.0 | 452.2 | 0.0 | | 137.8 | | |
| | | | | | CO3 | | | | CaHCO3 | CaCO3 |
| | 95 | | 104 | | 0.3 | | | | 0.0 | 0.5 |
| | | | | | | NaBr | | | Na2SO4 | CaSO4 |
| | 96 | | 105 | | | 2.2 | 0.0 | 0.0 | 3.3 | 2.0 3.0 |
| | 97 | | 106 | | | NaCl | 0.0 | | 0.7 | 6.1 |
| | 75 | | | 1.8 | H2O | 4.6 | | | | 0.6 |
| [e] [h] | 98 | | 107 | | | | | | | |
| | 99 | | 108 | Ca | 23.9 | | | | | |
| [e] | 5a | | | 130.0 | | | | | | |
| 65 | 100 | | 109 | Na | Cl | | | 18.8 | | |
| [h] | 101 | | 110 | 0.0 | 372.3 | 0.0 | 370.6 | 182.9 | | |
| [e] [h] | 103 | | 112 | | | | | | | |
| | 13a | | | 8.6 | | | | | | 0.9 |
| | 126 | | | 14.7 | Mg | 37.4 | | 222.8 | | 2.2 |
| | 105a | | 1 | | 0.1 | 98.3 | 0.0 | 0.0 | 0.4 | 0.7 0.5 |
| | 108 | | 4 | 38.8 | | | | 0.0 | 0.0 | 1.3 |
| | 111 | | 7 | 38.3 | SO4 | | | | | |
| | 112 | | 8 | 38.3 | 0.6 | | | | | |
| 66[g] | 21 | | | | | | | | | |
| | 114 | | | | Cl | 48.5 | 33.5 | | 0.0 | 7.1 |
| | 117 | | | | 53.9 | | | | | |
| [f] | 116 | | | | | | | | | |
| | 118 | | | | | 74.2 | 0.0 | 0.0 | 8.9 | 16.8 |
| | | 5 | 11b | | | | | | | |
| | 119 | 23 | 198 | 80.0 | | 203.4 | | 65.0 | | |
| | 120 | | 199 | 75.8 | | 192.7 | | 63.8 | | |
| | 121 | | 200 | 38.8 | | 98.6 | | 144.5 | | |
| | 122 | | 201 | 27.7 | | 70.4 | | 171.1 | | |
| | 123 | | 202 | 9.1 | | 23.1 | | 250.6 | | |
| | 124 | | 204 | | | 240.0 | | 4.2 | | |
| | 125 | | 205 | 60.1 | | 152.7 | | 117.5 | | 66.7 |

(a) A. R. Merz, analyst. (b) K only by Merz. (c) J. A. Cullen, analyst.
(d) From spring north of Woodward, Woodward Co., Okla. Collected by P. L. Clifton, 1910. (e) Data incongruous withdrawn.
(f) Same as *Bull.* **94**, p. 54, No. 17 and THIS JOURNAL, **4**, 832, No. 26. (g) Values represent parts per 1000, not per cent.

this laboratory, of certain American salines,[1] numerous inaccuracies, inconsistencies and typographical errors have been discovered which it is our desire to correct.

[1] *Bull.* **94**, U. S. Dept. of Agriculture, "The Occurrence of Potassium Salts in the Salines of the U. S." Extended abstracts, THIS JOURNAL, **4** (1912), 828 and 885; **5** (1913), 19.

The analyses have been recalculated by Mr. A. R. Merz, with the collaboration of Messrs. Gardiner and Cullen who have, in each case, inspected the results or approved them without inspection. The more serious of the errors encountered are set forth in the

table on page 688. Only the corrected figures and legends are recorded: reference is made to both publications, the first number being that assigned in *Bulletin* **94**, and the second, the Bureau of Soils number assigned in articles which appeared in THIS JOURNAL.[1]

To report in the conventional manner the results obtained in the examination of the various brines submitted for analysis was a concession to the supposed wishes of the laymen interested to whom the statement of results as ions conveys but slight information. This concession was made against our best judgment, since to report the various basic and acid radicles as combined is to abandon for the moment the best conception of the state of salts in solution. To calculate such analytical data to the saline combination is to juggle figures. As the basis for the conventional combination the respective solubilities of the component salts, which anciently were regarded as entities, have been taken. This, likewise, is a false basis, since the solubility of each salt when alone in solution is different from its solubility when in solution with the other salts. The latter solubility is determined by the equilibrium conditions obtaining for each system studied. The conventional combinations should represent, if anything at all, the solids precipitated on evaporation from the system studied, and should be recorded in the order of their precipitation. This could be determined only by an examination of the system under consideration.

The value of the results previously published is scarcely diminished by the errors introduced in the calculations previously published. However, the fact that the system of calculation from ionic to saline form is based on erroneous conceptions and therefore itself is erroneous does not excuse avoidable errors in the application of the system. For that reason it is desired to substitute the recalculations herewith presented.

BUREAU OF SOILS, U. S DEPARTMENT OF AGRICULTURE
WASHINGTON

[1] *Loc. cit.*

# LABORATORY AND PLANT

## A MODIFIED BURETTE CALIBRATING PIPETTE AND CERTAIN POINTS IN THE USE OF SUCH INSTRUMENTS[1]

By C. W. FOULK

Received March 23, 1915

Some months before this article was prepared for publication, the writer was told by the "Trouble Man" of a large chemical firm that the laboratory and factory control difficulties he was called upon to adjust were frequently caused by inaccuracies in the volumetric ware employed, and he added that in his opinion many young chemists and not a few old ones were unaware of this source of error. The "Trouble Man" must take the responsibility for his statement about chemists, but the author is willing to testify regarding the general depravity of uncertified volumetric ware. During the last ten years the calibration tables of several hundred burettes have been examined and errors of 0.1 cc. or more have been found the rule rather than the exception. Occasionally the corrections reach a truly surprising value. For example, at least three otherwise innocent looking burettes have been found with errors of over 0.4 cc. in the first 20 cc. of the scale. It, therefore, cannot be too strongly emphasized that all such measuring instruments must be calibrated before using.

If only one or two burettes are to be examined the method of weighing the water delivered from successive intervals is the simplest since it involves no special apparatus. If, however, a larger number are to be calibrated or if from time to time a few must be tested, some form of calibrating pipette will be found an advantage on account of the time saved and the simplicity and directness of the procedure. Several such pipettes have been described[2] but in every case an important point has curiously enough been overlooked, namely, the use of the two-way glass cock as an automatic zero adjustment. A modification employing this time-saving scheme will be described in this paper and in addition the general principles and procedures involved in the use and calibration of these calibrating pipettes will be given. It so happens that in previous articles there is not very good agreement as to the details of determining the capacity of the pipette itself and in some cases the methods of calculating the final values obtained for the different points on the burette scale are unnecessarily long. Many recent text-books also do not refer to the use of such calibrating instruments and, therefore, there is perhaps some justification for presenting in this place a more complete account of their advantages and use.

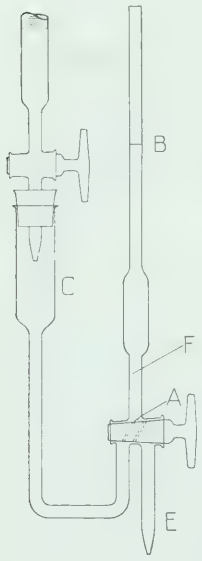
The instrument illustrated here is in its general operation like others that have been described, *i. e.*, it is a device for accurately measuring successive portions of water as they may be drawn from the burette under examination. It differs, however, from the previous instruments by its using the two-way glass cock as a zero adjustment instead of the usual mark on the lower stem. The enlargement at C may also be looked on as an improvement, since it furnishes a convenient place for attaching the clamp for holding it and also permits the use of a rubber stopper for connecting to the burette, which makes a more satisfactory joint than the gum tubing that would otherwise have to be employed.

All of the previously described pipettes of this sort have had a mark on the lower stem which served as a zero point, to which the water was adjusted before a portion was drawn out of the burette for measurement and at which the outflow was stopped when the pipette was emptied to make room for the next portion from the burette. The accompanying figure will illustrate this form of pipette if a mark around

[1] Pipettes of the design described in this article and provided with a 0.01 cc. division scale on the upper stem can be secured from the Kauffman-Lattimer Co., Columbus, O.

[2] Arndt, *Centralblat.*, **1856**, p. 865; Scheibler, *J. prakt. Chem.*, **76** (1859), 177; Ostwald, *Ibid.*, N. F., **25** (1882), 452; Morse and Blalock, *Am. Chem. J.*, **26** (1894), 479.

the stem be imagined at F. That such a mark is redundant and that the two-way cock can serve as a self-adjusting zero can be seen by reference to the figure, in which the cock is represented in the position of allowing the flow of liquid to take place from the burette into the pipette. It will be seen that, if the pipette has previously been filled and emptied, the flow will begin at the top of the boring through the plug of the cock as indicated at A. Furthermore, since the operation of the cock is such that the connection with the burette is closed before the outflow through the tip can begin and the outflow through the tip is closed before the inflow from the burette can begin, it is evident that, after the pipette is emptied and another portion of liquid is to be drawn from the burette, its flow will also begin at the top of the boring at A and so on for all succeeding portions. This makes the point A a zero mark to which the adjustment of liquid is automatically regulated by the position of the cock. Moreover, this zero point is more accurate than a mark around the lower stem would be on account of the smaller diameter of the boring.




GENERAL POINTS IN THE USE OF SUCH CALIBRATING PIPETTE

First, there can be no question of the accuracy of the method. Owing to the smaller bore of the stem of the pipette the readings are ten times more delicate than on the burette. In other words, differences of 0.001 cc. can be noted in the pipette as readily as 0.01 cc. in the burette. An error might possibly be introduced by carelessly allowing a considerable difference in temperature to occur between the water as measured in the burette and in the pipette. Ordinary care will, however, prevent such differences so that it is safe to assume the temperature of the water to be the same —within the limits required by the nature of the work. A similar assumption is made by the Bureau of Standards in its method of calibrating flasks by delivering into them measured volumes of water from standard pipettes.[1]

Secondly, there can be no question of the time saved by the use of these calibrating devices because adjusting the meniscus in the pipette when drawing off a portion of water from the burette is a brief operation compared with making a weighing, and finally because there are no temperature corrections to calculate. The pipette when once calibrated for the standard temperature (20°) for glass apparatus, may be assumed to retain a constant volume so far as ordinary laboratory temperature changes are concerned.

[1] Osborn and Veazey, *Bulletin B. of S.*, **4** (1908), 589.

THE CALIBRATION OF THE PIPETTE

It is evident that the capacity of the calibrating instrument itself must be determined with great care and that this must be done by weighing the water required to fill it. From this weight and the temperature of the water its volume can be calculated. The methods for making such calculations are to be found in any large text-book on quantitative analysis and, therefore, will not be repeated here. In this connection see also the Bulletin of the Bureau of Standards cited above.

At the outset, however, an important point in the calibration of such pipettes should be noted: the usual rapid rate of outflow of the ordinary burette must be restricted or the results will be in error. This is because in calibrating the burette, successive, small portions (pipettefuls) are drawn off with an interval of time between the readings while in an actual titration 30 to 40 cc. may be drawn off at once. The former method gives more water because, being the slower, there will be more drainage.[1] The difference due to variable drainage may amount to as much as 0.1 cc. in the lower part of the scale in burettes as ordinarily received from the manufacturers. If, however, the rate of outflow be sufficiently restricted (see footnote below) this difference in drainage between emptying the greater part of the burette in a series of small portions or all in one portion, becomes negligible. In earlier articles this point has received no mention, though the method of Morse and Blalock eliminates the error. These authors, however, do not discuss or even allude to this advantage of their plan. The same situation exists in the case of calibrating a burette by weighing. If successive small portions are drawn off in tandem the results obtained for the lower part of the burette will differ from those obtained by starting at zero, unless the rate of outflow is small. The Bureau of Standards, though recognizing the small size of the error occasioned by the tandem method of calibrating burettes with restricted outlets nevertheless follows the more accurate plan of starting at zero each time when drawing off the portion of water to be weighed.

Similarly, the author prefers the Morse-Blalock method for getting the capacity of the calibrating pipette. It has the merit of eliminating any possible tandem-error and at the same time is, if anything, a trifle shorter than other methods. As will be seen below, it does not give the true capacity of the pipette but rather the capacity corrected for any difference in drainage between emptying the burette in successive, small portions taken out in tandem, as compared with drawing out the same amount of water in one portion; for example, 0 to 5 cc., 5 to 10 cc., etc., to 45 to 50 cc. as compared with 0 to 50 cc. in one portion.

Morse and Blalock's procedure is to determine the capacity of the pipette in an indirect way, by dividing the volume of water delivered directly from zero to a mark near the bottom of the burette scale, by the

[1] Schloesser, *Z. anal. Chem.*, **46** (1907), 392

number of pipettefuls that can be drawn off to that mark. For example, with a pipette like the one shown here, the capacity of which is about 5 cc., it is evident that with a 50 cc. burette, 10 pipettefuls can be obtained if the capacity is less than 5 cc., or 9 pipettefuls if the capacity is a little more than 5 cc. Assuming the latter, let the reading of the burette be 45.23 cc. when the ninth pipetteful has been reached. To get the corrected capacity of the pipette, the burette is again filled to zero and the water allowed to flow out into a small flask to 45.23 cc. on the scale. This water is weighed, its temperature taken and its volume calculated. One-ninth of this is then the volume of the pipette to be used in calibrating burettes. It is not the true capacity of the pipette because the amount of water obtained by allowing the burette to empty itself at its normal rate from 0 to 45.23 is slightly less than the amount that would be gotten by drawing it out in nine portions with a considerable interval of time between each portion.

METHOD OF MARKING THE PIPETTE

The author of course hopes that no one will continue to put a mark on the lower stem of such calibrating pipettes, but there still remains the marking of the upper stem. This can be done as follows:

(1) A single mark arbitrarily placed is put around the upper stem. The exact capacity of the pipette from the stopcock to this mark is then determined by the method of Morse and Blalock. Such an instrument will measure successive portions of the same volume as they are drawn from the burette and the successive burette readings will correspond to the multiples of the capacity of the pipette. A variation of this plan consists in locating the mark on the upper stem so that it will correspond to some convenient whole number of cubic centimeters, such as 2 cc. or 5 cc. This is no advantage because, in any event, the burette readings will not fall on the marks of the burette representing such integral numbers or their multiples, and for plotting a correction curve the readings obtained by using an arbitrarily marked pipette would be of equal value with those obtained by the second method.

(2) A scale divided arbitrarily into small units approximating 0.01 cc. or so that each division corresponds exactly to 0.01 cc. may be combined with a major capacity mark which may be located in either of the ways described in (1) above. In using a pipette equipped with a scale, successive portions of the same nominal value, such as from 0 to 5 cc. on the burette, 5 to 10 cc. or whatever value the capacity of the pipette may be, are drawn out and their exact volume determined by measurement in the pipette.

"This appears to be an advantage, which is, however, more apparent than real, and will hardly pay for the extra labor required for the construction and location of such a scale unless a very large number of burettes are to be tested. In either case a correction curve can be made and the values corresponding to integral marks on the burette (1, 2, 3 cc., etc.) can be calculated upon the reasonable assumption that the bore of the burette does not change appreciably in a short length. Therefore, the error at any integral mark will be the same as at any reading in the immediate vicinity. Thus, if at 14.71 cc. the error is 0.05 cc., the same correction may be applied at 15 cc."

It might be interesting to compare the above method with the more laborious one employed in one of the previous articles on burette calibrating pipettes. The exact volume corresponding to the 50.00 cc. mark on a burette scale had been found to be 50.258 cc. and it was desired to find the volume corresponding to 49.52 cc. on the same scale. It was done by solving the proportion $50 : 50.258 :: 49.52 : x$, by which $x$ is found to be 49.7755 cc. (The figures are given as they are found in the article in question.) If instead of making this calculation, it had been assumed that the error of the burette at 49.52 cc. was the same as at the near-by point, 50 cc.—namely, +0.258 cc.—the true value of the scale reading 49.52 could have been found by simply adding the correction 0.258. This gives 49.7780 cc. which differs from the other value, 49.7755 cc. so laboriously obtained, by only 0.0025 cc., an amount which under the circumstances could introduce no error.

In order to show the necessary details in manipulation and calculation there will now be given the complete procedure for determining the capacity of the calibrating pipette and for using the pipette in finding the errors of a burette.

DETERMINATION OF THE CAPACITY OF THE PIPETTE[1]

The pipette and a burette, connected as shown in the drawing, are filled with distilled water. Both instruments can be supported on one ring-stand by the use of two clamps. Air bubbles in the connecting parts can be avoided by having the enlargement at C full of water before the stopper is inserted. This causes an overflow through the hole, and if now the tip of the burette is also filled before it is put into the stopper, no air will be entrapped. The level of liquid in the burette is adjusted to zero and the pipette (which must be full) is allowed to empty itself through the tip at E. This point of filling and emptying before an actual measurement is made is necessary because the capacity of the pipette is affected by the amount of liquid on the interior. This amount must obviously be the same for the first pipetteful as for the subsequent ones. In the manipulation of the stopcocks it will be found convenient to leave the burette cock open and control the flow of water entirely with the two-way cock of the pipette.

[1] Before beginning an actual calibration, the rate of outflow of both the pipette and the burette should be adjusted once for all by properly constricting the outlet orifice. The stopcocks can then be opened to their full extent and the rate of flow will be correct without further regulation. Specifications from the Bureau of Standards require the outflow of a burette with a scale 50 cm. long—about that of a 50 cc. burette—to be not less than 90 seconds nor more than three minutes, and the free outflow time of a 5 cc. pipette to be not less than 15 seconds nor more than one minute. The most convenient way of adjusting the orifice to a given rate of delivery is to draw out the tip in a flame so that it is smaller than desired. One can then gradually enlarge it by filing or grinding across the end. By this procedure trial can be made from time to time without the necessity of waiting for hot glass to cool or for drying the wet glass before heating again, as would be the case if the usual method of allowing the tip to contract in a flame were employed. Finally, everything must be thoroughly cleaned with chromic-sulfuric acid mixture and rinsed with distilled water before beginning work.

With the level of water in the burette at zero and the pipette emptied, the next step is to allow water to flow from the burette into the pipette till the mark at B on the upper stem is reached. This portion is then allowed to flow out through the tip at E. In this way successive pipettefuls are drawn off and wasted through E till a point is reached on the burette beyond which another portion would bring the level of the water below the scale. This last burette reading must be carefully noted and, though it is the only one necessary for the calibration of the pipette, the intermediate ones should also be made and recorded because they may subsequently be used in determining the errors of the burette and because it is the simplest way of insuring the same conditions in the calibration as in the subsequent use of the pipette.

The next step is to find the volume corresponding to the last reading on the burette as obtained above. This is done by disconnecting the pipette, filling the burette with water, adjusting the meniscus to zero and then allowing the water to flow out at its normal rate into a tared flask till the point corresponding to the last pipetteful is reached. This portion of water is then weighed to the nearest milligram and from its weight and its temperature its true volume in cubic centimeters is calculated. The above experiments should of course be repeated several times till closely agreeing results are obtained, the averages of which are then used for the final calculations as follows:

Suppose that the capacity of the pipette is such that the tenth portion drawn from the burette by its use brings the level of liquid to 49.82 cc. on the burette scale and that the weighing of the water delivered directly from zero to this point gave its true volume as 49.88 cc. Since this volume corresponds to ten pipettefuls, it is evident that the capacity to be assigned to the pipette is 4.988 cc.

### CALIBRATION OF A BURETTE

The calibration of a burette is carried out by connecting the pipette as described above and drawing off successive pipettefuls, noting the reading each time on the burette scale. Assuming a pipette with a capacity of 4.988 cc. and an average burette, readings would be obtained about as given in the first column of the table below. The second column gives the true

TABLE I

| 1 Burette readings | 2 Correct volume | 3 Corrections | 4 Burette reading | 5 Correct volume |
|---|---|---|---|---|
| 5.05 | 4.99 | —0.06 | 5.00 | 4.94 |
| 10.04 | 9.98 | —0.06 | 10.00 | 9.94 |
| 15.04 | 14.96 | —0.08 | 15.00 | 14.92 |
| 20.08 | 19.95 | —0.13 | 20.00 | 19.87 |
| 25.06 | 24.94 | —0.12 | 25.00 | 24.88 |
| 30.03 | 29.93 | —0.10 | 30.00 | 29.90 |
| 35.06 | 34.92 | —0.14 | 35.00 | 34.86 |
| 40.04 | 39.90 | —0.14 | 40.00 | 39.86 |
| 45.05 | 44.89 | —0.16 | 45.00 | 44.84 |

50 + Correction for 50.00 cc is found by the method illustrated in Table II

volume corresponding to the readings and is obtained by multiplying the capacity of the pipette by the serial number of the interval measured and rounding off the numbers to two decimals. Column 3 gives the corrections for the points in Column 1 and, since the corrections are the same for all points in the immediate vicinity of a given point, the numbers in Column 3 are also the corrections for the burette readings as given in Column 4. Column 5 gives the volumes corresponding to the "5 cc." points on the scale.

The above figures are from an actual burette and present a complication that may sometimes arise; namely, that when starting at zero the last pipetteful may bring the burette reading below the scale. This situation is, however, easily remedied by a simple trick of manipulation. Two or three sets of readings are wanted in any event in the interests of accuracy and when the first series shows that the last pipetteful brings the reading below the scale, the next series is started a little above the beginning of the second interval; in this case, for example, at 5.00 cc. on the burette scale. The burette readings are then as follows:

TABLE II

| I Burette reading | II Correct volume | |
|---|---|---|
| 5.00 | 4.94 | The correct volume corresponding to the burette reading of 5.00 cc. is taken from Table I |
| 9.99 | 9.93 | |
| 15.00 | 14.92 | |
| 20.03 | 19.90 | |
| 25.01 | 24.89 | |
| 29.98 | 29.88 | |
| 35.01 | 34.87 | |
| 40.00 | 39.86 | |
| 45.00 | 44.84 | |
| 49.98 | 49.83 | |

The true volumes corresponding to the readings are obtained by adding the appropriate multiple of the capacity of the pipette to the volume corresponding to the starting point which is taken from Table I and which must be checked by a separate experiment. This series of readings in Table II also gives the corrections for points in the immediate vicinity of those marks on the burette scale which are multiples of 5 and consequently may be applied at once to those marks. In other words, they are check readings on those of Table I, and in addition give the value of the correction for the 50 cc. mark.

If a correction curve is to be made, the above data are sufficient. In case it is desired to tabulate the corrections for each "cubic centimeter" mark on the scale of the burette the following procedure should be used: (1) The true volume of each 5 cc. interval of the burette is found by a series of subtractions based on the values in Table I, Column 5; (2) the value of 1 cc. in each interval is found by dividing the true volume of the interval by 5. Table III illustrates these two points.

TABLE III

| Interval on burette scale | Volume of interval | Value of "1 cc." in interval |
|---|---|---|
| 0 to 5 | 4.94 | 0.988 |
| 5 to 10 = ( 9.94 — 4.94) = | 5.00 | 1.000 |
| 10 to 15 = (14.92 — 9.94) = | 4.98 | 0.996 |
| 40 to 45 = (44.84 — 39.86) = | 4.98 | 0.996 |
| 45 to 50 = (49.85 — 44.84) = | 5.01 | 1.002 |

The final tabulation is made by adding these cubic centimeter values in Table III, the results being rounded off to two decimals. Table IV, below, covering part of the burette scale, shows this.

TABLE IV

| Burette reading | True volume | Burette reading | True volume | Burette reading | True volume |
|---|---|---|---|---|---|
| 1 | 0.99 | 8 | 7.94 | 44 | 43.84 |
| 2 | 1.98 | 9 | 8.94 | 45 | 44.84 |
| 3 | 2.96 | 10 | 9.94 | 46 | 45.84 |
| 4 | 3.95 | 11 | 10.94 | 47 | 46.84 |
| 5 | 4.94 | 12 | 11.93 | 48 | 47.85 |
| 6 | 5.94 | . | ..... | 49 | 48.85 |
| 7 | 6.94 | .. | ... | 50 | 49.85 |

If this plan is used, the tabulation should be made

on a stiff piece of paper or board so that it can be hung up near the burette.

CONCLUSION

In this article there has been described a modification of a burette-calibrating pipette that eliminates the mark on the lower stem and provides for the use of a two-way cock as an automatic zero-adjusting device.

A discussion of the principles underlying the calibration and use of such pipettes is also given.

DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY
COLUMBUS, OHIO

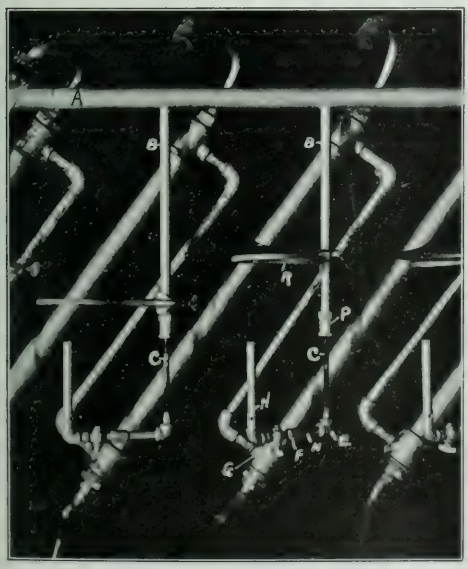
## AN ADJUSTABLE BURNER SUPPORT FOR CONDENSATION APPARATUS

By H. E. BISHOP

Received April 19, 1915

The condensation apparatus described by H. E. Barnard and H. E. Bishop in the *Journal of the American Chemical Society*, **28** (1906), 999, was designed for use with flasks of uniform size only. The burner and flask supports were so arranged that in changing the adjustment of the still it was necessary to move them as a unit. To overcome this difficulty the burner and flask support to be described was designed.

The condensation tubes, water connection and their supports were not changed. The gas supply was changed from a position under the flask support to the top of the supports for the condensing tubes *A*.




The gas pipe was already tapped for $^1/_8$ in. air cocks to which the burners were attached. The air cocks were replaced by $^1/_8$ in. close nipples. An 11 in. length of $^9/_{16}$ in. (outside diam.) brass pipe, *B*, was tapped at one end to fit the $^1/_8$ in. close nipple and attached to the gas pipe. This pipe, hanging in a perpendicular position, forms the rod for the ring which supports the flask.

Into this tube was fitted a brass tube, *C*, which would slide easily. The lower end of this sliding tube was soldered into a $^1/_8$ in. brass elbow, *E*. A 2-in. $^1/_8$ in. nipple, *N*, was screwed into the other side of the elbow; then a $^1/_8$ in. coupling, *F*, which in turn took the air cock, was attached. Another elbow was attached to the air cock *G* which took the nipple for the tube of the Bunsen burner *H*.

The gas joint, which allows the burner to be adjusted up or down, is similar to the old gas drop-light which was on the market before the use of rubber tubing was so general. The lower end of the tube *B*, which forms the ring support and the outside member of the extension tube, was threaded to take an ordinary packing box, *P*, similar to those used at the top and bottom of the condensing tubes. Ordinary candle-wick packing, well oiled, was used. The addition of a ring, *R*, from the regular ring stand, completed the apparatus.

The great advantage of the apparatus is its wide range of adjustment for individual operations. Flasks from 5 in. to 14 in. high can be used simultaneously. The sliding gas tube overcomes the necessity for rubber connections and if more heat is desired, two burners may be turned under one ring. The cost of construction is small and the upkeep is *nil*.

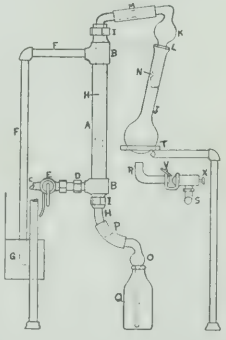
INDIANA STATE BOARD OF HEALTH
INDIANAPOLIS

## A NEW AND IMPROVED FORM OF KJELDAHL DISTILLATION APPARATUS

By ARTHUR D. HOLMES

Received March 9, 1915

A description was given in THIS JOURNAL, **6** (1914), 1010, of a Kjeldahl apparatus which has given satisfactory service in this laboratory. This apparatus as described, when set up on a laboratory table of the usual height, has been found somewhat too high for convenience when used by a person of short stature. To avoid this difficulty, the apparatus may be modified as indicated in the accompanying sketch, which should be substituted for Fig. II of the original article. The height may be decreased 6 to 8 in. by replacing the upright type of burner with a horizontal offset burner, and shortening the condenser pipe accordingly. It is well to make sure, however, that the diameter of this pipe, and the rate of flow of the water in it, are sufficient to insure condensation in the tube *H*.




The modification not only lessens height, but also obviates the disagreeable results which often follow

the breaking of a Kjeldahl flask during the distillation. Whenever this occurs, the upright burner must usually be dismantled and cleaned, as it is generally coated inside and out with a crust of alkali, which clogs the gas passages. While the solution may in some instances run down the tube of the offset burner, at the worst it merely coats that portion of the burner and does not clog up any of the parts necessary for adjusting the flames; consequently there is less confusion and interruption of distillations.

Attention is directed to the fact that the pipe sizes given in the original article (refer to Fig. II) are outside measurements rather than the inside dimensions customarily used in plumbers' specifications.

LABORATORY OF NUTRITION INVESTIGATIONS
OFFICE OF EXPERIMENT STATIONS
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON

# ADDRESSES

## LEST WE FORGET! WHO KILLED COCK ROBIN? THE U. S. TARIFF-HISTORY OF COAL-TAR DYES

By BERNHARD C. HESSE

Received June 24, 1915

In 1914 the textile industry[1] said to the chemists of this country:

"The appeal of the textile industry to the chemist at present is: 'We need dyestuffs, so get busy and make them; don't hem and haw, and make excuses, but get right on the job.' "

Again in 1914 the dye-users[2] said to the chemists of this country:

"Users of dyestuffs in quantity are more or less indignant over the fact that manufacturers in this country are dependent upon other countries, and Germany particularly for the dye supply. They ask: 'Why haven't our chemical companies experimented sufficiently to produce synthetic dyes, pharmaceutical products, essential oils and synthetic perfumes, in the production of which Germany seems to have had almost a monopoly?'

"The users of dyestuffs say that the General Chemical Company, with its cash resources and its extra cash and stock dividends yearly, and other companies in a similar position, ought to have had sufficient initiative to use a portion of their large profits in experimental work, which would have permitted us to manufacture synthetic dyes without recourse to other countries and would not have permitted American manufacturers to suffer severely when imports were checked by the war. They state that the interests of manufacturers of the country should have been placed ahead of large immediate profits and unusual dividend returns to stockholders."

In view of these statements the following excerpts from the official reports of the various Tariff Commissions and similar Committees, from 1882 forward, are not without present-day utility and interest.

The views of importers, users, economists and domestic chemical and dye-makers are given quite fully; repetition has been avoided as far as reasonably practicable. For fuller information the complete originals should be consulted.

These excerpts show beyond doubt that practically every argument advanced in 1914 as to why coal-tar dyes should theretofore *have been* made in this country, was previously presented to Congress in support of the view that they *should be* made here.

These excerpts are here presented in the hope that careful study of them by the chemists of this country will pave the way for tariff treatment of coal-tar products, inclusive of dyes, on as nearly a fair and equitable economic basis as all the circumstances may require.

[1] THIS JOURNAL, **6** (1914), 945.
[2] *Wall Street Journal*, Dec. 28, 1914.

### Report of the Tariff Commission, 1882

LONG BRANCH, N. J., July 26, 1882.

VOL. I—PP. 154–6. Mr. JOHN CAMPBELL, of New York City, a member of the firm of J. Levinstein, Campbell & Co., manufacturers of aniline dyes, appeared in response to the invitation of the Commission and made the following statement:

GENTLEMEN OF THE COMMISSION: We are importers and manufacturers of aniline dyes. We pay from 5 to 300 per cent duty on the different articles which we import. Our goods are used by paper makers, manufacturers of woolens and other textile materials, and in nearly every class of industrial pursuits. We are the third largest aniline-dye importers in this country, and pay annually duties amounting to nearly $100,000 upon the dyes we import. The duty now is 50 cents per pound, and 35 per cent ad valorem upon aniline dyes and colors, by whatever name known. With the exception of four small firms in the United States, who only manufacture two or three colors, out of two or three hundred imported, and who altogether do not employ more than fifty men, these dyes are all imported from Germany, England, France, and Switzerland.

As I have said, these colors enter into the consumption of nearly every manufacturer of textile fabrics, paper, leather, silk, ink, matches, soap, printers' and innumerable other trades. They cannot profitably be made in this country for various reasons: First, the raw material is here in only very limited quantities; second, the acids and other chemicals used for making these dyes are not made here; third, the skilled chemists who have grown up with this particular branch of industry are very few and are all engaged in Europe.

In every country in Europe, and even Canada, these goods are upon the free list. There is one dye, wool scarlet, a substitute for cochineal, which bears a duty of 135 per cent, while cochineal, the article it is a substitute for, is admitted free. This means a tax upon every 100 pounds of woolen or worsted yarn, dyed scarlet, of from $1.50 to $2, and to every manufacturer of hosiery (shirts and drawers knitted) 25 cents per dozen of shirts.

This compound duty of 50 cents and 35 per cent is a very unequal tax, as the bulk of the dyes are only worth abroad from 50 to 60 cents per pound, whereas at the time this duty was levied, scarlet dye was unknown, and the dyes then imported were worth from $2.50 to $10 per pound in Europe. I doubt if a single consumer of these dyes would advocate the retention of this portion of the tariff. I am in favor of the free importation of these goods, but still, if a duty be requisite for revenue, then I say make it ad valorem instead of specific and ad valorem, as the fifty cents per pound alone means upon some of these dyes 240 per cent duty, while upon others it means only 5 per cent.

I have no means of getting at the exact quantities imported into the United States, but from a list of the imports recorded in the *Oil, Paint and Drug Reporter*, which I take to be fairly

accurate, I find that from January 1, this year, to June 30, there were 532,000 pounds of aniline dyes imported into the city of New York, so that it would not be far from a correct estimate to place this year's imports into the United States at a total of 1,500,000 pounds, paying a duty of $1,500,000. If these goods are placed upon the free list it will go a long way towards enabling American home industries to compete successfully against foreign manufactures in foreign markets.

The three largest importers of these dyes are William Pickhardt & Kuttroff, of New York, agent for the Badische Aniline Company, of Stuttgart, Germany; Lutz & Movius, of New York, agents for Meister, Lucius & Brüning, Hoechst-on-Main, Germany; and ourselves. Our works are at Blackley, near Manchester, England.

These three firms import more than half of all the aniline dyes brought to the United States, while the remaining half are distributed between about twenty other firms.

Aniline dyes, although a manufactured article, are really and substantially, to the American consumer, a raw material. There has been, since the tariff was last framed, quite a revolution in this trade, which has brought them from the category of a luxury to a necessary and essential product, of great importance to the industries previously stated.

All the large carpet manufacturers use these goods, and the tariff is quite unequal. When it was first framed the duty was 30 to 40 per cent, but now the duty is 300 per cent very nearly on some of the articles.

By the PRESIDENT:

*Question.* Will you please state what the dyes you have referred to are made of, and whether they are manufactured in England any better than we could possibly manufacture them here?—*Answer.* Aniline dyes are manufactured from coal tar, or gas tar it is called in England. In England they are produced more extensively than here, for one reason that the material is not found in this country in such abundance as it is in England and for the several other reasons before mentioned. I understand that the coal found in this country does not contain so great a percentage of the light hydrocarbons as the coal found in England, therefore these dyes cannot be made here at such profit. In Germany and France they import their raw materials largely from England. Manchester is the center of production for aniline. There are four large firms engaged in the manufacture in Germany, two in France, and a few in Switzerland. The raw material at our command is not sufficient or cheap enough to enable us to make them at a profit at present, but if the duty is put up pretty high we will erect works and manufacture some of the dyes here ourselves. If the duty is taken off, this branch of industry will remain as it is at present.

*Q.* I would like to ask you as to the aniline dyes that are made in this country—whether their quality is good and whether you are limited to one color?—*A.* There are three colors made in this country. One is *magenta*, the raw material for which is imported from England. It is manufactured here and sold at a fair price, but the quality is not such as to enable it to compete with the imported article. The firm which manufactures it is located at Albany, N. Y. I do not think they employ more than about forty men altogether. There are three other concerns, employing a dozen men. That is the extent of the manufacture at present. They do not compete with the foreign goods at all.

*Q.* What amount of these goods are used by the different manufacturers of colored prints, for example; I mean of these aniline dyes?—*A.* I cannot tell you exactly the amount the different manufacturers consume, but the quantities imported last year were about 1,200,000 pounds, paying a duty of $1,200,000. These dyes take the place of almost every color. Cochineal has been generally used for dyeing woolen goods, but wool scarlet is used as a substitute for *cochineal*, which comes in free, while this has to pay 135 per cent duty. They replace also archil and other barks, woods, and extracts used for coloring purposes. This whole trade is yet in its infancy. The blue article that I introduced into this country enters into the manufacture of all the paper used by the New York dailies. It sold then at $4 a pound, and it took the place of *ultra marine*. All the paper-makers use it. Among the consumers of aniline dyes I might mention the following: All woolen manufacturers, who use it in the manufacture of bed-blankets, horse-blankets, carpets, shirts and drawers, flannels, hosiery, domestic woolen yarns, worsted piece goods, merinos, ladies' opera flannels, wool hats, overcoatings, &c. It is also used in the manufacture of dress goods, both woolen and cotton; ginghams, prints, and cotton yarns. It is also used in all classes of paper manufacture, not only for newspapers, but for paper used for wrapping purposes, for posters, envelopes, and wall paper; also in the manufacture of straw hats, willow and wicker work, leather for chair covers, and for printing inks, especially by all label press printers, and by matchmakers and jute-carpet manufacturers.

LONG BRANCH, N. J., July 26, 1882.

Mr. Joseph Wharton, of Philadelphia, representing the nickel interest, appeared before the Commission in response to its invitation and made the following statement:

VOL. I—P. 205. * * * * * * I also know something about aniline dyes, because I was invited to go into that industry, and had occasion to examine it at the time. I declined to go into it because I had so many other kinds of business on hand. The idea that we have not in this country the material for manufacturing aniline dyes is absurd. A small fraction of the waste of our gas-works would make all that the country wants. There is a lack of skill here to produce the dyes, and a certain amount of danger to life in the process of producing them. They are mostly made by the use of arsenic, which makes poisonous compounds, sometimes destroying the lives of healthy workmen, and perhaps destroying the lives of the persons who use aniline-dyed carpets or live in the rooms where the walls are covered with paper colored with aniline. But there is no trouble about the making of aniline dyes in this country. I think it is an industry that should have every measure of encouragement that the government sees fit to give to other industries * * * *.

LONG BRANCH, N. J., July 26, 1882.

VOL. I—PP. 207–8. Mr. HENRY BOWER, of Philadelphia, made the following statement before the Commission in regard to the subject of aniline dyes, in addition to his former statement on the general subject of chemicals, given on the 22d of July:

I would like to make a short additional statement on the subject of aniline dyes. Sometime ago, while this whole question was being discussed in a public way, I received a letter from Mr. H. K. Lansing, the treasurer of the Albany Aniline and Chemical Works, relating to this subject, which I will take the liberty of reading. It was as follows:

ALBANY ANILINE CHEMICAL WORKS,
Albany, N. Y., February 8, 1882.

DEAR SIR: We desire to inform you that the manufacture of colors (aniline) commenced in this country, we think, in 1866 by T. and C. Holliday, who subsequently sold out to the Albany Aniline and Chemical Works, a company incorporated in April, 1868, with a capital of $25,000, and increased to $100,000. After expending all their capital on machinery and experiments in the manufacture of fine aniline colors, they reduced the capital to $25,000, and confined their attention to the production of aniline red until about two years ago, when new premises were purchased and some $60,000 expended for machinery. Chemists were brought from Switzerland and England, and we are now engaged in the manufacture of all the fine aniline blues, and

expecting ere long to make all the finer colors made in Europe. As an illustration of the benefit the country has derived from our efforts, we can state that large crystals of red were sold in 1868 at $6.50, gold. We now supply the trade with an acknowledged better color at $2.50 per pound. Blues were sold one year ago at $4. Since we commenced making the price has dropped to $2.50. We think we deserve the sympathy and encouragement of the powers that be.

Very respectfully yours,

H. K. LANSING, *Treasurer.*

I will state that I have notified Mr. Lansing of the hearing that is going on before you, and he will appear in person and make a statement on this subject.

I desire also to add that it appears that in 1880 there were 563,932 pounds of aniline dyes of foreign manufacture, of value, with duty added, $1,600,166.48, entered for consumption, while during the last census year only 80,518 pounds were produced in the United States, in value amounting to $107,282. These figures are the most exemplary that can be given to show the depressing effect on an industry of an unpremeditated reduction of duty. Had the other 50 cents per pound been allowed to remain, the position of aniline dyes would doubtless have been about the same as licorice and borax, and the country would have been independent in this regard. Not only has the reduction of this duty prevented the manufacture from growing until quite recently, but the danger of having another 50 cents per pound lopped off has naturally aided in hindering it, as one house sank $50,000, another $30,000 to my knowledge, following the reduction.

I am informed that the manufacture of aniline dyes in Europe is practically controlled by an English monopoly, which buys a large amount of material for this manufacture in this country, sending it to Germany and Switzerland, where these colors are produced by the poorest paid labor in Europe, and shipped to England and America. Already an extensive English house has made overtures to parties in this country, looking to the control of these products, and thus to deprive us of the raw material after present contracts have expired. I could name other articles of chemical manufacture which are held in about the same prospective condition if the large European combinations should succeed in breaking through the barriers of our protective system.

LONG BRANCH, N. J., July 26, 1882.

Mr. EVERETT P. WHEELER, of New York, representing the New York Free Trade Club, appeared before the Commission, in response to its invitation, and made the following statement:

VOL. I—P. 223 * * * *. I use in illustration of this the facts stated by Mr. Campbell in regard to aniline dyes. It was shown by him clearly, and I think there is no dispute about that, that the cheapening the cost of production of these goods abroad has not benefited to the extent it ought the parties in this country who use them, because the duty being a fixed one of so much a pound instead of being based on a sliding scale, the price has been kept up instead of being diminished. And, as a consequence, all of us who use printed goods of any description, or paper of any description, have to pay more in the long run than we otherwise should have done if the manufacturers could have bought a cheaper dyestuff.

P. 229 * * * * *. Why should not, then, the third class of wools, the heavy wools, be put on the free list? That certainly would be a great benefit to the carpet manufacturers of America; and if this other suggestion made by Mr. Campbell to you should be carried out, and these aniline dyes should be put on the free list as well, the production of American carpets would be cheapened to such a degree that they could compete with great success in the South American market and in other markets. The goods we make are good in quality; a great deal of money is expended in designs for them, and I think any one who has examined the American carpets of recent make has been astonished at the amount of taste shown in the designs * * * *.

P. 230. Let me make just one suggestion on the question of dyestuffs. I want to call attention to the census bulletin in regard to the manufacture of chemicals. You will observe in regard to these dyestuffs that they have almost entirely displaced the vegetable dyes. The duty in many cases amounts to more than 100 per cent *ad valorem*. Even if it were possible for us in this country to prohibit for the next ten years the importation of these colors, would it be a wise policy for us to do it, considering the extent to which you have been shown they enter into all manufactured goods? Would it be a wise policy for us to build up a manufactory of aniline dyes in this country when they can be made more cheaply abroad because the raw material is found in a cheaper condition in England? The English coal, as everybody knows, is richer in the hydrocarbons or inflammable matter than our American coal, and it is well known that we do import to some extent English coal to make gas, although the duty on it is a high one. The only objection that has been or could be made in regard to that would be that if we got into a war with some of the European countries we should be at a disadvantage in regard to these colors. I suggest that that is a very contingent and remote disadvantage; that the probabilities of such a war are insignificant. These goods are made not only in England, but in Germany, and if the worst came to the worst, and we were cut off from our European supplies, we could fall back on the vegetable dyes that came from South and Central America before aniline dyes were invented * * * *.

PP. 236–237. In regard to one suggestion which was made, which goes to the whole root of the matter, that it was the object of the government to lay a tax to enable people to do a business which would be profitable, which otherwise would not be profitable, I will say this: Where that applies to large amounts of money invested, that is one thing; but where it applies to a creating of a new business that is not necessary and that the country can do without, we should pause before committing ourselves to that proposition. If there were an embargo, and we could not import anything, I suppose all sorts of industries would spring up here at once. In regard to the aniline dyes, it was said to be a poisonous business, and the people engaged in it suffered very much on account of the poisonous materials used. If that is so, why should we desire to build up a business of that kind? The gentlemen from Albany, Mr. Hendrick, spoke of a 35 per cent ad valorem duty. Certainly, in the present condition of that business, considering the existing rate, I should not contest that proposition, so far as the aniline reds are concerned; I should not oppose, but consider it just to put the duty at that figure. But I should object to keeping all aniline dyes at the rate of 35 per cent so that Mr. Hendrick might be enabled to build up a new business for the purpose of increasing the cost of all articles that are made with those dyes.

LONG BRANCH, N. J., July 27, 1882.

VOL. I—PP. 253–256. Mr. James Hendrick, president of the Albany Aniline and Chemical Works, Albany, N. Y., appeared before the Commission, upon its invitation, and made the following statement:

The history of our business is simply this. In 1866 my attention was called to the manufacture of aniline dyes, and I considered it a legitimate manufacture in this country which ought to be developed. Some gentlemen associated themselves together and we purchased the establishment of T. and C. Holliday, the only establishment of that kind then in this country, and began the manufacture in Albany of this article, putting in at first about $25,000 and subsequently increasing the amount to $100,000. We lost that amount of money and $50,000 additional in the business. In 1872 I took personal

charge of the manufacture, and, applying to it practical business principles, found it could be made a success in certain directions. I emasculated everything from the manufacture except the article of "aniline red." We continued the manufacture of aniline red for seven or eight years and made an article, acknowledged by all manufacturers in this country as well as those who know of it in Europe, to be equal to anything made abroad. The price of it at that time was $6.50 in gold. We are selling it now at $2.25, and are supplying the manufacturers of New England, and today they are giving us orders for more than we can make of it. As I presume you are all aware, all these aniline colors are made from an oil procured from coal tar—the benzole made from coal tar. We have been obliged to import that because of the difficulty of getting it in this country in large enough quantities to distil it. We have been importing all of this oil that we required, but now we are manufacturing it a little. I have in my pocket a sample of aniline oil manufactured from benzole, which is, in turn, manufactured from the residuum of petroleum. I have also a sample of cloth dyed with the various colors that we make ourselves. These dyes we make in our factory, but not in large quantities. We are putting up machinery now which will enable us to manufacture on a larger scale.

The Pacific Mills and other like manufactories in this country express the strongest hope that we shall receive from you the encouragement we are entitled to. In a letter addressed to me within a week by Mr. Saltonstall, the treasurer, he said there were some importers, or the agents of foreign color companies going through the mills in New England, expecting to get a petition signed in favor of the reduction of the duty on aniline colors, and he said they would have no sympathy from them and cautioned me against them. I have no doubt you will have an application to this effect. I have not come here to tell you what you shall do. I can only point you to the evidence we have of what we have done in our little way toward reducing the price from $6.50 to $2.25, and we propose continuing that warfare. We have not made a large amount of money, and every dollar we have made, we have spent in improving the manufacture of these colors, so that the investments we have made from the year 1866 up to the present time, have not yielded us 1½ per cent on our money. But we are developing the business we have helped to create and the country is getting a benefit. I will leave you samples of these colors I have referred to.

By Commissioner AMBLER:

*Question.* As I understand the matter, this is the product you obtain from the residuum of petroleum, and you are still continuing your experiments endeavoring to extend the number of colors to be made?—*Answer.* Yes, sir.

*Q.* I do not understand that you now make a multitude of colors, so as to be able to put them on the market?—*A.* Not all of them. We are manufacturing the colors I have exhibited.

*Q.* From these experiments which you have made you think you can make a variety of colors, and are putting in the machinery now for that purpose?—*A.* Yes, sir.

*Q.* It has been suggested here that the raw material for making these colors is not obtainable in the United States. Is that the fact, and, if so, what is the cause of it?—*A.* It is a fact, for this reason: That, as I endeavored to explain, the gas-tar was not gathered in sufficient quantities in this country to make the benzole, and the expense of distilling benzole into aniline oil has been too large for any party to engage in it. But there are two parties now making benzole, the New York Coal-Tar Company and one other, and they are exporting benzole, and we are importing the oil. If we get the oil industry started, as we expect to do, we shall not be dependent on foreigners for our oil, but they will be dependent on us.

*Q.* Have you taken any steps towards producing this aniline oil?—*A.* Yes, sir; contracts are out for $35,000 worth of apparatus with which to manufacture it, and I have a chemist here from France to superintend the work.

*Q.* How long have you been making these other colors? I do not mean the aniline red.—*A.* Not more than about two years.

*Q.* Are there any other firms in the United States engaged in the manufacture of these aniline colors?—*A.* There are three or four, I think. There is the firm of T. & C. Holliday, in Williamsburg, N. Y., another one in West Virginia, and one in Buffalo, N. Y. Those are the only three I know of; I have heard of others.

*Q.* Up to this time, as I understand you, this has been an unprofitable experiment?—*A.* I cannot say that; but we have been spending a large amount of money.

*Q.* Have you been able to make aniline red at a profit?—*A.* Yes, sir; we have been making it at a profit, but all the profit we have reinvested. We have upwards of $250,000 invested in the business in buildings and machinery, and this will be the result of the profits for the last ten or twelve years.

By Commissioner KENNER:

*Q.* Are these colors fast colors?—*A.* They are as fast as colors can be made. All aniline colors are a little fugitive; that is to say, the sun will fade them somewhat. All the red garments you wear are made from them, every one of them. We have everything in this country that is necessary to manufacture aniline dyes. We have brains enough to do it; and I think we are as able to make them as any foreigner is.

By Commissioner AMBLER:

*Q.* I am requested to inquire of you (and your answer can be given now, or hereafter, in writing) what you would regard as a sufficient duty for the protection of your manufacture?—*A.* My individual opinion would perhaps be of no more value than the opinion of any other person. We do not want to make a great fortune by large protection. I think, perhaps, that a fixed duty of $1 per pound would be preferable to the duty of 50 cents per pound and 35 per cent ad valorem.

*Q.* Would not that operate very unequally in this respect, that some of these colors are very much more expensive to produce than others?—*A.* Yes, sir.

*Q.* Have you any remedy to propose as to that; that is, can you suggest any mode of making the rates equal?—*A.* No, sir; if I were to suggest a plan I should say let well enough alone; let the business go along until it is better developed, and it will regulate itself by and by. I believe the great curse of the country today is change in these laws; and I think the less we change the tariff, as it affects commercial and manufacturing interests, the better. It is a trite saying, attributed to President Lincoln, that you should never swap your horses when crossing a stream. I think that principle should apply in this case, and that when we are trying to develop a business it is not well to change the laws affecting it too often.

*Q.* It is complained that this is an unequal duty. The only purpose I had in asking the question was to ascertain whether you had anything to suggest which would make it an equal duty; and I now ask you specifically, would an ad valorem duty, at a proper percentage, be a fair duty?—*A.* It would if you could get at the ad valorem; that is the great difficulty. The manufacturers on the other side of the water are exceedingly smart, and they will tamper with colors, and represent one color to be a different color; and the difficulty is in getting competent men who know the value of an article, and will place the true ad valorem on it. I have heard of expensive colors being introduced under a new name in order to get rid of the duty. Therefore, I say the other way is the more equitable method.

By Commissioner GARLAND:

*Q.* I understood you to say, in regard to the supply of the

raw material, that you were importing it from abroad?—*A*. We have imported all the raw material of which we make these colors, and are doing so today.

*Q*. Is there not enough material in this country, if it was collected properly, to furnish the supply, or what is the difficulty?—*A*. The difficulty has been that it was not profitable to go into that branch of the business. The tar yields 3/4 to 1 per cent of benzole, both the American and the English tar.

*Q*. Is the English tar better adapted to the purpose?—*A*. It is one-eighth of 1 per cent richer, that is all. But we think the American tar would be quite as good, the only difficulty is in getting it together and carrying it from one place to another, which would add the cost of transportation.

*Q*. Then I understand there is enough of that material in this country, but the difficulty is in getting it together?—*A*. Yes, sir. Even if this product of petroleum fails, which I think it will not do, there would be an abundance for our own use and that of Europe besides; I mean of the benzole extracted from tar.

By Commissioner McMahon:

*Q*. If it should be decided to apply an exclusively ad valorem duty, what rate would you recommend?—*A*. I think about 35 per cent would be fair; that is my impression about it. I should make as few changes as I could.

By Commissioner Underwood:

*Q*. Would it be possible for you to furnish the Commission with a schedule of duties on these different articles which would enable the government to collect duties without ambiguity and the commission of fraud?—*A*. Not unless you can make men perfectly honest. If we had honest men everywhere, there would be no trouble. There would be no difficulty in enforcing such a schedule in case men did not resort to dishonest practices. In that case I think 35 per cent would be about a fair rate. I think we could live if it were fixed at that figure.

By Commissioner Boteler:

*Q*. You think specific duties are better for the government and for the parties concerned?—*A*. Yes, sir. Specific duties I believe in, because they are easily collectible, and men have no disposition to be dishonest; but with ad valorem duties the temptation to fraud is greater. That is my view of that matter. I will leave you these samples that I have referred to in my statement, and, if you desire, I will give you any further information I possess, from our books or in any other way.

Long Branch, N. J., August 21, 1882.

VOL. I—PP. 565–568. The following communication, regarding duties on aniline dyes and coal-tar products, was received from Mr. V. G. Bloede, representing the American Aniline Works of Parkersburg, W. Va.:

Gentlemen: Having found it impossible, during my recent hurried visit to New York, to accept your invitation to appear in person before your committee, I adopt this method of communicating my views upon some of the matters you now have under consideration.

The firm of Bloede & Rathbone, of which I am a member, is engaged at this point in the manufacture of various chemicals, chiefly such as are used in the dyeing and printing of yarns and textile fabrics. Our firm is also largely interested in the business known as the American Aniline Works, and it is particularly in this line of manufacture that I feel competent to communicate important information to your committee. The production of aniline colors from our native crude materials is a business, the benefits of which seem to me to belong most legitimately to this country, and forms a fitter subject for heavy, even prohibitory, duty than many other branches of trade depending exclusively upon imported crude material. Strange to say, although we have all of the chief crude materials in this country, it is only within the last two or three years that the production of colors exclusively from our native products has been attempted. Prior to this time a few small works had been engaged in the manufacture of a few simple coal-tar dyes, but they worked exclusively with a crude material, combined and manipulated by European skill and imported into this country, duty-free, in a half finished condition, *i. e.*, in the form of arseniate of aniline. To produce this material, American benzoles and other coal-tar products are shipped abroad in a crude state at a heavy expense, manipulated by foreign skill and labor at another heavy expense, and returned to us still as a crude product, but largely enhanced in value. The entire profits of manipulating our own crude material have thus for years been lost to our country. I believe I am correct in stating that the American Aniline Works, which I have the pleasure of representing, was the first concern in the United States which succeeded in producing on a large scale the base used in the manufacture of these colors, *i. e.*, aniline oil, from the crude coal-tar products of our own country, and exclusively by home labor. It is not necessary for me to dwell upon the almost insurmountable difficulties encountered in a new manufacture of this kind in a country totally devoid of skilled labor and experience. It generally means one of three things: first and generally, a total failure; second, the importation of skilled labor from the other side (a class of labor which seldom flourishes under the business conditions here existing), or, as the American Aniline Works have done, the *redevelopment*, as it were, of the entire process of manufacture by a long series of difficult and costly experiments. One thing that is retarding the utilization of our home products more than anything else is the fact that, by the grossly unjust and arbitrary provisions of some sections of our tariff, aniline oil, and the half finished product known as arseniate of aniline, have been hitherto admitted free of duty, a provision wholly and exclusively to the benefit of the foreign producers. The natural result has been that no American manufacturer could be found willing to devote his time and capital to the development of a branch of industry in which Europe has the advantage of twenty-five years' experience. To insure the utilization of our own coal-tar products under the best possible conditions for success, I would most urgently request that your Commission recommend a duty to be placed upon the two crude materials named, as well as any others that can be produced here, so as to insure to our country the benefits derived from the consumption of our own coal-tar products. In my opinion, had our tariff not been defective in this vital particular, and aniline oil and its compounds had early paid duty, the manufacture of the articles from our own crude coal-tar products would have been an assured fact years ago. I believe that our people are fully competent, not only to hold their own against the competition of other nations in any manufacture, but that they are their superiors in many essential particulars. At the same time it is absolutely necessary that a new enterprise of this kind, in order to compete successfully against the products of a quarter of a century of European research and experience, be liberally protected until our own manufacturers have acquired sufficient knowledge and experience to enable them to hold their own against these odds. I would therefore urge that aniline oil, arseniate of aniline, and other salts of the base be protected with a specific duty of from five to ten cents per pound. I would also urge that the duty on the intermediate products, such as nitrobenzole, and binitrobenzole, and its homologues, be maintained. The duty on nitrobenzole is now two cents per pound, while binitrobenzole, which is merely nitrobenzole combined with more acid, pays a duty of 20 per cent. I would recommend that the duty upon all nitro compounds of benzole and its homologues be made a uniform one of 10 cents per pound, as in the case of nitrobenzole.

I have carefully examined some of the statements made before your Commission, and must say that some of those presented on behalf of the foreign manufacturers are certainly extraordinary misstatements of facts. Mr. John Campbell, for instance, appeared before your Commission, and, unless the press misrepresented him, made the remarkable and wholly erroneous statement that a color costing $1 per pound in England would, under the present duties, cost $4 per pound laid down on this side. This is such a very gross misstatement of the facts that I hesitate to believe it was seriously offered to your Commission. Such a color as Mr. Campbell speaks of, after payment of all duties, freights, and the like, would cost less than one-half that sum, say $1.90 per pound. The result of home competition is already so strongly felt in some lines, for instance fuchsine and other reds, as almost to have stopped all importation, and it is my opinion that within a short space of time these colors can be made as cheaply in the United States as in any country of Europe. This is the direct result of protection and the stimulation of home enterprise, and there is no reason whatever why, within ten years, or even a much shorter period, if we are only able to avail ourselves, by means of a liberal protection, of our domestic wealth in crude material, all other coal-tar colors should not be in the same position.

Whatever course your committee may take as regards the older chemical industries of this country, I would urge that the aniline branch be liberally protected at least for a few years. As before stated, it is an industry so new that up to two years ago not one pound of the base used in the manufacture of these colors was made in the United States.

A great deal has been said, and with much force, upon the nature of the duties imposed on aniline dyes, and the injustice resulting therefrom. A duty like the present one, of 50 cents per pound and 35 per cent ad valorem, I believe to be wholly wrong. It annually deprives our government of thousands of dollars of legitimate revenue, and entails an enormous and unnecessary expense in collection. Many of the manufacturers on the other side have resident partners here, and it is the general impression that an enormous amount of color finds its way into this country under the ad valorem system at a very great undervaluation. That this system of collecting duties at least opens the way to a great deal of fraud will be seen at a glance by your Commission, when I state that the various aniline blues, for instance, range in price from $2 to $15 and $20 per pound. The difference is not one of strength, but only of purity and quality of shade, some high-priced colors being actually weaker in point of strength than others of a low price. These colors are sold under arbitrary names and marks, such as B, BB, &c., up to 5 B or 6 B. Now, suppose an unprincipled person wishes to undersell his competitor, all that he has to do is to mark his 5 B, or 6 B, or other mark, worth, say, $12 per pound, down to B or BB, worth, say, $3; the result is the evasion on his part of 35 per cent duty on $9 of each pound of this color, or the enormous sum of $3.15 on every pound. It is utterly impossible for the largest corps of experts the government can command so to test the samples as to make such frauds impossible. The interests of the government, the consumer, and the honest dealer, require a change of this system to one of *specific* duty, or so much per pound of color. The average value of the aniline dyes imported into this country we will say is $6 per pound. Under the present system, such a color would pay a duty of $2.60 per pound, and I would recommend that a uniform duty of from $1.50 to $2 per pound be imposed upon all aniline dyes of whatsoever name or quality. While it is true that such duty would be prohibitory as regards the cheaper grades, the answer to this is, that such dyes can and are already produced in this country at a price to exclude, or almost exclude importation, even under the present system of duty. By adopting a specific duty a large expense would be saved the government in the collection of the duties, a larger revenue would result, the consumer would be largely benefited by the higher grade of the colors, and honesty on the part of the importer would be insured, as it would necessarily break up the system of undervaluation, or cost invoicing, adopted by many of the European manufacturers having resident partners on this side. Should an ad valorem duty be continued, I would urge your committee to move a Congressional investigation having for its object the breaking up of the system now in vogue for the evasion of duty.

Some efforts have been made to show that the present rate of duty on these dyes is very onerous to the consumer and the public; such is not the case, however, for two reasons: first, because the branches of business consuming them are themselves protected by almost prohibitory duties, and lastly and chiefly, because the quantity of dye used per pound of cloth or yarn is almost infinitesimal. Taking the case of fuchsine, for instance, a color costing only $2 per pound, but four or five ounces are required for every 100 pounds of carpet-chain; this means a tax through present duties of only 3 or 4 cents on an average size rag carpet. The fact is that while a removal of the duties would deprive the government of a large revenue, and kill the home industry outright, no one class, except the foreign manufacturer, would be benefited. This was shown a few years ago in the case of artificial alizarine. By the assistance of the consumers the duty was removed from this article, ever since which time the said consumers have to pay about as much again for the article as their foreign competitors, and the large revenue that would have resulted to our people by a duty was absorbed by the foreign manufacturers and their agents. It is therefore desirable that neither the government nor the consumer be again inveigled into such action on behalf of a wholly foreign industry.

Before closing I would call the attention of your committee to the fact that, owing to the vitality the American aniline manufacture is beginning to show in the last year or two, the foreign manufacturers of these dyes have combined for a concerted action, and are making extraordinary efforts looking to the repeal of the duties and the killing of this promising industry Among other devices adopted, is the one of obtaining signatures to petitions among the consumers of these dyes, asking for a repeal of the duties. These petitions have been gotten up by the New York representatives of a large foreign corporation, and are being extensively circulated for signatures. I state this so that when such petitions are presented, it will be understood that they are not the sentiments of the American consumers of these dyes, who, as far as my knowledge enables me to speak, are *universally* in favor of and willing to pay their quota towards the successful introduction of this manufacture in the United States. The actual disposition of the largest consumers of the anilines is fairly represented by the following sentence in a letter recently received by me from one of these consumers: "The representatives of a large European aniline works are making a great push to have the duties on anilines reduced. I inclose you their circular which they are sending to all the manufacturers to obtain signatures. What do you as a manufacturer think of it, and what would you propose? We can stand it as it is, and, having all the protection we need on our manufactures, are willing to give all that is required to others."

I have the honor of remaining, very truly yours,

V. G. BLOEDE.

PARKERSBURG, W. Va., Aug. 10, 1882.

BOSTON, MASS., August 24, 1882.

VOL. I—PP. 661–663. Mr. HENRY A. GOULD, of Boston, refiner of camphor and manufacturer of aniline dyes, addressed the Commission as follows: * * * *

I hope that the Commission will be able to recommend a reduction of the duty upon aniline colors. The duty now, as

you well know, is 50 cents a pound, specific duty, and 35 cents a pound ad valorem. I represent a house in Germany, with a capital of $10,000,000 or $12,000,000, and we sell the goods in the original package in this country. I have reason to know that the duty is so high that it leads, in the first place, to corruption and misrepresentation of goods brought into this country. Without desiring to make any definite statement, I may say that I feel that goods are, owing to this high duty, often brought in on a wrong valuation in many respects. The argument on this question has been gone over before you very fully by Mr. Campbell, but I may say, in brief, that a duty of 20 or 25 per cent would answer all the purpose of protection, as I have instanced in regard to the matter of camphor, and would help the manufacturer, without being a burden on the manufacturer of textile articles. I paid a visit to South America last summer, and while there could see the reason why they imported their goods from England rather than from this country. The 3 or 4 per cent which is added on to the cost of American goods by reason of this heavy duty on the raw materials used in their manufacture is the cause of it. Our house in South America imports hundreds of packages of goods from Manchester and other sections of England that we should import from this country if the prices were lower. Of course, every tax of this kind that is added to the original cost of the goods acts as a prohibition upon trade from this country. We have a house in South America for which we import largely from England. The freights on goods exported from this country to South America are much larger than they are on goods exported from England, and, of course, the percentage of cost for these pigments and colors add very largely to the cost of the print or the manufactured article. I think a moderate duty would do away with the tendency to undervalue these colors when they are imported. At the present rate of duty it is certainly a very great temptation to fraud.

By the PRESIDENT:

*Q.* How much does the duty on aniline colors affect the price of the ordinary American prints, for instance?—*A.* I am not prepared to answer that question exactly; but I know that we have very carefully prepared tables showing the cost of prints imported from Manchester and the cost of prints and other colored goods made in this country, and the difference is considerable; and, of course, as you can see, every additional tax on the manufacturer adds to the cost of the manufactured article. A duty of 25 per cent would answer all the purposes of protecting the American manufacture of aniline colors, as I have instanced in the case of camphor, without adding as heavy a tax to the user of aniline colors. As Mr. Campbell has said, there are from one to two million pounds of colors, representing millions of dollars in value, imported annually into the country, but yet the business is in its infancy. I imported in 1866 the first aniline colors ever brought into this country.

*Q.* What colors were they?—*A.* They were blues and reds. I had very hard work to dispose of my first consignment of 1,000 pounds; it took me nearly six months to do it. But in the next six months I sold from $50,000 to $75,000 worth, and the business has increased very rapidly ever since. I am satisfied we cannot manufacture these dyes in this country as well as they can abroad, unless there is a change in the prices of labor and in other particulars. In Germany laborers are paid from 60 cents to $1.12 a day, while the same laborers in this country receive from $1.50 to $2.50 a day. Alcohol is very cheap in Germany, while here it is loaded down with taxes. Nitric acid there is cheap, while here it commands a very high price per ton. And so I might go through the whole catalogue and name the elements that enter into the production of these colors. I should be very glad to see them made in this country, and even as an importer would readily submit to a fair rate of protection in order to develop that industry. There are only three or four companies in this country manufacturing these colors, and with every advantage of protection they have kept the price up as high as the tariff would allow them to, and made the manufacturers pay a royal price for their colors, and the textile manufacture has not been benefitted by it, and they never have been able to make one or two of the last colors. My house, in Germany, manufactures some two hundred colors, while such concerns as the one in Albany, the one at Buffalo, and one or two in Philadelphia manufacture only one or two colors. There are a dozen companies in Europe having a capital of from $12,000,000 to $15,000,000, some of them; even the smallest of them have at least a million dollars capital, and in that way they can manufacture to very great advantage. I am speaking now of aniline colors, without referring to alizarine, for that is a monopoly under a patent.

*Q.* Is the price of alizarine due to the high tariff?—*A.* No, sir; it is a free article; it is due to the control by one house of the patent under which it is made; it is a monopoly. We represent a manufacturing house in Austria which makes it, but we are prohibited selling it in this country, under a decision given by Judge Lowell. The decision is regarded in Europe as unsound, but nevertheless we have to abide by it.

*Q.* How much lower are the European users able to buy this alizarine than American users?—*A.* I could not answer that question, because since we were enjoined from selling the article I have not followed the price of it. I only know that after the decision of Judge Lowell the manufacturers here raised their price over 100 per cent in a very few months.

The PRESIDENT. I wanted to bring out the fact that the high price of alizarine, one of the most important of the aniline colors, is not due to the tariff.

The WITNESS. A specific duty in one sense would be an unjust one because of the fact that the colors are valued at different prices. A low ad valorem duty of 20 or 25 per cent, it seems to me, would answer every purpose and protect the American manufacturer. As it is now the profits all go into the pockets of these few manufacturers. A reduction of the duty would reduce the price to the consumer, and enable him to procure the better article which is made abroad. I suppose there are some things that we cannot make in this country, which we shall have to let other people in other countries make for us.

BUFFALO, N. Y., August 30, 1882.

VOL. I—PP. 749–750. Mr. J. F. Schoellkopf, Jr., of Buffalo, manufacturer of aniline dyes, addresses the Commission as follows:

GENTLEMEN: In addition to my communication of July 27, 1882, I desire to call your attention to the following circumstances: Coal tar is procured from bituminous coal; benzole, the raw material for aniline oil, is gained from coal tar by distillation. Now, benzole pays a duty of 40 cents per gallon, whereas aniline oil comes in free. These facts certainly must have been misrepresented at the time the present tariff was framed, for it is evident that if the raw material, benzole, is protected, the manufactured article, aniline oil, is justly entitled to the same privilege. Aniline oil, which is used directly for printing black (on cotton), cannot be manufactured as cheaply here as in Europe, owing to higher labor and high prices for acids (sulfuric and nitric acids) used in its manufacture.

I have learned that New York and Boston parties are circulating a petition among the larger consumers of aniline dyes, with the intention of reducing the duty on such dyes to 25 per cent ad valorem only. This would leave domestic manufacturers virtually without protection. We must have an *absolute* protection, and this can be realized only by a specific duty. I would suggest the raising of the specific duty 25 or 50 cents per pound and dropping the ad valorem duty altogether. This

would enable home manufacturers to compete with foreign producers.

By Commissioner AMBLER:

*Question.* Would not that operate inequitably by reason of the fact that there is a great difference in these dyes? Some of them, I understand, are cheap and others are expensive.—*Answer.* Yes, sir.

*Q.* How do they range in price?—*A.* From $1 to $5 per pound; the principal colors.

*Q.* I would suggest that a specific duty per pound, to afford any protection at all on the $5 article, would be too much on the cheaper article.—*A.* But, as I mentioned in my former communication, if we have protection, the domestic competition will reduce the price to a proper level. There are only five manufacturers of aniline dyes in the United States at the present time.

*Q.* Is it not a fact that any rate that operated as a protection on the $5 article would amount to a prohibition on the article that costs $1?—*A.* It does not seem so, for they are still importing fuchsine, which is a color worth from $2 to $2.50 a pound.

*Q.* Did you mention any specific amount of duty per pound which you think would be proper?—*A.* Yes, sir; the rate of duty now is 50 cents a pound, and 35 per cent ad valorem, and I suggest dropping the ad valorem rate and raising the specific rate 25 or 50 cents per pound.

*Q.* You mean, raise it 25 or 50 cents above the present duty of 50 cents?—*A.* Yes, sir.

*Q.* That would amount to a duty of 100 per cent on $1 dyes, and a duty of 20 per cent on $5 dyes?—*A.* Yes, sir; but, as I mentioned in my former communication, under these ad valorem duties imported dyes are liable to be undervalued.

*Q.* Are they generally undervalued?—*A.* I do not know, but I think they are, because it cannot very well be detected. I suggest this high duty in order to give the home manufacturers a start. After five or ten years it would not matter if the duty were taken off; but we must have a large protection to enable us to start. When I was in Europe this spring I was told that if the duty was not taken off in this country the manufacturers there would start establishments in this country, so that we would have plenty of competition.

By the PRESIDENT:

*Q.* Will you please repeat that statement; do you say that the foreign manufacturers themselves would begin the manufacture in this country?—*A.* Yes, sir. The president of the largest manufactory in Europe, the Badische Aniline Factory, at Mannheim, told me personally that if the duty was not taken off they would be obliged to start factories over here. I think that shows that the price today in this country is as cheap as it can be.

*Q.* How many dyes does that establishment now make?—*A.* They make almost all the known colors. Dyes can be made here, in time, as cheaply as in Europe; but we must have a chance to start the business.

NEW YORK, October 7, 1882.

VOL. I—PP. 1960–1962. The following communication from Mr. A. KLIPSTEIN, of New York, in regard to the duties on dyestuffs and chemicals, was ordered to be printed:

I would recommend putting upon the free list every dyestuff and chemical used in dyeing, calico printing, &c., and every chemical used in making paper, soap, and glass, in bleaching and other industries. These articles may be fairly classed as raw materials for the use of these industries. If these various industries could get their dyestuffs and chemicals free, the saving to them would be so considerable that they would be upon a much better footing for competing with the foreign manufacturers, and it would lead to a large increase of the export trade in their products * * * * *.

Aniline dyes and colors should be made free. They pay now the enormous duty of 35 per cent ad valorem and 50 cents per pound. At the time the tariff was framed these colors were comparatively little known, and their importance not recognized. Their price was at that time very high, and the 50 cents per pound specific duty was not felt so much. Since then great progress has been made in the manufacture of these dyes, the prices have been very considerably reduced, and large quantities are used.

The difference in duty which our print works, woolen mills, dyers, &c., have to pay is in many instances very considerable, many mills using large quantities, and the saving would amount to each of them to many thousand dollars per year.

The duty on the lower-priced colors, in consequence of the 50 cents per pound specific duty, amounts to 130 per cent. Notwithstanding this enormous duty, there is only a very small quantity (comparatively) of aniline colors made in this country, and the industry has made no progress here in twenty years. This is owing to many circumstances.

What is made at Albany, N. Y., and at some other small factories in the United States, is only the first stage, *viz.*, fuchsine (red). The higher class of colors are not produced, and it is not likely that they will be made of good enough quality.

It is not just that large industries (like the cotton, woolen, silk, calico printing, &c.) should be taxed heavily to support these small factories.

Other dyestuffs and chemicals are used in dyeing, calico printing, &c.—some of these are already on the free list, while others are taxed for no apparent reason. It does not appear, for instance, reasonable that such articles as archil and extract of archil, cudbear or extract of cudbear should be free of duty while the following articles are taxed; for if a high enough duty was imposed on the above, no doubt they would also be made here * * * * * * * *.

Through these tariff restrictions our manufacturers of textiles, &c., are prevented from using to advantage many articles like carmines, lakes, and other special preparations for calico printing, &c., which their competitors in Europe can employ.

Madder lake is taxed 25 per cent, but on the other hand extract of madder is free; naphthalene yellow and naphthalene brown pay 35 per cent and 50 cents per pound, as aniline colors, under the similitude clause, although they are not aniline colors, not any more than other products now assimilated to aniline colors and paying the same duty.

If every article used in dyeing and calico printing were put on the free list, this would do away at once with the many vexatious difficulties resulting in appeals to the Secretary and in lawsuits, which are caused by the present complicated state of the tariff.

PHILADELPHIA, PA., October 16, 1882.

The following report of Mr. Geo. C. Tichenor, special agent of the Treasury Department, addressed to the Secretary of the Treasury, in regard to importations of foreign goods, having been referred to the Commission for its information, was ordered to be printed:

VOL. I—PP. 2486–2488. PAINTS AND DYES—ANILINE DYES AND COLORS (1350 Heyl)—Like the preceding provision, concerning "statuary," this one has provoked much discussion and controversy; has been variously construed by customs officers; has resulted in lawsuits, and has caused the department a vast amount of trouble and vexation. The tariff act of June 30, 1864, provided that "aniline dyes" should pay duty at one dollar per pound and thirty-five per centum ad valorem. At the period of the passage of this act the industry devoted to the production of these dyes was in its infancy and had scarcely developed beyond an experimental state. The products were

then derived exclusively, I believe, from a single hydrocarbon resulting from the distillation of coal tar, then exceedingly expensive, and which was called aniline—a mere arbitrary and accidental name, which owes its origin to the circumstance that its coloring principle was, I believe, first discovered by a Portuguese chemist, through the destructive distillation of indigo, which is known as "anil" in the language of Portugal. At that time (1864) these so-called aniline dyes were enormously expensive, had not entered into general use in the arts of dyeing and printing, and it was not thought that the high rate of duty would burthen our textile industries or be at all generally felt. It was also, probably, the intention to encourage and foster the production of these dyes in this country. It should also be borne in mind that we were then in the midst of the war period, and were legislating to increase our revenues. Dyes that were then worth in Europe say $30 per pound are now scarcely worth $3. So that at that time the specific rate of $1 per pound was a comparatively trifling matter.

The act of July 14, 1870, fixed the duty on "aniline dyes and colors, by whatever name known," at 50 cents per pound and 35 per cent ad valorem. Although great progress in the industry had been made by this time, and the cost and price of the dyes had been much reduced, they were still of high price, were being produced from the same source, and had not come into general use. Efforts had also begun to be made to build up the industry in this country, and the protective idea was in consequence perpetuated in the new act.

Within the twelve years past far greater progress has been made in this industry in Europe than in all previous time. In addition to reducing the cost of production and selling price of the original aniline dyes proper to a fabulous extent, and thereby vastly extending their use, a vast field of new and useful dyes have been produced from naphthalene and other coal-tar derivatives, which, coming from a cheaper source than aniline, have been produced at still diminished cost, and have come into quite general use as substitutes for many of the old vegetable and other organic dyes, including cochineal, logwood, and indigo, while madder has been almost entirely supplanted by a dye called alizarine, produced from anthracine; this latter dye having been originally classified as a manufactured article not otherwise provided for at 20 per cent ad valorem, the other newly-discovered dyes, produced from other coal-tar derivatives than aniline, were entered and largely passed under the same classification as alizarine, which also led to entering many colors mainly produced from aniline at the same rate of duty, while others again were entered and passed as paints, &c. The Department's attention having been brought quite fully to the subject, it was held in numerous decisions that dyes or colors produced from derivatives of coal tar other than aniline were subject to duty as "aniline dyes and colors," in accordance with the provisions of Section 2499 Revised Statutes, from which decisions and assessment of duties numerous appeals have been taken, and some suits brought for the recovery of duties in excess of 20 per cent.

Alizarine, so-called, was taken out of the controversy by the act of February 8, 1875, by being placed on the "free list" with "madder and munjeet," which it had largely superseded. All these coal-tar dyes are familiarly—commercially—known as aniline dyes, or aniline colors, and I can see no reason for putting alizarine on the free list that would not apply both to its older and younger associates, a number of which pay duty in excess of their actual cost in the country of production. I think no candid man who understands the subject will contend for a moment but that all these dyes, "by whatever name known," coming from any of the series of coal-tar hydrocarbons, should be subject to the same rate of duty so long as they remain dutiable; they all come from the same parent source, take the same place substantially in the arts, and are used for the same purposes; those being for coloring silks, woolens, cottons, jute, flax, leather, and other substances, as well as for the manufacture of different colored writing and printing inks, artists' and painters' colors, &c., in which manufactures they are in the nature of raw materials. It requires expert knowledge of the very highest order, aided by most exhaustive chemical analysis, to determine whether one of these dyestuffs, as imported, comes from aniline, naphthalene, or some other coal-tar product; so that they should all be included under one and the same head in the tariff. I incline to think a provision in substance as follows would meet the case, *viz.:* "All paints, dyes, and colors produced in whole or in part from coal tar or its derivatives." This, it will be seen, would include some articles, notably alizarine and picric acid, now on the free list, and hence would admit of a large reduction in the rate of duty without decreasing the aggregate amount of duty derived from dyestuffs. And since all these dyestuffs enter into the same uses as the large number of organic dyes and coloring matters now on the free list there is apparently no good reason why the latter should not, as well as the former, pay duty.

The experience of the last eighteen years has, I regret to say, shown that a high protective duty has not resulted in the building up of anything worthy of the name of an aniline color industry in this country, notwithstanding it is understood that there is an abundance of the raw materials here, and aniline oil and arseniate of aniline have been admitted free of duty. There are, to be sure, a few small concerns making certain classes of colors, but these employ so few people and produce such limited quantities of dyes as hardly to amount to an industry worth protecting at the expense, at least, of burthening and crippling the vast industries devoted to the manufacture of textile fabrics, as well as to putting a tax upon the consumers of such fabrics.

Having, after much inquiry and experience, ascertained beyond question that aniline dyes imported into the country have been largely undervalued, and that it is practically impossible to prevent such undervaluation so long as they are subject to an ad valorem duty high enough to present any inducement of consequence for undervaluing, I am convinced that it would be advisable to retain the specific feature with an ad valorem rate sufficient only to serve as an equalizer, and not to exceed 15 per cent. I have thought that 25 cents per pound and 15 per cent ad valorem would be as high rate as could be asked for purposes of protection. This would amount to near 40 per cent on a very liberal proportion of the dyes most used, and to about 60 per cent upon some of them.

I was informed while in Europe that the use of arsenic in the manufacture of all coal-tar dyes had been prohibited by the German Government, and perhaps by others, not only on account of the danger to the life and health of those engaged in their production, but also to those who wear garments and live in rooms where the carpets, curtains, and papered walls have been dyed or printed with such arsenic colors

### Revision of the Tariff
### Hearings before the Committee on Ways and Means, 1889–90

NEW YORK, December 10, 1888.

PP 393 398. *The Subcommittee on the Tariff of the Senate Committee on Finance:*

The undersigned manufacturers of coal-tar dyes beg leave to present the following statement with regard to the tariff bill now under discussion:

The great difference in the cost of raw material, both imported and domestic, and the still greater difference in the price of labor between here and Europe, makes it impossible for the home manufacturers to successfully compete with those of Europe, even if the duty of 35 per cent be actually paid.

Annexed schedule will show clearly the disadvantages under which we labor.

We also submit a statement of one of the largest factories in Europe showing their consumption of raw materials and products for one year, thus illustrating the importance of this industry for the United States, if fully developed by a protective policy.

In order to give the domestic manufacturer a safer protection, to enforce a strictly honest entry of values, and to insure the importation of the best quality of goods only, we suggest that a specific, or at least a partly specific duty be imposed.

To overcome the apparent difficulty of equalizing the duty on the various priced goods more justly, we propose to separate coal-tar dyes into two classes, which can easily be distinguished, and which would also separate the high-priced colors from the cheaper ones, *viz.*:

COAL-TAR DYES AND ACIDS OR BASES OF COAL-TAR DYES

*Class I*—Azo colors, picric acid, and naphthole yellow, 25 per cent ad valorem and 10 cents per pound gross weight.

*Class II*—Non-azo colors, 25 per cent ad valorem and 25 cents per pound gross weight.

Our authority for this classification is the list of coal-tar dyes as compiled by Gustave Schultz and Paul Julius, and published by R. Gaertner, at Berlin, in the year 1888.

This book not only gives the scientific and trade names, but also a description of the outward appearance of all coal-tar colors and their action when treated with certain named reagents, thus clearly establishing the identity of the respective dyes.

Very respectfully,

ALBANY ANILINE COMPANY
SCHOELLKOPF ANILINE AND CHEMICAL COMPANY
HELLER & MERZ
HUDSON RIVER ANILINE COLOR WORKS

We also beg to call your attention to the following: Under "paragraph 974" aniline oil is free. We would suggest to strike out the words "aniline oil" and insert the words "commercial aniline oils." All aniline oils are mixtures of several products, but the law as it now stands is liable to be misconstrued by the custom-house officials.

SCHEDULE SHOWING THE CONSUMPTION OF RAW MATERIAL AND PRODUCTS FOR THE YEAR 1887–'88, BY FARBWERKE, VORM. "MEISTER, LUCIUS AND BRUENING," AT HOECHST-ON-THE-MAIN

| | Long tons | | Long tons |
|---|---|---|---|
| Coal | 64,230 | Pyrites | 12,661 |
| Coal-tar products | 3,624 | Iron borings | 1,503 |
| Caustic soda | 2,112 | Methylated and ethylated spirits | 309 |
| Different potash salts | 350 | Various chemical products | 1,635 |
| Soda | 1,610 | Rock salt | 10,518 |
| Nitrate of soda | 1,905 | Lime | 4,312 |

Should this factory be located in the United States 93 per cent of the above material would have to be produced in our country, 2 per cent nitrate of soda would come from South America, and of the remaining 5 per cent, consisting of "coal tar" and various chemical products, a large part, if not the whole, would also be manufactured in America.

To ship the manufactured products of above factory the following packages were used:

| | | | |
|---|---|---|---|
| Casks | 25,310 | Bottles | 803,200 |
| Tins | 1,962,000 | Cases | 25,310 |

The effect on the carrying of such an establishment can well be imagined.

This house was founded in 1863, and commenced operations with one 3 horse-power steam engine and 7 employees, which have been increased in the comparatively short time of twenty-five years to 1,840 horse-power and 2,062 employees.

SCHEDULE SHOWING EFFECT OF THE PROPOSED CHANGE OF DUTY ON THE PRICE OF THE MOST IMPORTANT COLORS NOW ON THE MARKET

| CLASS I—Azo colors, etc. | Cost in Europe Cents | 35% Cents | 25% and 10 c. per lb. Cents |
|---|---|---|---|
| Orange Y | 22 | 29.7 | 37.5 |
| Orange R | 25 | 33.75 | 41.25 |
| Orange No. 4 | 60 | 81.5 | 85 |
| Metanil yellow | 75 | 101.25 | 103.75 |
| Chrysoidine | 40 | 54 | 60 |
| Bismarck brown | 72 | 97.2 | 100 |
| Scarlet 2 R | 27 | 36.35 | 43.25 |
| Scarlet 3 R | 34.5 | 46.57 | 52.1 |
| Fast red | 22 | 29.7 | 37.5 |
| Crocein scarlet | 47 | 63.5 | 68.75 |
| Benzo-purpurine, 4 B | 100 | 135 | 135 |
| Chrysamine R | 100 | 135 | 135 |
| Hessian purple | 100 | 135 | 135 |
| Hessian yellow | 100 | 135 | 135 |
| | 824.5 | 1113.52 | 1169.10 |

Cost in Europe, 100 per cent.
Present duty cost in United States, 135 per cent.
Proposed duty cost in United States, 142 per cent.

| CLASS II—Non-azo colors | Cost in Europe | 35% | 25% and 25 c. per lb. |
|---|---|---|---|
| Auramine | $ 2.00 | $ 2.70 | $ 2.75 |
| Victoria green | 0.72 | 0.972 | 1.15 |
| Acid green | 1.00 | 1.35 | 1.50 |
| Victoria blue | 1.40 | 1.89 | 2.00 |
| Fuchsine | 0.84 | 1.13 | 1.30 |
| Violet crystals | 1.67 | 2.25 | 2.34 |
| Violet 3 B | 0.80 | 1.08 | 1.25 |
| Cotton blue 5 B | 2.90 | 3.91 | 3.875 |
| Cotton blue B | 1.50 | 2.02 | 2.125 |
| Methylene blue | 2.11 | 2.85 | 2.89 |
| Eosine | 1.25 | 1.635 | 1.81 |
| Erythrosine | 3.00 | 4.05 | 4.00 |
| Rhodamine | 5.00 | 6.75 | 6.50 |
| | 24.19 | 32.637 | 33.49 |

Cost in Europe, 100 per cent.
Present duty cost in United States, 135 per cent.
Proposed duty cost in United States, 138.4 per cent.
$(142 + 138.4) \div 2 = 140.2$.
$140.2 - 135.0 = 5.2$.
$\therefore$ Average higher duty under proposed duty = 5.2 per cent.

VIEWS OF FRED. KOEHLER

WASHINGTON, D. C., December 13, 1888.

*The Subcommittee on the Tariff of the Senate Committee on Finance:*

Mr. Pickhardt, in his statement regarding the manufacture of aniline colors in this country, having alluded to myself to sustain his assertion of the impossibility to make said dyes here, I beg leave to submit the following:

I was employed as chemist in the largest aniline-color factory in Germany and in the world from 1874 to 1883, and as such have had in my hands and am familiar with the manufacture of all aniline colors known up to that date. I subsequently was engaged for over five years in the aniline-color manufactory in this country, and I therefore believe myself more competent to judge about the possibility or impossibility of making colors here than Mr. Pickhardt. This gentleman having never been a manufacturer of coal-tar dyes himself, can only express the views of his friends in Germany about this matter or possibly the views they wish to impress upon your committee. If they really are convinced that aniline colors never can be profitably produced here, why are they not willing to let the American manufacturers die a natural death instead of trying to kill them quickly by having the duty removed, trying it even to the point of raising money among the German aniline-color manufacturers for that purpose? I, for my part, am firmly convinced that aniline colors can and will be made here, and, as a matter of fact, about 20 per cent of the home consumption are actually made here.

I am further convinced that had the duty not been lowered in 1883 not one pound of aniline color would be imported today.

It is true we did not succeed nearly as well as I expected, but that does not prove the impossibility to succeed finally. In the light of my knowledge of the circumstances under which this industry exists here and abroad, I find the reasons for its slow progress here chiefly as follows:

(1) In the very large difference in wages. An ordinary laborer in German aniline factories receives at the utmost 58 cents for

eleven hours' work, while we must pay from $1.25 to $1.75 for ten hours.

(2) In the large difference in the cost of raw material.

(3) In the difficulty we have in selling our goods. There are now about twenty agents of foreign manufacturers established in this country, who until recently have had practically the whole market, and whom we must undersell materially in order to procure any share of the market.

In conclusion, I would reiterate my statement that it is my firm belief that coal-tar colors can be made here, and it rests wholly with your honorable body to make the industry prosper or die out by tariff legislation.

Respectfully,

FREDERICK KOEHLER.

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REMARKS ON MR. WILLIAM PICKHARDT'S TESTIMONY GIVEN BEFORE THE SUBCOMMITTEE ON THE TARIFF OF THE SENATE COMMITTEE ON FINANCE, DECEMBER 5 AND 6, 1888

Mr. Pickhardt does not contradict our statement that he charged $1 per pound over the European price. We are informed by the defendants in the suit that the patent had two years longer to run when the adverse court decision came, and other alizarine importers stated that Mr. Pickhardt could have had the patent two years longer if he had permitted the defendants and one or two others to share in the profits.

*Page 8, b, line 8*—Anthracene was formerly made here and could be made here again.

*Line 16*—The coal tar produced here is practically the same as that produced in London.

*Page 9, b, line 9*—Considerable coal-tar products are made in this country and used for coal-tar dyes and other purposes n spite of Mr. Pickhardt's decisive "No."

*Page 12, line 15*—How can the woolen mills of Rhode Island be retarded when the duty on the whole importation of coal-tar dyes used for cotton, wool, silk, paper, jute, lake colors, etc., only amounts to $400,000 per year? On all these articles the quantity of color used can not average 1 pound of dye to 100 pounds of material.

*Page 13, line 8*—If Mr. Pickhardt calls the stuff the New York Coal-Tar Company distills benzine, he tries to mislead. He must know this is commercial benzole—50 and 90 per cent used in the manufacture of coal-tar products. In fact, these are the standard grades produced by coal-tar distillers for the trade.

*Line 13*—On a previous page Mr. Pickhardt describes the process of distillation very minutely, and here he does not know what comes off first.

*Page 14, line 17*—Mr. Pickhardt says that his factory was only making 10 per cent on their capital. For the last four years they declared dividends of from 12½ to 25 per cent after deducting large amounts for wear and tear, reserves, etc. His statement that an aniline factory would be useless for any other purpose is absolutely true. Mr. Pickhardt's statement that all azo dyes are made from naphthole and naphthalene and the aniline colors from aniline is incorrect and shows how very little he understands of the real nature of coal-tar dyes. The very first azo color discovered—amidoazo benzole—is a pure aniline color and contains not a trace of naphthole or naphthalene. The true characteristic of an azo dye is the fact that it contains the azo group N-N.

*Page 15, line 10*—If the patent has nothing to do with the price it is singular that alizarine red should have dropped $1 per pound as soon as the patent was practically declared void, page 7.

*Page 19, line 9*—Mr. Pickhardt's assertion that transportation from London to New York is as low as from London to Germany is not correct. It costs three times as much to New York as to Cologne on the Rhine.

*Page 21, line 20*—It is singular that Mr. Pickhardt can not state the difference in price of soluble and insoluble alizarine blue, as he imports and sells both. We protest against putting the alizarine colors on the free list. These colors, with free alizarine red, can be produced here as well as any of the coal-tar colors.

*Page 5, c, last line*—The Buffalo people never tried to sell their factory to Mr. Pickhardt or anybody else. The reason why the industry did not develop is because the duty was lowered in 1883 but not because we can not get the proper help.

*Page 7, c*—The reasons for the decline in prices of aniline colors are, first, cheaper raw material; second, improved methods and principally on account of the enormously increased output. Farbwerke, Meister, L. and M. produced in 1863, 10 to 14 pounds of magenta per day; in 1873 they produced 770 pounds per day.

*Mr. Pickhardt's reply to Mr. Randall's letter*—In 1883 Heller & Merz's ultramarine factory was about the third largest in the world and probably furnished 10 per cent of the world's consumption. The labor in aniline factories in the United States ranges from $1.25 to $1.75 per day for ordinary laborers.

We estimate the production of aniline dyes in the United States at 500,000 pounds, and the value at $500,000.

Mr. Pickhardt's statement regarding the number of men employed in this industry is probably correct. In this connection we may say that the Buffalo factory employed over one hundred men before the last reduction in duty. They now employ about one-half that number.

The production of aniline colors in Germany last year was in round numbers 13,000,000 pounds. Of this, one-ninth is exported to the United States. Seven-eighths of the entire output is exported.

The following is a pretty complete list of coal-tar dye factories in Europe: Germany, 18 factories; England, 6 factories; France, 6 factories; Switzerland, 6 factories.

It would be very desirable to have free alcohol, but for many purposes it should be free from admixtures such as methyl alcohol, camphor oil, etc.

*Page 14*—There is a decided difference between dye-wood and coal-tar colors. The first named are products of agriculture, while the latter are wholly manufactured articles.

*Page 18*—Mr. Pickhardt says here that in 1872, when he contemplated starting an ultramarine factory, nobody else had thought of it up to that time. He seems to have forgotten that he bought ultramarine from Heller & Merz several years before the date mentioned.

*Pages 19 and 20*—Not everybody seemed to have been of Mr. Pickhardt's opinion regarding the foolishness of starting an aniline factory here. As late as 1882 the general manager of Mr. Pickhardt's factory told Dr. Koehler that he considered America a good field for that industry then and he would come over himself if he had been younger. He told Dr. Koehler he did not consider the Americans crazy enough to lower the duty. Another authority on this subject is G. Schultz, who, in his book on coal-tar dyes, edition of 1882, says: "The tar in Russia and especially in America is developing. The latter country may soon be a serious competitor in this line to Europe."

*Page 22*—Mr. Pickhardt evidently wishes to convey the impression that our raw material is almost finished color. This is not the case by any means, as Mr. Pickhardt knows. With the exception of a few of the very largest, all the European factories buy their material in the same state as we do.

SCHEDULE SHOWING THE PRINCIPAL RAW MATERIALS USED IN AMERICAN COAL-TAR DYE FACTORIES, AND THEIR PRICES HERE AND ABROAD

| Price per pound in | Europe | United States |
|---|---|---|
| Sulfuric acid 66° | $ 0.45 | $ 0.95 |
| Nitric acid 40° | 4.75 | 5.50 |
| Muriatic acid 20° | 0.30 | 1.10 |
| Aniline oil for blue | 16.33 | 18.00 |
| Aniline oil for red | 15.00 | 16.50 |
| Toluidine | 15.00 | 19.50 |
| Binitrobenzole | 14.70 | 18.00 |
| Binitrotoluol | 14.70 | 18.00 |
| Bichromate of soda | 7.00 | 9.50 |
| Salt | 0.10 | 0.25 |
| Naphthole | 14.40 | 18.00 |
| Nitrite soda | 5.77 | 7.72 |
| Alkali, 58 per cent | 1.10 | 1.40 |
| Iron borings | 0.50 | 0.75 |
| Caustic soda, 74 per cent | 1.74 | 2.84 |
| Labor per week | 4.04 | 10.00 |
| Total | 115.88 | 148.01 |

The above list shows that we have to pay for our raw material and labor on an average 28 per cent more than it costs on the other side. If it is further considered that we are obliged to undersell imported dyes from 5 to 10 per cent, that our plant costs at least twice as much, the higher interest on capital and insurance, on plant and wear and tear of same, and the difference in scientific and clerical help, it will be plain to everybody that 35 per cent, even if fully collected, is an entirely inadequate protection. This assertion is borne out by the schedules given below, showing the different costs of a few of the principal colors in this country and abroad:

| One week's production of safranine | Cost in Europe | Cost in U. S. |
|---|---|---|
| 600 lbs. aniline oil | $90.00 | $99.00 |
| 150 lbs. nitrite soda | 8.64 | 11.58 |
| 2,400 lbs. muriatic acid | 12.00 | 24.00 |
| 600 lbs. iron borings | 3.00 | 4.50 |
| 960 lbs. whiting | 3.84 | 5.76 |
| 1,110 lbs. bichromate soda | 77.70 | 105.42 |
| 30,000 lbs. salt | 30.00 | 75.00 |
| Labor | 16.16 | 40.00 |
| Total | 225.18 | 325.26 |
| Wear and tear | 11.26 | 32.52 |
| | 236.44 | 357.78 |
| Per cent | 100 | 151 |

| One week's production of Bismarck brown | Cost in Europe | Cost in U. S. |
|---|---|---|
| 900 lbs. binitrotoluol | $132.30 | $162.00 |
| 1,910 lbs. muriatic acid, 20° | 9.55 | 19.10 |
| 702 lbs. alkali, 58 per cent | 7.72 | 9.83 |
| 2,400 lbs. iron | 12.00 | 18.00 |
| 222 lbs. nitrite soda | 12.81 | 17.14 |
| 1,200 lbs. salt | 1.20 | 3.00 |
| Labor | 12.12 | 30.00 |
| Total | 187.70 | 259.07 |
| Wear and tear | 9.38 | 25.90 |
| | 197.08 | 284.97 |
| Per cent | 100 | 145 |

| One week's production of orange | Cost in Europe | Cost in U. S. |
|---|---|---|
| 660 lbs. aniline oil | $107.79 | $118.80 |
| 1,710 lbs. sulfuric acid, 66° | 4.29 | 16.25 |
| 345 lbs. alkali, 58 per cent | 3.81 | 4.83 |
| 270 lbs. lime | 0.54 | 0.54 |
| 396 lbs. nitrite soda | 22.86 | 30.57 |
| 720 lbs. naphthole | 103.68 | 132.60 |
| 600 lbs. caustic soda | 10.44 | 17.04 |
| 2,100 lbs. salt | 2.10 | 5.25 |
| Labor | 12.12 | 30.00 |
| Total | 267.63 | 325.88 |
| Wear and tear[1] | 13.38 | 32.58 |
| | 281.01 | 358.46 |
| Per cent | 100 | 128 |

| One week's production of fuchsine | Cost in Europe | Cost in U. S. |
|---|---|---|
| 4,188 lbs. aniline oil | $628.20 | $ 691.02 |
| 17,400 lbs. salt | 17.40 | 43.50 |
| 210 lbs. alkali, 58 per cent | 2.31 | 2.94 |
| 2,664 lbs. muriatic acid | 13.32 | 29.30 |
| 1,900 lbs. nitrobenzole | 190.00 | 237.50 |
| Labor | 40.40 | 100.00 |
| Total | 891.63 | 1,104.26 |
| Wear and tear[1] | 44.58 | 110.42 |
| | 936.21 | 1,214.68 |
| Per cent | 100 | 130 |

[1] In Europe 5 per cent; in United States 10 per cent.

| | | |
|---|---|---|
| TOTAL PER CENT FOR FOUR DYES | 400 | 554 |
| AVERAGE PER CENT FOR FOUR DYES | 100 | 139 |

All of above calculations do not include salaries for chemists and office help, insurance on plant, interest on capital invested, etc., all of which items form a large part of the cost of the finished product, and cost at least twice as much here as they do in Europe.

## Tariff Hearings before the Committee on Ways and Means, 1896–7

MONDAY, December 28, 1896.

PP. 57–61. Mr. SCHOELLKOPF submitted the following paper:

COMMITTEE ON WAYS AND MEANS, Washington, D. C.:

The undersigned coal-tar dye manufacturers of the United States respectfully submit that the following changes be made in the present tariff law:

Paragraph 14, which reads as follows: "Coal-tar colors or dyes, by whatever name known, and not specially provided for in this act, 25 per cent ad valorem," should be changed to read as follows:

"Coal-tar colors and dyes of every description not specially exempted by name, 35 per cent ad valorem."

The change in phraseology increases the clearness of the paragraph, and the increase in duty to 35 per cent is absolutely necessary to put the industry on a footing which will enable it to compete successfully with the foreign makers.

Article 443: "Coal-tar, crude, and all preparations except medicinal coal-tar preparations and products of coal tar, not colors or dyes, not specially provided for in this act, free."

This article should be changed to read as follows:

"Coal tar and all products and preparations of coal tar, not colors or dyes, except medicinal coal-tar preparations and such other coal-tar products and preparations which are specially exempted by name, free."

This phraseology makes the paragraph much clearer without, in any way, changing its meaning, and will avoid differences of opinion as to where certain products belong.

Article 368, which reads as follows: "Alizarine, natural and artificial, and all alizarine colors and dyes, free," should be changed to read as follows: "Alizarine, natural and artificial, free."

This is the way the paragraph stood in the act of 1883, and there is no reason whatever why alizarine colors, which are nothing more nor less than coal-tar colors, should be put on the free list any more than any other class of coal-tar colors.

The tariff of 1890 left the domestic coal-tar dye manufacturers in a very unfortunate position, with the duty of 35 per cent on the colors and 20 per cent on coal-tar preparations, which constitute a large percentage of the raw material for the colors. This, in addition to the higher prices we are compelled to pay for labor and other domestic chemicals, precluded any real progress of the American manufacturers in their struggle against the aggressive competition of the well-equipped German factories. The Wilson bill placed the coal-tar preparations on the free list, but by reducing the duty on the colors to 25 per cent did not improve the position of the domestic makers We feel confident that the slight increase asked for which makes the rate what it was under the tariff act of 1883 and 1890, will enable us, with the experience we have gained under adverse circumstances and with the great domestic progress in scientific chemistry, to successfully compete against the imported goods and in time supply the home market.

THE HELLER & MERZ CO.,
Henry Merz, *Treasurer.*
THE SCHOELLKOPF ANILINE AND CHEMICAL CO.,
By J. F. Schoellkopf, JR.
HUDSON RIVER ANILINE COLOR WORKS,
Louis S. Waldman, *President.*

The CHAIRMAN. What is the extent of this industry of coal-tar colors in this country?

Mr. SCHOELLKOPF. There are three plants with an aggregate capital of about a million dollars.

The CHAIRMAN. And how many employees?

Mr. SCHOELLKOPF. About 150 direct. Of course, the coal-tar dye industry is very large, in fact the largest consumer of crude chemicals, such as acids, etc., and in that way gives employment to a large number of hands indirectly.

The CHAIRMAN. About what proportion of the consumption of this country is produced here now?

Mr. SCHOELLKOPF. I would say about 20 to 25 per cent.

The CHAIRMAN. I see that the imports last year amounted to about $3,000,000.

Mr. SCHOELLKOPF. Well, I think that includes the alizarine red, also, as well.

The CHAIRMAN. It includes all dutiable coal-tar colors?

Mr. SCHOELLKOPF. Yes; I think that alizarine colors, which are coal-tar colors, of course, are included in that.

The CHAIRMAN. I presume so.

Mr. SCHOELLKOPF. I would like to mention that in this percentage I was not referring to alizarine red, which is on the free list now and always has been on the free list.

The CHAIRMAN. Are alizarine colors made in this country?

Mr. SCHOELLKOPF. They are not at present. They are on the free list at present and, of course, can not be made here. They could be made.

The CHAIRMAN. No attempt has been made to make them?

Mr. SCHOELLKOPF. They could be made.

The CHAIRMAN. Are there any special difficulties in the manufacture of these colors in this country?

Mr. SCHOELLKOPF. There are not now.

The CHAIRMAN. Growing out of the technical education which is required?

Mr. SCHOELLKOPF. That used to be the case formerly, but, of course, as I have stated in my paper, we have overcome these difficulties and are in a fair shape to capture the home market if we are sufficiently protected; and aside from the coal-tar products, which are on the free list, we consume vast quantities of other chemicals which are made in this country and can not be imported, such as acids, etc.

The CHAIRMAN. There is a great difference in the value of these materials?

Mr. SCHOELLKOPF. Yes, sir.

The CHAIRMAN. Therefore an ad valorem duty, perhaps, could be applied better than a specific duty could be applied?

Mr. SCHOELLKOPF. It would be rather difficult to apply a specific duty.

The CHAIRMAN. The prices ranging from what to what?

Mr. SCHOELLKOPF. Running from 20 to 25 cents a pound up to $15 a pound.

Mr. MCMILLIN. What will be the value of the product which will be affected by the change of from 25 per cent ad valorem to 35 per cent?

Mr. SCHOELLKOPF. You mean the value at present of the products of this country?

Mr. MCMILLIN. Yes, sir.

Mr. SCHOELLKOPF. I should say about $600,000 or $700,000.

Mr. MCMILLIN. And the present duty being 25 per cent, 10 per cent added to that is an increase of more than 20 per cent of the present rate. That would be a difference of between $100,000 and $200,000 added to the value of that product?

Mr. SCHOELLKOPF. I doubt very much whether it would add that much to the direct cost at the present time. We are not really able to compete at all, and while we are selling our colors we are not making anything on them, and we can not possibly make anything on them, and it is not so much we ask an increased duty to increase our prices greatly but simply to be better able to compete. It is not so much we want to increase the prices one or two hundred thousand dollars, but if we can increase our production we can produce cheaper if we are sure of this market, but if we must compete against twenty-five or thirty importers in New York, each one of whom represents a large manufacturing establishment on the other side, we must compete on even their terms and we must expect to get our proportion of the business which will be about 5 or 10 per cent, because this is our only market, and we can not manufacture on a sufficiently large scale to produce cheaply.

Mr. MCMILLIN. How many hands does your concern employ?

Mr. SCHOELLKOPF. We employ at the present between 60 and 70 hands.

Mr. MCMILLIN. And there are three concerns, representing the business of this country, I believe you stated, who employ about 150 hands?

Mr. SCHOELLKOPF. Some gentleman here can state that better than I can.

The CHAIRMAN. From what source of supply is crude tar product obtained—the residuum of the manufacture of gas?

Mr. SCHOELLKOPF. Yes, sir.

The CHAIRMAN. It comes from no other source in commercial quantities. Is it a by-product of the manufacture of gas?

Mr. SCHOELLKOPF. Yes, sir.

The CHAIRMAN. Has the supply of coal tar of this country been diminished by the extensive manufacture of water gas instead of coal gas?

Mr. SCHOELLKOPF. It has.

The CHAIRMAN. Is the supply insufficient in this country?

Mr. SCHOELLKOPF. The raw materials we use are an intermediate product between coal tar and coal-tar colors. There are certain products of coal tar which are intermediate, and those are the products which we use.

Mr. MCMILLIN. Is any considerable portion of this raw material imported?

Mr. SCHOELLKOPF. A very considerable proportion.

Mr. MCMILLIN. But you get your raw material free?

Mr. SCHOELLKOPF. Yes, sir.

Mr. MCMILLIN. You do not seek to add a duty to that?

Mr. SCHOELLKOPF. No, sir; we do not. In fact, we could not.

The CHAIRMAN. The reason is there is an insufficient supply of the by-product?

Mr. SCHOELLKOPF. That is one reason. Of course, we could not get along without a duty on colors. We would have to have an additional duty on colors if we put an additional duty on the raw material.

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### ANILINE COLORS AND DYESTUFFS

Statement of F. E. Atteaux & Co., of Boston, Mass.

BOSTON, MASS., January 9, 1897.

COMMITTEE ON WAYS AND MEANS:

We beg leave to present in brief our reasons for requesting that a duty be placed upon all colors commercially known as alizarine colors, with the exception of true chemical alizarine.

We are domestic manufacturers of so-called alizarine colors and dyestuffs, and have our works at South Boston, Mass. Our plant there is valued at about $75,000. We have been in this business a number of years, and are manufacturing a line of colors which come into competition with the so-called alizarine colors which are imported to this country. In the last ten years we have spent over $20,000 experimenting, and we are now able to make a considerable number of colors which do the work of the imported colors. We feel that we are entitled to consideration and that our interests ought to be considered by your committee in framing this bill.

#### BENEFITS THE DOMESTIC CONSUMER

In 1890, when we commenced to manufacture the color which we call alizarine violet, and which took the place of the foreign alizarine violet, the imported color was sold in this market at 75 cents a pound. Today it is being sold at 28 cents a pound, and the reduction has been largely due to our competition. We make in the same way alizarine green, so called, and this comes in competition with the imported veridine, or coeruline. The importers were selling this color at that time at about 48 cents a pound. Today, largely in consequence of our being able to manufacture a similar color, the price has fallen to 25 cents a pound. These are only two instances of cases which may be amplified to show your committee what has been the effect of our presence as manufacturers in this market. In addition to these two colors we are now manufacturing five other so-called alizarine colors, to wit, Blue B., Blue G. S., Blue R., Brown O., and Brown R. These colors come into competition with and take the place of imported alizarine blue and brown.

The foreign colors are patented, as is well known, and the prices charged here and abroad for the same article have greatly varied, at the expense of the American consumer.

It is well known to the coal-tar color trade that prior to 1888 a certain firm of importers in this country was charging $1.25 per pound for alizarine which was sold all over Europe at 25 cents. As long as we are not able to produce these colors, the complete control of the market will enable the foreigner to charge a price without reference to the cost, and based entirely upon the needs of the consumer and his inability to obtain the color from any other source. In this connection, we beg leave to refer your committee to the statements made and testimony taken July 7, 1888, before the subcommittee on the tariff of the Senate Committee on Finance, and printed on page 268.

The fact that the imported colors are patented does not make it impossible for us, under equal conditions, to compete with these articles, as we have been able in the past and expect in the future to make colors which will do the work of the imported colors and not infringe upon their patent rights. If we can do this, it will be seen that it will be of large benefit to the domestic consumer, as the patent has been in the past the means of keeping up the prices artificially in this country. As soon as we have been able to make a color that did the work of a foreign color we have found that the importers have been compelled to bring their prices down and to sell at or below our price; and this price of ours being based upon the cost of manufacture has given the consumer the benefit of a large reduction in the artificially sustained price.

DUTY ON RAW MATERIAL AND NOT ON THE MANUFACTURED ARTICLE

In our industry we are confronted with conditions imposed by the tariff which are a reversal of the usual methods of protection. We are paying 25 per cent duty on the articles which we import and use as the material for making our colors. We are compelled to sell the colors which we manufacture in competition with the so-called alizarine colors which are entered without duty by the importers. We use at present as our raw material imperial blue, chrome orange, and naphthol yellow, and on these we pay at the custom-house 25 per cent duty as coal-tar colors.

In addition to this, it may be stated that our labor costs at least double that of Europe, we paying $1.50 a day while the same class of labor can be had there at 75 cents a day. As we have heretofore stated, this is a direct reversal of the theory of protection of a new industry, and we feel that if we are compelled to pay a duty of 25 per cent for that which enters into our complete product the article which is not manufactured and with which we are now competing should pay at least the same rate of duty * * * *.

**Tariff Hearings before the Committee on Ways and Means, 1908–1909**

WEDNESDAY, November 11, 1908.

VOL. 1—PP. 128–130. Mr. SCHOELLKOPF. I represent the Schoellkopf, Hartford, Hanna Company, of Buffalo, N. Y., and the Heller & Merz Company, of Newark, N. J. I have prepared a short brief, which I will read.

(Reads:)

BUFFALO, N. Y., November 9, 1908.

Hon. SERENO E. PAYNE,

*Chairman Ways and Means Committee.*

DEAR SIR: The undersigned respectfully request that at the impending revision of the tariff the minimum duty on coal-tar colors and dyes be increased from 30 per cent to 40 per cent ad valorem, and that all coal-tar products and preparations not colors or dyes used in the manufacture of these dyes be placed on the free list.

In submitting this request we do so with the understanding that it is the intention of Congress so to adjust import duties as to give the domestic manufacturer adequate protection against his foreign rival; or, in other words, the duties imposed shall cover the difference in cost of the article protected when made in America as against the same article when made abroad.

In asking for free entry of all coal-tar products and preparations used in the manufacture of coal-tar colors, no American industry will be injured, as these articles are not made in the United States, nor can they be manufactured profitably under existing conditions.

In order to prove that our demands, as outlined above, are not unreasonable we have prepared the following tables:

*Table A*—Showing cost of coal-tar dye plant in America and Germany, designed for a yearly output of 3,000,000 pounds; also showing the cost for depreciation on buildings and wear and tear on machinery and interest on investment.

*Table B*—Showing number of employees required and their salaries for such a plant in America and Germany.

*Table C*—Showing material required to produce 3,000,000 pounds of color and cost of same under present tariff; also under tariff as proposed by us; also cost of same material in Germany.

*Table D*—Showing comparative cost of 3,000,000 pounds of color when produced in Germany; also cost when produced under present tariff; also cost when produced under tariff as proposed by us.

By referring to Table D it appears that taking the cost of colors in Germany at 100 per cent, the same colors cost to produce in America under the present tariff 144.1 per cent, and in case all coal-tar preparations should be admitted free, the cost would still be over 134.4 per cent. That our figures are correct is positively proven by two highly significant facts.

*First.* These same colors are now being imported from Germany and sold in this market for less than it costs us to produce them, even omitting charges for depreciation and interest on investment.

*Second.* By the fact that German manufacturers do not manufacture in the United States because, as people high in authority state openly, they can 'manufacture the colors in Germany and lay them down in the United States, with duty of 30 per cent and manufacturer's profit added, at a lower price than they could manufacture the same colors in America.

By referring again to the same table it appears that under the proposed tariff the cost of colors would be only 35 per cent higher than the same colors when made in Germany, while we are asking for a duty of 40 per cent. It should be borne in mind, however, that in the first place the American manufacturer, in order to secure the home market, must be in a position to undersell the importer, and in the second place, the foreign manufacturer, when driven to it, will always assume part of the duty himself. The result would be that with a duty of 40 per cent the American manufacturer could not hope to realize more than 30 per cent in excess of what the same goods are sold for in Germany, and probably considerably less. In any event, therefore, even with a 40 per cent duty, the American manufacturer would have to content himself with a considerably smaller profit than his German rival.

Since the present tariff went into effect American coal-tar dye manufacturers have striven strenuously to capture the home market, and while they have succeeded in increasing very materially their output, they have done so at no profit to themselves. Whenever the domestic production of any one color increased sufficiently to interfere seriously with the sale of the imported product, the foreign manufacturers dropped prices to a point that compelled the American manufacturer to sell at cost or even lower.

On the other hand, colors not made in America and controlled by the foreign manufacturers, either through patents or combinations, were not only not reduced, but in many instances

actually increased in price. Eliminate American competition, and prices, even with a reduced duty, will rise and not fall. We refer to such products as alizarines, aniline salt, aniline oil, beta naphthol, etc., which during the past few years have been advanced from 15 to 50 per cent, although the cost of production has not risen.

TABLE A—SHOWING COST OF COAL-TAR DYE PLANT DESIGNED FOR A YEARLY OUTPUT OF 3,000,000 POUNDS; ALSO SHOWING THE COST OF DEPRECIATION OF BUILDINGS AND WEAR AND TEAR ON MACHINERY, ETC.

| Cost of plant in | U. S. | Germany |
|---|---|---|
| For land | $50,000 | $50,000 |
| For buildings | 100,000 | 60,000 |
| For machinery, tools, etc. | 380,000 | 250,000 |
| For working capital | 500,000 | 350,000 |
| Total cost of plant | 1,030,000 | 710,000 |
| Depreciation on buildings, 5 per cent. | 5,000 | 3,000 |
| Wear and tear on machinery, etc., 10 per cent. | 38,000 | 25,000 |
| Interest on investment, 6 per cent. | 61,800 | 42,600 |
| | 104,800 | 70,600 |

TABLE B—EMPLOYEES NEEDED FOR A COAL-TAR DYE PLANT WITH A YEARLY CAPACITY OF 3,000,000 LBS.

| | United States | | Germany | |
|---|---|---|---|---|
| | Rate | Amount | Rate | Amount |
| 1 general manager | $10,000 | $10,000 | $5,000 | $5,000 |
| 2 head chemists | 5,000 | 10,000 | 2,500 | 5,000 |
| 4 chemists | 1,500 | 6,000 | 1,000 | 4,000 |
| 1 chemist | 1,300 | 1,300 | 800 | 800 |
| 1 chemist | 900 | 900 | 600 | 600 |
| 3 dyers | 1,144 | 3,432 | 390 | 1,170 |
| 1 helper | 468 | 468 | 160 | 160 |
| 1 helper | 312 | 312 | 135 | 135 |
| 2 boys | 208 | 416 | 78 | 156 |
| 1 head bookkeeper | 2,500 | 2,500 | 1,200 | 1,200 |
| 1 clerk | 1,800 | 1,800 | 900 | 900 |
| 1 clerk | 1,200 | 1,200 | 600 | 600 |
| 3 clerks | 900 | 2,700 | 450 | 1,350 |
| 1 clerk | 780 | 780 | 350 | 350 |
| 2 boys | 500 | 1,000 | 250 | 500 |
| 1 telephone operator | 364 | 364 | 160 | 160 |
| 1 superintendent | 1,560 | 1,560 | 750 | 750 |
| 1 shipping clerk | 1,200 | 1,200 | 450 | 450 |
| 2 engineers | 1,040 | 2,080 | 520 | 1,040 |
| 6 firemen | 780 | 4,680 | 390 | 2,340 |
| 2 watchmen | 728 | 1,456 | 390 | 780 |
| 2 teamsters | 624 | 1,248 | 390 | 780 |
| 4 carpenters | 780 | 3,120 | 390 | 1,500 |
| 2 machinists | 936 | 1,872 | 468 | 936 |
| 2 blacksmiths | 676 | 1,352 | 468 | 936 |
| 4 helpers | 624 | 2,496 | 260 | 1,040 |
| 10 foremen | 718 | 7,180 | 390 | 3,900 |
| 83 laborers | 540 | 44,820 | 300 | 24,900 |
| TOTAL | | 116,236 | | 61,493 |

TABLE C—MATERIAL REQUIRED FOR 3,000,000 LBS. OF COAL-TAR DYES AND COST OF SAME

| CHEMICALS USED | Quantities in lbs. | Cost in U. S. under Present tariff | Cost in U. S. under Proposed tariff | Cost in Germany |
|---|---|---|---|---|
| Nitrite soda | 385,803 | $29,899.74 | $29,899.74 | $23,919.79 |
| Muriatic acid | 1,369,125 | 10,268.43 | 10,268.43 | 8,214.74 |
| Sulfuric acid | 122,814 | 409.38 | 409.38 | 327.50 |
| Carbonate soda | 790,875 | 7,592.40 | 7,592.40 | 6,073.92 |
| Caustic soda | 111,942 | 2,417.94 | 2,417.94 | 1,934.35 |
| Common salt | 3,371,280 | 5,899.74 | 5,899.74 | 4,719.79 |
| Sulfide sodium | 4,800 | 65.61 | 65.61 | 52.49 |
| Ammonia 26° | 2,880 | 144.00 | 144.00 | 115.20 |
| Mono - ethyl - alpha naphthylamine | 4,437 | 1,668.30 | 1,387.89 | 1,110.31 |
| Aniline oil | 139,041 | 16,128.75 | 16,128.75 | 12,903.00 |
| Paranitroaniline | 68,445 | 16,426.80 | 13,680.00 | 10,951.20 |
| H-acid | 593,145 | 206,414.46 | 172,605.21 | 138,084.17 |
| Alpha naphthylamine | 54,270 | 4,205.94 | 4,205.94 | 3,364.75 |
| R salt | 29,295 | 4,247.79 | 3,544.71 | 2,835.77 |
| Amido-G—salt | 35,910 | 9,605.91 | 7,989.96 | 6,391.96 |
| Freund's acid | 9,630 | 1,661.16 | 1,396.35 | 1,117.08 |
| Cleve acid | 4,032 | 695.52 | 584.64 | 467.71 |
| Gamma acid | 12,420 | 5,464.80 | 4,558.14 | 3,646.51 |
| Salicylic acid | 18,720 | 4,867.20 | 2,822.97 | 2,258.38 |
| A B Sp Sa | 47,952 | 5,591.19 | 5,072.22 | 4,057.78 |
| A A Tm Ba | 19,908 | 4,411.62 | 4,081.14 | 3,264.91 |
| A A Bm Ba | 104,625 | 22,965.18 | 21,228.09 | 16,982.47 |
| A A Tm S | 23,400 | 7,317.18 | 5,974.02 | 4,779.22 |
| Tolidine | 25,740 | 8,494.20 | 8,494.20 | 6,795.36 |
| Benzidine | 218,340 | 66,047.85 | 66,047.85 | 52,838.28 |
| TOTAL | 7,568,889 | 442,911.09 | 396,508.32 | 317,206.64 |

TABLE D—COST OF PRODUCING 3,000,000 LBS. OF COAL-TAR DYES

| Materials, labor, fuel, etc. | When made in United States under present tariff | When made in United States under proposed tariff | When made in Germany |
|---|---|---|---|
| Materials | $442,911.09 | $396,508.32 | $317,206.64 |
| Fuel | 20,250.00 | 20,250.00 | 27,000.00 |
| Labor | 116,236.00 | 116,236.00 | 61,493.00 |
| Interest on investment | 61,800.00 | 61,800.00 | 42,600.00 |
| Depreciation of plant | 43,000.00 | 43,000.00 | 28,000.00 |
| Taxes, fire insurance, and incidentals | 8,000.00 | 8,000.00 | 4,000.00 |
| | 692,197.09 | 645,784.32 | 480,299.64 |
| Per cent | 144.1 | 134.4 | 100 |

TABLE E

| PRESENT WORDING | NEW WORDING SUGGESTED |
|---|---|
| SEC. 15—Coal-tar dyes or colors, not specially provided for in this act, 30 per cent ad valorem; all other products or preparations of coal tar, not colors or dyes and not medicinal, not specially provided for in this act, 20 per cent ad valorem. | Coal-tar dyes or colors, not specially provided for in this act, 40 per cent ad valorem. |
| **FREE LIST** | |
| SEC. 469—Alizarin, natural or artificial, and dyes derived from alizarin or from anthracin. | No change suggested. |
| SEC. 524—Coal tar, crude, pitch of coal tar, and products of coal tar known as dead or creosote oil, benzol, toluol, naphthalin, xylol, phenol, cresol, xylidin, toluidine, cumidin, binitrotoluol, binitrobenzol, benzidin, tolidin, dianisidine, naphthol, naphthylamin, diphenylamin, benzaldehyde, benzyl chloride, resorcin, nitrobenzol, and nitrotoluol; all the foregoing not medicinal and not colors or dyes. | Coal tar, crude, and all products or preparations of coal tar, not colors or dyes and not medicinal, not specially provided for in this act |
| SEC. 580—Indigo. | No change suggested. |

In conclusion, we beg to state that the figures and tables contained in this document are taken from our books, and represent actual conditions, and if desired we are prepared to prove the correctness of same in every particular.

On a separate sheet annexed hereto, marked Table E, we suggest the wording of the sections in the tariff which we desire to have changed.

Respectfully submitted,

SCHOELLKOPF, HARTFORD & HANNA COMPANY
THE HELLER & MERZ COMPANY

P. 143. NEW YORK, November 20, 1908.

Hon. SERENO E. PAYNE,
*Chairman Committee on Ways and Means,*
*House of Representatives.*

At a meeting of the firms interested in and dealing in "coal-tar colors or dyes" and "coal-tar products not colors or dyes, not otherwise specially provided for," held here to-day, the following resolution was unanimously adopted:

*Resolved*, That we, the undersigned, protest against any increase in the duties on coal-tar colors or dyes, by whatever name known, or coal-tar products not colors or dyes, not otherwise specially provided for, and request an opportunity to be heard individually at such time and place as is convenient to the committee of Congress.

H. A. METZ & Co., H. A. Metz, *President.*
CASSELLA COLOR COMPANY, G. W. J. Matheson.
BADISCHE COMPANY, Adolf Kuttroff, *President.*
FARBENFABRIKEN OF ELBERFELD COMPANY,
Y. Rellmerling, *President.*
A. KLIPSTEIN & Co., G. O. Klipstein, *Treasurer.*
BERLIN ANILINE WORKS, E. O. Patz, *Second Vice-President.*
GEIGY ANILINE AND EXTRACT COMPANY,
Alfred Küblein, *Vice-President.*
WALTER F. SYKES & Co., Jno. A. McGuire, *Attorney.*
GEISENHEIMER & Co.
C. BISCHOFF & Co.
KALLE & Co. (incorporated), Wm. Junker, *Secretary.*

P. 146. MEMORIAL AND PROTEST IN OPPOSITION TO ANY ADVANCE IN DUTIES ON COAL-TAR COLORS AND DYES

WASHINGTON, D. C., December 20, 1908.

COMMITTEE ON WAYS AND MEANS,
*Washington, D. C.*

GENTLEMEN: Your memorialists, cotton manufacturers, consumers of coal-tar dyes for the coloring of various cotton fabrics (the largest consuming industry of coal-tar dyes in the country) respectfully submit:

*First.* We desire to protest against any advance in the rates of duty on coal-tar dyes or colors under Section 15 of the present tariff on the ground that such advance would—

(*a*) Increase the cost of manufacturing colored cotton goods in the United States.

(*b*) Increase the price to the consumer in the United States.

(*c*) In the case of export trade an advance in the cost of any of our raw materials adds to our burden and minimizes our opportunity to compete with foreign cotton manufacturers in foreign markets.

*Second.* We further petition that, for the same reasons, alizarines and dyes derived from alizarin and anthracene, as well as indigo, be left upon the free list, and that no change be made in the following schedules now on the free list:

Section 468. Alizarin, natural or artificial, and dyes derived from alizarine or from anthracene.

Section 580. Indigo (meaning vegetable and synthetic).

Very respectfully,

AMOSKEAG MFG. CO.,
F. C. Dumaine, *Treasurer*, Manchester, N. H.
HAMILTON MFG. CO.,
Franklin D. Williams, *Assistant Treasurer*, Lowell, Mass.
PACIFIC MILLS,
Edwin F. Greene, *Treasurer*, Lawrence, Mass.
MASSACHUSETTS COTTON MILLS,
Edward Lovering, *Treasurer*, Lowell, Mass.
MERRIMACK MFG. CO.,
Herbert Lyman, *Treasurer*, Lowell, Mass.
COCHECO MFG. CO.,
H. DeF. Lockwood, *Treasurer*, Dover, N. H.
AMERICAN PRINTING CO.,
B. H. Borden, *Treasurer*, Fall River, Mass.
THE UNITED STATES FINISHING CO.,
J. H. Wright, *President*, New York.
THE APPONAUG CO.,
J. H. Wright, *President*, Apponaug, R. I.
GARNER & CO.,
Oscar Hutley, *Vice-President*, Pleasant Valley, N. Y.
PASSAIC PRINT WORKS,
Edward E. Poor, *Treasurer*, Passaic, N. J.
ARNOLD PRINT WORKS,
W. A. Gallup, *Treasurer*, North Adams, Mass.
WINDSOR PRINT WORKS,
D. A. Russell, *General Manager*, North Adams, Mass.
RENFREW MFG. CO.,
Ira S. Ball, *Assistant Treasurer*, Adams, Mass.
QUEEN DYEING CO.,
B. J. Horton, *Treasurer*, Providence, R. I.
S. H. GREENE & SONS CORPORATION,
Francis W. Greene, *Treasurer*, Riverpoint, R. I.
THE ASPINOOK CO.,
L. Johnson, *Treasurer*, Jewett City, Conn.

The hearings of 1913 both before the Committee on Ways and Means and the Senate Finance Committee were of the same general tenor as the statements just given.

The duties on coal-tar dyes in the different tariff revisions were:

1864—Anilin dyes $1.00 per lb. and 35 per cent.
1870—Anilin dyes 50 c. per lb. and 35 per cent.
1883—Anilin dyes 35 per cent. Alizarin, free.
Anilin oil and salts, free. Indigo, free.
1890—Same as 1883 with alizarin *dyes* added to Free List.

| 1894—Coal-tar dyes, 25 per cent. | 1897—Coal tar dyes, 30 per cent. |
|---|---|
| Alizarin dyes & indigo, free. | Alizarin dyes & indigo, free. |
| Anilin oil & salt, free. | Anilin oil & salt, free. |
| 1909—Same as 1897. | |
| 1913—Alizarin & alizarin dyes, free. | Coal tar dyes, 30 per cent. |
| Indigo & indigo dyes, free. | Carbazol dyes, free. |
| Anilin oil and salts, toluidin, xylidin, etc., 10 per cent. | |

It is therefore clear, in the light of the above tariff-enactments, that the preceding arguments of dye-users *against* suitable tariff-enactments on coal-tar dyes so as to enable their manufacture in this country, were more persuasive with Congress than the arguments of domestic dye and chemical makers *on behalf* of such favorable tariff-enactments.

Will the awakening of the American public since August, 1914, alter this situation?

90 WILLIAM STREET, NEW YORK CITY

## THE HEATING OF COTTONSEED—ITS CAUSES AND PREVENTION

By E. H. R. Barrow
Received June 19, 1915

On the subject of heating and deterioration of cottonseed in storage, and the accompanying reactions, there has been very little work and no published data, so far as I have been able to find. The losses which may be directly attributed to this deterioration have been enormous during the course of development of the cottonseed industry, frequently amounting to many millions of dollars in a single season, and diverting from its natural uses as edible products, many millions of tons of products which thus become suitable only for the soap kettle and as fertilizer. The heating of cottonseed has been regarded as the inevitable result of conditions beyond the control of the producer or manufacturer, and until quite recently little thought has been given to controlling these conditions and arresting the tendency of cottonseed to heat, and in this manner conserving the edibility of the resultant products.

It is generally known, however, that the heating of cottonseed is due, primarily, to excess of moisture. The cottonseed is composed, essentially, of a germ or embryo, together with a supply of reserve material from which the future plant is derived. The embryo is the only living portion of the seed—destroy this embryo and the life of the seed is destroyed. While the presence of moisture induces germination, other important circumstances materially effecting the process are temperature, access of oxygen, and removal of carbon dioxide.

The presence of moisture is very essential and sufficient moisture is necessary to induce germination, the effect being one of softening and swelling of the cellular structure, accompanied by a rise in temperature. As a general rule seeds of all kinds undergo very little change when they do not contain an excess of moisture; when not already dry, they continue to lose moisture until a relatively normal equilibrium of moisture content is established, in which condition they are subject to little change and retain their vitality for long periods. We are familiar with the ordinary keeping qualities of cottonseed stored in a good sound condition, without excess of moisture, when for a period of several months there is very little change in the physical characteristics and only slight increase in the amounts of free fatty acid. The presence of the fine coating of closely adhering lint makes the cottonseed peculiarly susceptible to the absorption and retention of relatively high percentages of moisture. The results of many moisture determinations of the separated kernels and hulls are conclusive evidence that the hulls to which the lint adheres are almost invariably from 1 to 5 per cent higher in moisture than the kernel, as illustrated by the averages of several thousand seed analyses covering the past six years.

| MOISTURE IN | HULLS | KERNEL | SEED | |
|---|---|---|---|---|
| 1914..... | 13.82 | 9.48 | 11.42 | Bad |
| 1913..... | 13.88 | 8.38 | 10.84 | Bad |
| 1912..... | 13.02 | 8.17 | 10.29 | Good |
| 1911..... | 13.84 | 10.20 | 11.82 | Bad |
| 1910..... | 11.96 | 7.58 | 9.51 | Good |
| 1909..... | 12.85 | 7.63 | 9.88 | Good |

Concurrent with the averages showing the highest moisture content is the fact that the seed of those years showed a marked tendency to rapid heating and deterioration, whereas in the other years there was very little low-grade product made, due to heating. As to the normal moisture content of cottonseed, or the

limit of moisture which seed may contain without undergoing heating, it is not possible to say with positiveness in the light of our present knowledge and insufficient data, but that a definite relationship does exist between the moisture content of seed and their keeping qualities is an indisputable fact. My observations have been that it is not safe to store for any length of time seed containing 10 per cent of moisture, and that a moisture content of 11 per cent or over would cause the seed to heat very rapidly. More extended observations and investigations along this line would be valuable.

When the moisture content is above the normal, thus providing suitable conditions to induce germination, and the seeds are accumulated in large bulk, the chemical changes are set in motion in the embryo of the seed, and these reactions are accompanied by a rise in temperature, at first slowly, then, as a flame spreads, so the combustion proceeds more rapidly, involving larger areas and may produce a warmth favorable to the incipient germination of seed containing even a normal amount of moisture. This result has frequently been observed in seed sheds where perhaps one car-load of wet seed will get into a large pile, commence heating and rapidly spread to other parts of the pile, even though composed of sound seed. It is also common knowledge that heating once begun will infect larger areas unless promptly checked, out of which knowledge has grown the common practice of using long steel rods in seed piles, and promptly "working up" the hot seed located in this manner. If all of the circumstances favorable to germination were present in the seed pile the process would go on there as it does when the roots and leaves are developed in the soil; in other words, the seed would "sprout." However, the compactness of the seed pile prevents the free access of the air, or oxygen, and the exhaling of carbon dioxide, two essential details of germination, and as a result of the slow embryonic combustion, the fats and carbohydrates are partially consumed, whereas the proteid matter remains undiminished in quantity.

As a practical illustration of this phenomenon the oil yield of badly damaged, heated seed is often reduced from 5 to 15 gallons per ton less than normal, whereas the by-product cake will analyze as high in nitrogen as undamaged seed, but of course the color would be dark.

Again it must be borne in mind that seed germination can take place only within definite temperature limits and that this range of temperature is different for different seeds, as a rule there being no germination below 35° F., or above 115° F. Then how must we account for the much higher temperature to which cottonseed will heat under favorable conditions, if left undisturbed?

As a further contributing cause to the deterioration of cottonseed must be added the important influence of microörganisms. We know that not only aerobic but the spores of anaerobic microörganisms are present everywhere so that it is only necessary to furnish favorable conditions and all the latent life collected in millions of bacteria will start to act, developing the reactions which we commonly call putrefaction. In putrefaction we find both oxidation and reduction processes. It is comparable to digestion where, in the body, the heat and energy is derived from the breaking up and utilization of the complicated molecules of fat, carbohydrates and proteids of our food. Likewise the decomposition, or putrefaction of similar molecules in the supplies of reserve material found in the seed, is accompanied by the evolution of heat. When the heat developed by the destruction of the complicated organic molecules has reached a temperature favorable for the process of oxidation we find pure chemical reactions which may raise the temperature to the point of ignition.

The presence of large proportions of fat in the seed, under the influence of moisture and the rise in temperature induced by embryonic and enzymic changes, brings about a concomitant reaction, whereby the glycerides of the fat are broken up into their corresponding fatty acids, and glycerine set free, accompanied by the evolution of heat. This action is accelerated by the presence of the cellular substance of the seed.

I have kept accurate records of the rise of temperature in various piles of seed and have found that from 60 to 85° F. the rise is very gradual, sometimes requiring from 2 to 3 weeks; however, when 85° is reached the rise becomes very rapid, showing increases of 10° or more in 24 hours. This readily accounts for the fact that many have observed where rods pulled from a seed pile one morning and showing "barely warm," may be found next day to be "hot," according to the crude method of controlling seed in storage. I am not prepared to name the maximum temperature to which cottonseed may heat, but I have recorded temperatures of 190° F. I am not aware of any cases of spontaneous combustion in piles of cottonseed, but it is of course well known that spontaneous combustion frequently occurs in cottonseed hulls in bulk. Allen records a maximum temperature of 284° C. in 1 hour and 35 minutes; in experiments with cottonseed oil in Mackey's "Cloth Oil Tester,"[1] all oils that attain a temperature of 200° C. in less than 2 hours in this test are regarded as dangerous. Spontaneous combustion of waste saturated with cotton oil frequently occurs.

Having reviewed briefly some of the fundamental causes of the heating of cottonseed in storage we shall now look to the control and prevention of this condition.

Cottonseed will not heat if given free access to air by spreading in thin layers upon a floor surface or dividing the storage shed into small compartments, whereby a ventilation of the seed may be obtained. But on account of the enormous space requirements either of these plans have been found impracticable without enormously increasing the storage capacity. Other systems of ventilation have been tried with little success, such as perforated pipes distributed at intervals through the pile and providing a means of circulating a current of air. Removing the excess of moisture by drying has been given some attention recently, and there is now on the market a drying apparatus which has found some favor and is being operated in some mills. The chief objections to this system are its cost of installation and operation, its limited tonnage capacity, the heavy loss in weight due to evaporation of moisture and the "setting" of the color of the oil if the drying is permitted to go too far.

The keeping qualities of cottonseed may be greatly improved by thoroughly cleaning before storage, and removing all bolls, dirt, trash, etc.—a practice to be commended where the seed receipts of a mill would not overtax the capacity of the seed cleaning machinery.

For a number of years I have given much thought to this subject and conducted numerous experiments along the lines above mentioned, with the result that my researches led to the conclusion that the ideal control of the heating tendency of cottonseed would be a method adaptable to all of the varying conditions in different mills, of unlimited tonnage capacity, of small working cost and without the necessary tying up of capital in expensive machinery operative only when seeds are in bad condition—a method by which the heating tendency would be checked or overcome without incurring enormous manufacturing losses in weight and whereby the quality of the resultant product would not be impaired or rendered unmerchantable.

Various chemicals and substances having hygroscopic properties were tried out with varying successes, concurrent with carefully observed records of temperature and analyses of the seed at different stages. These experiments included the use of iron sulfate, sodium nitrate, copper sulfate, salicylic acid, borax and boracic acid, sodium carbonate, calcium chloride,

[1] *J. Soc. Chem. Ind.*, **15** (1896), 90.

formaldehyde, magnesium carbonate, pipe clay, and sodium chloride (common salt).

In each instance the results obtained with different percentages of salt and salt brine were highly gratifying and led to further and more elaborate experiments along these lines. These experiments extended over relatively long periods of time and the effect of the treatment was so salutary that an effort was at once made to adapt the experiments to a larger and more practical scale. Then it was that one of the usual vicissitudes of an inventor was encountered; not owning an oil mill myself, and finding even my most intimate friends to be skeptical, and indifferent to becoming pioneers, it was with great difficulty that an opportunity was found to reduce the process to treatment. About this time a providential act occurred in the sinking of the steamboat Shiloh at the Memphis wharf. As part of its cargo this boat carried 4000 sacks of cottonseed. In the opinion of insurance adjusters and experienced oil mill men these seeds were regarded as a total loss even should they be recovered from the wreck. Although it seemed a foolhardy experiment, a proposition was made to attempt to preserve these seeds for oil milling purposes should they be secured. After being submerged from 10 days to 3 weeks, part of this seed cargo was brought to the surface and stored upon the levee, finally being removed to an old warehouse where the treatment was applied. During the few days on the levee these seed rapidly attained temperatures ranging from 100° to 160° F. and were completely saturated with water.

Sacks of these seeds untreated became a foul-smelling mass of decomposed substance in a very few days. The effect of the treatment was to immediately check the tendency to heat, and by occasional stirring, notwithstanding the enormous excess of water, the semblance of the seed was retained, and they were kept in this manner for a period of three months. On account of the large quantity of water present, which it was never possible to materially reduce, a number of mechanical difficulties were encountered in the working of them, and of course the quality of the product was "off." It is very probable, too, that the cost of handling these seeds did not make it profitable, nor is it recommended that this method be adopted to prove the efficacy of this process. However, admitting the severity of the test, it is quite remarkable that anything remained at the end of three months but a foul-smelling mass of putrefaction and decomposition. This experiment served its purpose.

At the opening of the season 1914–15 many mills, despite a warning, loaded up on hot seed. In the meantime more plausible experiments had demonstrated the means of successfully controlling this tendency to heat. In the application of this treatment I have found that it is best to apply the salt in the dry powdered form as the seeds are passing through the conveyors, either in unloading from the cars or in moving from one place to another in the seed shed. A very simple proportioning machine, devised by Mr. F. C. Holly of Memphis, was found to give excellent results in making the application. The agitation of the conveyor produces a very thorough mixing, resulting in each seed being given a thin coating of salt, provided of course, the particles are fine enough. Three important details are very essential to the successful operation of the treatment: (1) the initial temperature of the seed in storage; (2) the salt must be very finely divided; (3) the salt must be dry and loose.

It must be borne firmly in mind that this treatment is not curative, but preventive; and that the quality of the seed can be made no better than they are at the start. For the most part seed treated the past season had already undergone considerable damage from heating. In unloading from cars or moving these hot seeds in the house through the conveyors, there is always a marked reduction in temperature, due to the airing. The longer the conveyor, and the lighter the feed, the greater the drop in temperature.

(1)—It is possible to handle seed showing 150° F. through 100 feet or more of conveyor, and by regulating the feed reduce them to atmospheric temperature. This is the usual method applied in mills having hot seed, except that there being nothing added to check the heating tendency, after a short time these seed usually become heated again. It has already been pointed out that seeds heat very slowly up to 80° F., then commence to heat very rapidly; therefore in applying this treatment it is very important to cool the seed in the conveyor as much as possible, and always below 80° F. This gives time for the saline solution to permeate the seed and get in its work.

(2)—In order that the seed may be thoroughly coated without using too large a quantity of material, it is necessary to have the salt very finely ground. The commercial grades on the market were found to be too coarse to give successful results, and as the tendency of finely ground salt is to absorb moisture, become lumpy, and eventually solidify, it was found necessary to manufacture a special grade for this purpose.

(3)—The function of the salt being to absorb part of the contained moisture of the seed it is very important and quite essential to success to have a loose, very dry material. Again the commercial grades were not satisfactory, and it was necessary to add certain harmless drying substances to counteract the deliquescence of the salt, and retain for a reasonable time the original condition of the manufactured product, thereby improving its effectiveness and cost of handling without materially adding to its cost.

The first effect of the application of the preserving material is to the average oil mill man quite alarming. The moisture of the seed is rapidly brought to the surface and for a period of from one to three weeks the seed go through a "sweat," and appear very damp and moist. The salt has now partially gone into solution in the moisture of the seed, forming a saturated brine solution. By continual contact this saline solution gradually permeates the seed coating by osmosis. Salt being an enemy to the process of germination and antiseptical towards the enzymic ferments or decomposing microbes within the cellular structure of the seed, the process of heating is thereby checked by arresting the cycle of developments due to chemical and bacterial activities. As to the proportion of salt preservative to be added, good results have been obtained with approximately 5 per cent by weight, proportionately to the seed; however, the exact proportioning is not important, and it is only necessary to have an excess in order that the seed may again become dry after going through the initial "sweat." This excess adhering to the outer surface of the seed is removed during the various seed-cleaning operations before the seeds are passed to the mill to be crushed.

Only such salt remains in the seed as is actually absorbed and is approximately as follows:

| | Per cent | Per ton seed |
|---|---|---|
| Whole seed, 1 ton | 1.25 | 25 lbs. |
| Lint, 80 lbs. | 5.00 | 5 lbs. |
| Hulls, 750 lbs. | 2.5 | 16.5 lbs. |
| Meal, 850 lbs. | 0.5 | 4.2 lbs. |
| Oil | None | None |

Of the 100 lbs. applied per ton of seed, approximately 25 lbs. are taken up by the seed, the remainder, 75 per cent, being removed in cleaning. Moisture determinations in the impure salt recovered average 10 per cent. Therefore, assuming that the salt was originally moisture-free, there is removed from the seed 7.5 lbs. moisture and a gain in absorbed preservative of 25 lbs. representing a net gain in weight of 17.5 lbs. per ton of seed.

During the past season's operations such data as were available have been collected. However, by reason of the fact that the bulk of the treated seed was worked by mixing with untreated seed, the opportunity for the collection of a large amount of comparative data was not altogether favorable. Especial attention has been given to the possible effect of this treatment

upon the manufacturing losses and with particular reference to the quality and grade of the manufactured product. Careful observations have also been made of the manufacturing problems, if any, which might be encountered in working the treated seed. In this latter respect the experience of the operating superintendents has been unanimous that the difficulties encountered are far less, by comparison, than the many difficulties of working heated seed. The only objection so far offered was a slightly diminished capacity of conveyors; a tendency to occasionally clog the boll screens at one mill, and the alleged tendency of the salt to rust certain exposed parts of the operating machinery and gin ribs at another. It is generally admitted by these superintendents that these difficulties were immaterial and could be easily remedied by allowing the seed to remain long enough to be in condition, and working a few tons of untreated seed before the "clean up."

### COTTONSEED

A number of analyses were made of the seed at the time of treatment and when working to ascertain the per cent of damaged and the available oil content. These analyses showed practically no increase in damaged seed and no falling off in available oil yields.

### COTTONSEED MEAL

The regular analyses of the mills showed no falling off in the extraction of oil when working treated seed and in every mill as good analytical results were shown on meal from treated seed as untreated. Quantitative estimations of chlorine have shown the presence of from 0.1 to 0.8 per cent of sodium chloride. It has been claimed by Dr. Battle that a small percentage of salt added to the meals in cooking increased the flow of oil and gives a better extraction. I have so far failed to note this effect in working treated seed. The addition of about 1 per cent of salt to most manufactured feeds increases their palatability and tends to prevent fermentation and moulding; therefore, the presence of these small amounts in the meal would be a decided advantage.

### COTTONSEED HULLS

The application of the preservative being external, as would be supposed, the larger percentage of sodium chloride is found in the hulls, and lint. The hulls being used principally as a roughage feed, in quantities from 10 to 15 lbs. per day, the amount of salt contained therein is important. It has been found that the absorptive properties of different lots of cottonseed vary so that the percentage of sodium chloride found in unmixed treated seed has ranged between the limits of 0.5 to 4 per cent. In feeding hulls from treated seed it would not be necessary for the feeder to supply the usual quantities of salt to his stock and the purchaser should be informed by the mill that the hulls contain all the salt necessary. Careful inquiry has been made of dairymen and feeders using these treated hulls. They have invariably reported no injurious results but on the other hand that the stock apparently ate the hulls with greater relish. Aside from increasing the palatability the presence of the salt unmistakably adds to the keeping qualities of the hulls and prevents the well-known tendency of excessive moisture hulls to heat and deteriorate. At one of the mills in Memphis a pile of about 100 tons of hulls from treated seed remained cool and sweet in storage, while in the same shed another pile of hulls from untreated seed was hot and smoking and had to be forked over to prevent spontaneous combustion. The fact that salt is also frequently used in fireproofing inflammable materials should make it evident that treated seed and hulls would constitute a lower fire risk, and that the process would have the endorsement of fire underwriters.

### LINT

At first no appreciable effect was noticed upon the lint. As the treatment progressed further, attention was called to comparison of linter samples from the same mill working untreated and treated seed. This comparison both as to color and texture appeared most favorable towards the lint from treated seed and it was actually found that buyers were willing to pay a better price for such lint, on account of the peculiar firmness of texture imparted by the treatment. Microscopic examination failed to show the presence of but occasional minute salt crystals, whereas by chemical analysis from 2 to 5 per cent of sodium chloride was found to be present. This amount is undoubtedly held partially in solution in the capillary wall of the lint, and being a saturated solution would tend to deposit minute salt crystals with any loss in moisture. At ordinary temperatures 100 parts of water dissolve 36 parts of salt; consequently about 4.5 per cent of sodium chloride would indicate a saturated salt solution if the lint contained 12 per cent of moisture.

### CRUDE OIL

Only minute traces of salt have been found in the oil from treated seed and a number of samples failed to show a qualitative reaction. The property of salt to coagulate albuminous matters is well known. Its effect, if any, upon the meal would be to act concurrently with the heat of cooking in the coagulation of the proteid matters, with the result that the expressed oil would contain less impurities which hasten its deterioration and increase the refining loss. Coincident with this theory is the average result of 12 oil samples compared with average results of 50 oils of the previous season containing the same amount of free fatty acid and reported by different operators.

| | Average of 50 samples Oil season 1913–14 Analyzed by different operators | Average of 12 samples Treated seed From Mill No. 1 |
|---|---|---|
| Free fatty acid..... | 6.93 per cent | 7.1 per cent |
| Refining loss..... | 20.5 per cent | 17.1 per cent |
| Color (red)..... | 15.35 | 12.1 |

Insufficient data make it impossible to substantiate this theory further at the present time. It is a common practice in refineries to use salt for the improvement of flavor of oils and aid in the process of refining, so that its presence in treated seed would tend to improve its quality.

The process, as described, is the very essence of simplicity. Its intelligent use may prove the means of overcoming in the future the great losses which many mills have incurred from this source in the past. The protection of this work by Letters Patent is to conserve its use to the great number of oil mill interests in this great industry.

MEMPHIS, TENN.

# OBITUARIES

## JOSEPH A. HOLMES

Dr. Joseph A. Holmes, Director of the United States Bureau of Mines, died in Denver, Colorado, Tuesday, July 13th, at 1 o'clock in the morning, after an illness of about one year. His death was due to tuberculosis which it is thought was brought on through a too great devotion to his duties.

Dr. Holmes was born at Laurens, S. C., November 23, 1859. He graduated at Cornell University in 1880.

During and following his college course, Dr. Holmes devoted especial attention to chemistry, including the chemistry of explosives, and to metallurgy, geology, electricity and general physics, surveying, and mining. He visited mining regions and

examined iron, copper, and other metal mines, coal mines, quarries, etc., and plants for the treatment and preparation of mineral products in many parts of the United States, in Germany, France, Belgium, and Great Britain.

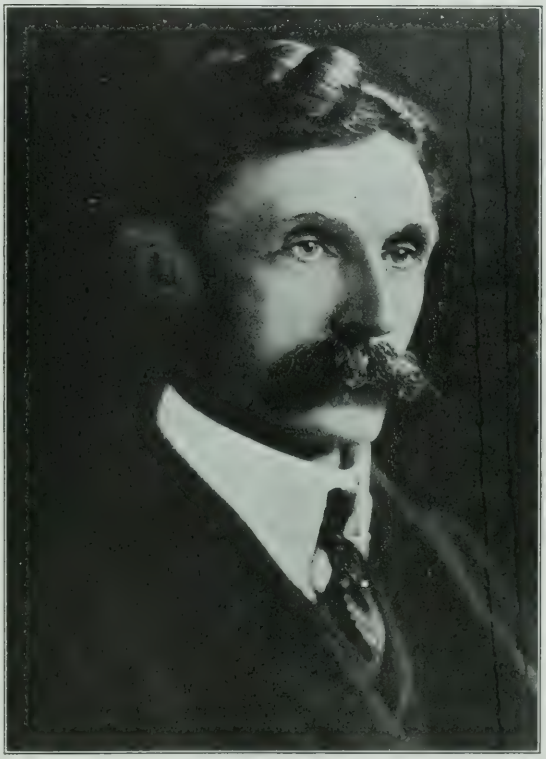
In these foreign countries, as well as in the United States, Dr. Holmes studied the methods of mining with special reference to lessening the loss of life and waste of resources. For ten years, from 1881 to 1891, he was professor of geology in the University of North Carolina and State Geologist from 1891 to 1903. As professor of geology, he examined many mines in a professional way and gave much attention to quarrying, metal mining, and metallurgical operations.

In 1903 and 1904, he organized and had charge of the Department of Mines and Metallurgy at the St. Louis World's Fair, planning the exhibits of mining and metallurgical operations.

In 1904, when the government fuel investigations were authorized by Congress, Dr. Holmes, having planned the work, was offered its supervision, but being unable to give it the necessary time, at his request the supervision was placed under a committee consisting of two members of the Geological Survey and Dr. Holmes. Under this committee the investigations were carried on to the end of 1904.

Early in 1905, the Director of the Survey appointed Dr. Holmes to take individual charge of the fuel investigations as enlarged and continued, and of the investigations of mine explosions, that were first authorized in 1907. These, developed during 1905 to 1910 under the Geological Survey, were on July 1, 1910, transferred to the newly-created Bureau of Mines. The work under the Geological Survey was carried on by the Technologic Branch, of which Dr. Holmes was chief. During this time and before the Bureau of Mines was created, Dr. Holmes examined the mine-experiment stations and mine-rescue stations in Great Britain, France, Belgium and Germany, studying their equipment and methods, and as a result of his study inaugurated the movement for mine-rescue work in this country by private operators, by States and by the Federal Government.

At that time he planned the establishment of three State mine-rescue stations in Illinois and of the Government mine-rescue experiment stations located at points accessible to the principal coal fields of the country. Afterwards he extended these mine-rescue experiment stations until they are now located in both coal-mining and metal-mining regions of the country.



JOSEPH A. HOLMES

In 1907, on Dr. Holmes' recommendation, President Roosevelt secured the appointment by the governments of Great Britain, Germany and Belgium of one distinguished engineer from each of these countries to visit the United States; and in company with these engineers Dr. Holmes visited the more important coal fields of the country to determine the extent to which safety practices used in other mining countries might be introduced in the United States.

On the basis of their findings, Dr. Holmes organized and directed the government investigations of mine explosions, of explosives used in mining, and the use of electricity in mining. He took personal part in the rescue work after many of the mine disasters occurring in the United States from the beginning of the work under the Geological Survey until about one year before his death.

In connection with his work for the Geological Survey, Dr. Holmes had charge of the structural-materials investigations which were inaugurated during the Louisiana Purchase Exposition. While this work was under his direction, he conducted a number of notable investigations into the value of various structural materials with especial reference to their fire-resisting qualities. He was perhaps the pioneer in calling general attention to the large per capita fire waste in this country and undoubtedly aided much in the campaign which has been continued ever since to reduce it. Under his initiative, the United States Geological Survey at the time issued a report entitled "The San Francisco Earthquake and Fire of April 18, 1909, and Their Effects on Structures and Structural Materials," a report that has since served as a guide to foreign countries in rebuilding cities destroyed by earthquakes. Other important publications on structural materials were: "The Fire-Resistive Properties of Various Building Materials," and "The Fire Tax and Waste of Structural Materials in the United States."

When the Bureau of Mines was created in 1910, the structural-materials investigations were turned over by Congress to the Bureau of Standards, which has carried them on ever since.

Dr. Holmes' work under the Geological Survey also included fuel investigations which were started by him at the Louisiana Purchase Exposition and led to a remarkable quickening of public interest in the values of fuels. The work of the coal-testing plant at the Exposition was reported in Professional Paper 48, "Report on the Operations of the Coal-Testing Plant of the United States Geological Survey at the Louisiana Purchase Exposition, St. Louis, Missouri, 1904," and several other papers.

After the close of the Louisiana Purchase Exposition, the United States Geological Survey under the direction of Dr. Holmes continued work at the fuel-testing plant at St. Louis, Mo., and as a result published a number of important papers. Bulletin 339, "The Purchase of Coal under Government and Commercial Specifications on the Basis of Its Heating Value, with Analyses of Coal Delivered under Government Contracts," published in 1908, gave impetus to a movement throughout the United States for the purchase of coal under specifications as to quality as shown by analysis. The plan was adopted by the United States Government which today purchases $8,000,000 to $10,000,000 worth of coal yearly on such a basis.

With the creation of the Bureau of Mines and the appointment of Dr. Holmes as Director, the work he had planned under the Geological Survey developed rapidly. Congress widened the scope and enlarged the purposes of the bureau, and authorized a work more nearly commensurate with the importance and the needs of the world's greatest mining industry.

The chief work of the Bureau of Mines under Dr. Holmes has been the investigation of problems having to do with the cause and prevention of coal-mine explosions and the safeguarding of the lives of coal miners.

Dr. Holmes found that both the improper use of explosives and the use of improper explosives had resulted in coal-mine disasters; he demonstrated, what many mining men had doubted, that coal dust might be as dangerous to the miner as firedamp, and after some time he established a list of "permissible" explosives for use in mines in which dust or gas were a menace to the miner. These explosives were designated as permissible after they had passed rigid tests at the experiment station of the bureau, which had been established at Pittsburgh, Pa., and when used as prescribed by the bureau. The protection these explosives give the coal miner is shown by a statement of the bureau's engineers that since 1908 there has been only one serious explosion in a mine where permissible explosives were used. Dr. Holmes also took up the investigation of better lights for miners and established a permissible list of portable electric lamps for use in dangerous mines. Thousands of these lamps are now in daily use.

Dr. Holmes in developing rescue work introduced in this country the so-called oxygen-breathing apparatus, and as a result of his efforts such apparatus is not only widely used but is being adopted by manufacturing establishments and by city fire departments. There are today six mine-rescue stations and eight mine-rescue cars and one rescue motor truck operated by the bureau, and there is federal legislation to increase the number of stations each year. Today 170 mining companies have individually or through the association of two or more companies established 76 mine-rescue stations at which there are now 1,200 sets of artificial breathing apparatus besides the auxiliary equipment for first-aid and fire-fighting work. There are also 12 mine-rescue cars now operated by individual mining companies about their own property—all of these the result of the incentive given by Dr. Holmes to this work.

The investigations of the Bureau of Mines into causes of disasters and the recommendations made by the bureau and the coöperation received from the State mine inspectors, mine operators and miners have resulted in a decreasing death rate in the mines since the work was taken up by the Federal Government.

It was Dr. Holmes who aroused the coal-mining industry to the danger of dust explosions. At the experiment station of the bureau in Pittsburgh through his efforts a large steel tube was constructed for demonstrating the explosibility of coal dust. While foreign countries had paid much attention to the danger of coal dust and while it was known in this country that coal dust was dangerous, little attention was being paid to the prevention of such explosions until Dr. Holmes demonstrated how violent they might be. As some mining men were unconvinced of the great danger from coal dust, believing that what happened in a tube might not happen in a mine, Dr. Holmes developed an experimental coal mine at Bruceton, Pa., twelve miles from Pittsburgh, the only experimental mine in the world. For more than four years demonstrations have been going on in this mine until today the entire mining industry, including operators and miners, has a well-settled idea of the danger of coal dust, and mine operators and State officials are following the recommendations of the bureau to prevent dust explosions.

In the last two years, the work of the bureau under Dr. Holmes has included metallurgical investigations which are of especial importance to the West. These investigations have so far been confined to general inquiries and to a few investigations dealing with such topics as smelter-smoke wastes at smelters and other metallurgical plants, and wastes in the treatment of rare minerals and metals. Under the supervision of Dr. Holmes, chemists and engineers of the bureau have demonstrated that a process they have devised for the extraction of radium from its ores can be successfully used on a commercial scale and will prove more efficient than that used by the largest foreign producers of radium. Through this process it is possible that the cost of radium to the consumer will be greatly reduced. The process is to be patented and dedicated to the public.

Dr. Holmes on many occasions showed the need for such investigations and told the mining industry that the total wastes or losses in mining and utilizing our mineral resources amount to more than $1,000,000 a day.

He told the country that the coking of coal in bee-hive ovens is resulting in an annual loss of $75,000,000. The progress made in reducing some of this loss through the use of by-product ovens and the utilization of the by-products is described in a recent report of the Bureau of Mines.

The Director showed also that the annual waste of metals in brass-furnace practice amounted to over $4,500,000 and the bureau issued a report showing how this waste can be largely prevented by practical means.

Dr. Holmes organized the first national mine-safety demonstration which was held in Pittsburgh, Pa., 1911, before President Taft and other notables and 20,000 miners. The slogan "Safety First" was used for the first time generally at this demonstration and shortly afterwards spread rapidly throughout the mining industry and now it is known throughout every industry in the country.

In 1908, when President Roosevelt took up the question of conservation of our natural resources, Dr. Holmes was made a member of the National Conservation Commission and had charge of the inventory of the nation's mineral resources.

Dr. Holmes was a member of the Mining Legislation Commission of Illinois; American Institute of Mining Engineers; American Society for Testing Materials; Elisha Mitchell Society; Washington Academy of Science; Academies of Science of St. Louis and North Carolina; American Society of Mechanical Engineers; Cosmos Club of Washington; Engineers' Club of New York; and a fellow of the Geological Society of America.

He received a degree of D. Sc. from the University of Pittsburgh, and that of LL. D. from the University of North Carolina, both degrees being conferred as a result of Dr. Holmes' efforts in behalf of the mining industry.

In the death of Dr. Holmes, the people of the United States lose one of their most remarkable and efficient public servants. And the saddest part of it all is that Dr. Holmes is a victim of overwork, a too great devotion to the duties which had been assigned to him in behalf of the safety of the million miners in the United States. He was one of the most enthusiastic, indefatigable workers I ever had the pleasure of associating with. His mind was continually upon the yearly death toll of the miners, and although taken away in the prime of his life he has already

accomplished much in reducing the terrible death rate. In the last five years of his life he saw a slowly but steadily decreasing death rate and while it gave him much joy, it only added to his almost superhuman efforts in behalf of the men.

It is thought that Dr. Holmes' frequent visits to mines in which there were disasters and his continual insistence on going where only his trained rescue crews should go, sharing the dangers that should have gone only to more robust men, seriously affected his health. On his trip to Alaska two years ago to learn concerning the great coal fields there he met with many hardships and severe exposure and it is believed that this hastened his end.

Dr. Holmes is indeed a martyr to the cause of safety among the miners, and his name is added to the honor roll of three bureau rescuers who in the past gave up their lives to this cause. The mining industry suffers a keen loss in his death.

VAN. H. MANNING

## ALBERT PLAUT

The death of Albert Plaut, on June 17th, at his apartments in the Hotel Ritz-Carlton, New York, was a great shock to his large circle of friends and business acquaintances, and a serious loss to the chemical profession, in which he was so well and favorably known. He was an active member of the American Chemical Society and of the Society of Chemical Industry. He served as a delegate, appointed by President Taft, to represent the United States at the Seventh International Congress of Applied Chemistry in London, and was a member of the Executive Committee and Chairman of the Entertainment Committee of the Eighth International Congress held in New York.

Mr. Plaut gave much time and energy to the development of the Chemists' Club of New York. He was personally active in the building of the present new Club House and was at the time of his death Treasurer of the Club and a member of its Board of Trustees. The portrait of Priestley, which hangs in the social room of the Club, was presented by him, and many other features of the Club owe their origin or existence to his interest and generosity. At a special meeting of the Board, held on the day after his death, the following minute was adopted:

"The death of our Treasurer and fellow member of this Board, Albert Plaut, inflicts upon the Chemists' Club and its members a very great loss. His unflagging interest in the Club's affairs, his generous helpfulness on every occasion that offered itself, his keen interest in the work of chemists, and his encouraging appreciation of those efforts, his sturdy maintenance of what he regarded as right, together with his gracious good fellowship, all endeared him to the large number of us who knew him. And while we record our poignant grief at his passing, we are glad to acknowledge both appreciation and pleasure in that ours was the privilege to be associated with one who ordered his life to such good ends and whose friendship was indeed a benediction to those who shared it.

"This Board extends its sincere condolences to his bereaved family, and directs that a copy of this minute, properly engrossed, be sent to it."

At a special meeting of the Directors of the Chemists' Building Company held June twenty-first, the following Minute was unanimously adopted:

"In the death on June seventeenth, one thousand nine hundred and fifteen, of Mr. Albert Plaut, Vice-President of this Company, a Director since its organization, and one of the moving spirits in the generous group that made possible the present club house for the chemists of this country, not only this Board has suffered the loss of a close friend, and wise counsellor, but the chemical world as well is deprived of one whose integrity of purpose, genial personality and wide interests have made for him a lasting place in the hearts of all who enjoyed the privilege of knowing him.

"*Resolved*, that a suitably engrossed copy be transmitted to the bereaved family of our lamented fellow, with the expression of this Board's personal grief and deepest sympathy in their loss."

ALBERT PLAUT

Mr. Plaut was preeminently successful in his commercial undertakings, and was recognized as a leader among the merchants of New York. The firm of which he was the head became, under his administration, one of the leading pharmaceutical houses in America. He was Past-President of the National Wholesale Druggists' Association, First Vice-President of the Merchants' Association, a founder of the Metropolitan Drug Club and of the Druggists' Supply Corporation, an active member of the New York Drug and Chemical Club, and past-chairman of the Drug and Trade Section of the New York Board of Trade and Transportation.

Born in Eschwege, Germany, in 1858, Mr. Plaut came to the United States with his parents when eleven years old and received his education in the public schools of New York City, the College of the City of New York, and the New York College of Pharmacy. He served a five-year apprenticeship with his father, Isaac Plaut, in the drug business, after which he entered the firm of Lehn & Fink as a stock clerk. He was admitted to

partnership in this Company in 1886, on the retirement of Mr. Lehn. In 1910 Lehn & Fink was incorporated, with a capital of $600,000, and Mr. Plaut became President of the concern. The business structure at 120 William Street was erected by Mr. Plaut in 1901 and the factory and general laboratory in Brooklyn were established by him in 1906.

Mr. Plaut showed a keen interest in educational work. He served many years as trustee of the New York College of Pharmacy and was at the time of his death First Vice-President and Chairman of the Committee on Instruction of that institution. In 1914 he founded the Isaac Plaut Travelling Fellowship, in memory of his father, to be awarded annually to the post-graduate student who had shown special aptitude for original investigation. The holder of the fellowship receives a stipend of $500 for a year's study in some foreign university. Mr. Plaut also established an endowment fund of $5,000 for the Princeton Chemical Club in order to enable its members to enjoy the advantages of outside lectures on special chemical topics. During his lifetime he was a generous supporter of many other charitable and educational institutions in New York.

He left a large estate which, after ample provision for his employees and numerous charitable bequests, is to be shared by his son, Edward Plaut, who succeeds to his business interests, and his daughters, Mrs. M. J. Falk and Miss Constance Plaut.

The funeral services were held at the Society for Ethical Culture Hall, and the interment was made in the cemetery at Point Pleasant, New York. The honorary pallbearers were I. Frank Stone, President of the National Aniline & Chemical Co.; Thomas F. Main, President of Tarrant & Co.; Wm. J. Schieffelin, President of Schieffelin & Co.; William C. Breed, President of the Merchants' Association of New York; Berthold Levi and Francis F. Holliday, representatives of the National Wholesale Druggists' Association; Professor M. C. Whitaker, President of the Chemists' Club; Frederick William Fink, former partner in the Lehn & Fink Corporation; Franklin Black, of Charles Pfizer & Co.; and F. L. Lavanburg.

M. C. WHITAKER

# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

## WORLD TRADE IN FERTILIZERS

*L'Institut International d'Agriculture* has published in Rome (September, 1914) a pamphlet containing very complete data, chiefly in tables, of the production, movement and consumption of various classes of fertilizers.

Those figures which concern the United States are the following, the amounts being given in metric tons (approximately equal to United States long tons):

| | 1912 | 1913 |
|---|---|---|
| PRODUCTION | | |
| Natural phosphates: | | |
| Extracted | 3,231,636 | 3,202,636 |
| Sold | 3,146,573 | 3,020,905 |
| Ammonium sulfate | 149,700 | 176,900 |
| Calcium cyanamide(*a*) | 14,000 | 14,000 |
| Sulfur | 308,328 | 316,575 |
| Copper sulfate | 17,908 | 24,643 |
| IMPORTS | | |
| Guano | 19,467 | 19,411 |
| Bone meal, etc. | 34,704 | 35,173 |
| Potassium sulfate | 44,071 | 40,172 |
| Potassium chloride | 218,751 | 217,191 |
| Manure salts(*b*) | 694,133 | 600,168 |
| Sodium nitrate | 444,134 | 635,876 |
| Ammonium sulfate | 54,016 | 59,670 |
| Synthetic nitrogenous fertilizers | 2,339 | .... |
| Sulfur | 27,315 | 14,870 |
| EXPORTS | | |
| Natural phosphates | 1,225,824 | 1,388,362 |
| Potassium chloride | 620 | 708 |
| Miscellaneous fertilizers | 75,780 | 73,911 |
| Sulfur | 27,315 | 14,870 |
| Copper sulfate | 3,097 | 1,910 |
| CONSUMPTION | | |
| Artificial fertilizers | 5,575,392 | 6,169,736 |
| Potassium-containing products(*c*) | 215,966 | 231,690 |
| Sodium nitrate | 441,047 | 589,187 |
| Nitrogen fertilizers: | | |
| As sodium nitrate | ..... | 485,000 |
| As ammonium sulfate | ..... | 235,000 |

(*a*) Capacity of plants. (*b*) Min. 20 per cent $K_2O$.
(*c*) Calculated on basis of pure potash.

. The pamphlet also contains tables showing market prices at different times and places and concludes with an extensive bibliography.

## TOLERANCES IN TESTS OF PERMISSIBLE EXPLOSIVES

At the invitation of Van. H. Manning, Acting Director of the United States Bureau of Mines, a number of the prominent manufacturers of permissible explosives used in coal mines met in conference at the Bureau of Mines offices in Washington, June 7th, to discuss the tolerances that may be permitted in tests of field samples or manufacturers' samples of permissible explosives.

At the request of Mr. Manning, Dr. Charles E. Munroe, consulting explosives chemist of the Bureau of Mines, presided at the conference and explained its objects. Addressing the manufacturers he said: "Today there are 133 different explosives on the permissible list. There have been others admitted to the list and later removed. In all, over 150 explosives have been tested by the various methods and the results carefully recorded in the archives of the bureau. It was found that the bureau could not rest content with simply testing the original samples submitted and saying that hereafter that was a permissible explosive provided it was used in the manner described by the bureau. It was felt that in order that the bureau might know that the explosives were of the proper kind, samples should be obtained in the field and that such samples should be tested by the same methods. When this was undertaken, the question came up as to how nearly the tests should conform to the results of the tests made on the original samples. It is well known that it is physically impossible for a man to exactly duplicate results in two tests. After a large amount of data had been gathered, a committee was appointed by the Director to consider the problem; the committee has been working on the matter for a long time, the data have been tabulated, and have been thoroughly investigated by the members of the committee. The results were set forth in a report to the Director, a copy of which has been sent to all manufacturers of permissible explosives and you are here to discuss that report today. The committee felt it was necessary to determine these tolerances before proceeding with the investigation of explosives in the field and before saying that they did or did not conform to the requirements. We should have complete agreement between the manufacturers and the Bureau of Mines in regard to this retesting of explosives."

The questions submitted by the committee of the bureau were taken up in detail and the tolerances recommended and agreed upon at the conferences are as follows:

In order to define more exactly what is meant by the phrase "similar in all respects" in the definition of a permissible explosive, *viz.*: "An explosive is called a permissible explosive when it is similar in all respects to the sample that passed certain tests by the United States Bureau of Mines, and when it is used in accordance with the conditions prescribed by this bureau," the following tolerances are recommended for field samples or manufacturers' samples of explosives, beyond which such lot of explosives can not vary and still be considered permissible for use in coal mines: *Provided*, that where the Bureau of Mines finds a sample which does not come up to the tolerance limits, the bureau shall simply declare that particular lot of explosives not permissible, and a copy of the notification to the

consumer or owner shall be furnished the manufacturer, the notification to state that the explosive did not meet the tolerance requirements for moisture or ingredients.

CHEMICAL ANALYSIS

MOISTURE, to be fixed by a sliding scale of from 1.5 per cent at zero to 4 per cent at 10 per cent of moisture in original sample, this tolerance being on total percentage of moisture in the explosive.

OTHER INGREDIENTS (or their equivalents) in quantities not exceeding 60 per cent, according to attached curve. For ingredients in quantities of 60 per cent or more, the tolerance shall be plus or minus 3 per cent: *Provided*, that the ingredients of a permissible explosive shall be considered to be those substances reported as found by the Bureau of Mines in the original sample of that explosive submitted for test as to its permissibility; and *Provided further*, that an equivalent shall be considered to be a substance which would not materially alter the properties of the explosive and which would produce the same result as the original substance.

PRODUCTS OF COMBUSTION (determined by Bichel gauge test): The volume of poisonous gases from 680 grams of the explosive including its wrapper must be less than 158 liters, except that in case the first test yields 158 liters or more of poisonous gases per 680 grams of the explosive (including its wrapper), the average result of three tests agreeing within 5 per cent of each other shall be taken and no explosive shall remain permissible when this average for poisonous gases exceeds the above standard limit.

PHYSICAL TESTS

RATE OF DETONATION (the average of three trials with Mettegang's recorder): plus or minus 15 per cent.

UNIT DEFLECTIVE CHARGE (the average of three trials with the ballistic pendulum): plus or minus 10 per cent.

GRAMS OF WRAPPER per 100 grams of explosive (average of four determinations): Plus or minus 2.0 grams; *Provided*, that the manufacturers shall submit samples of all different sized cartridges, to be considered as part of the original sample, the amount of wrapper to be determined for each size of sample; and, *Provided further*, that the tolerances as suggested shall be made in comparison with the various diameters as submitted with the original sample.

APPARENT SPECIFIC GRAVITY of cartridge, by sand (average of four determinations): plus or minus 7.5 per cent; *Provided*, that actual density shall be determined on cartridges of the same diameter as the standard, and, *Provided further*, that manufacturers shall be required to submit samples of all sizes.

GAS AND DUST, GALLERY NO. 1. No ignition must be obtained in each of one or more trials. *Note:* In the retesting of permissible explosives by tests 1, 3, and 4, the charges of the explosives fired will be reduced 10 per cent in weight from the weights originally used in order to eliminate any likelihood of a failure being due to the natural variations in the gallery conditions.

PENDULUM FRICTION TEST: Each explosive must pass a test of ten trials under the same conditions as originally tested, except that the height of fall of the wood fiber shoe will be reduced by 10 per cent in order to eliminate any likelihood of a failure being due to the natural variations in test conditions.

The following persons were present at the conference: John H. Feeman and Willard Young, Atlas Powder Company, Wilmington, Delaware; G. R. McAbee and C. T. Crone, McAbee Powder & Oil Company, Pittsburgh, Pa.; W. H. Blumenstein, W. H. Blumenstein Chemical Works, Pottsville, Pa.; W. C. Anderson and J. S. Burton, Burton Powder Company, Pittsburgh, Pa.; A. M. Comey, E. I. du Pont de Nemours Powder Company, Wilmington, Delaware; and Herbert Talley, Hercules Powder Company, Wilmington, Delaware. The bureau was represented by Van. H. Manning, Acting Director, Dr. Charles E. Munroe, consulting explosives engineer, George A. Hulett, consulting chemist, S. P. Howell and C. G. Storm, explosives chemists.

## THE RISE IN PRICES IN THE GERMAN CELLULOID INDUSTRY

According to the *Berliner Tageblat*, because of the rise in cost of the raw products of the celluloid industry towards the beginning of November, especially of Japanese camphor and Chili saltpeter, the manufacturers were forced to raise their prices considerably. While synthetic camphor offers a substitute for the Japanese article, unfortunately the manufacture of synthetic nitric acid has not progressed to a point where it affords the necessary supply. The celluloid manufacturers were caught entirely unprepared, with the result that they bought up all the available raw products on the market, forcing prices still higher. Although it was known at the outbreak of the war that these raw products would be liable to seizure by the government for the army, exact information on this point was not to be had, and this also affected prices. While some qualities could have stood a slight rise in price, the hundred per cent increase demanded was out of the question for most consumers, and many canceled the orders they had already given. Since celluloid is chiefly used in the manufacture of luxuries rather than necessities, economic conditions also tended to cut down the demand for it. The great falling off in demand must eventually bring down to some extent the price of the raw materials.

## ENGLAND'S TRADE IN MAY, 1915

The British Board of Trade report for the month of May shows imports into the British Isles of $358,022,000, against $299,950,000. Exports were $198,090,000, compared with $210,255,000 last year.

The increase in the value of imports was due largely to gains in food, drink, and tobacco, amounting to $40,580,000; cotton, $13,685,000; manufactured iron and steel increased $1,395,000. Other metals and their manufactures increased $8,145,000.

The largest decreases in exports were $11,100,000 in manufactured cotton, $7,780,000 in machinery, $4,490,000 in coal and coke, and $4,210,000 in iron, steel, and the manufactures thereof.

England's imports and exports by months during the past year compare with one year ago as follows:

| | Imports | | Exports | |
|---|---|---|---|---|
| | 1915 | 1914 | 1915 | 1914 |
| May | £71,604,400 | £59,990,000 | £39,618,000 | £51,421,577 |
| April | 73,678,288 | 61,626,830 | 42,126,787 | 50,736,066 |
| Mar | 75,982,845 | 67,339,845 | 39,829,000 | 54,171,870 |
| Feb | 65,265,744 | 62,050,744 | 36,405,778 | 51,490,778 |
| Jan | 67,401,006 | 68,005,009 | 35,143,057 | 57,403,108 |
| | 1914 | 1913 | 1914 | 1913 |
| Dec | 67,100,000 | 71,111,857 | 36,055,000 | 53,055,443 |
| Nov | 55,900,918 | 68,480,918 | 32,606,807 | 52,756,807 |
| Oct | 51,562,000 | 71,732,893 | 38,158,000 | 56,178,843 |
| Sept | 45,056,086 | 61,359,086 | 33,527,877 | 49,277,877 |
| Aug | 42,362,034 | 55,975,704 | 28,631,104 | 52,261,228 |
| July | 59,383,792 | 61,783,683 | 52,231,296 | 55,475,551 |
| June | 58,272,042 | 58,309,519 | 48,626,410 | 51,377,685 |

## AMERICAN STEEL RAILS

The American Iron and Steel Institute reports that the production of steel rails in the United States declined last year to 1,945,095 tons—the smallest production for any year since 1908. The contraction of the output in 1914 as compared with that of 1913 was no less than 1,557,000 tons, or 44 per cent. The yearly production has been as follows during the decade ending with 1914 inclusive:

| Year | Tons | Year | Tons |
|---|---|---|---|
| 1905 | 3,375,929 | 1910 | 3,634,029 |
| 1906 | 3,977,887 | 1911 | 2,822,790 |
| 1907 | 3,633,654 | 1912 | 3,327,915 |
| 1908 | 1,921,015 | 1913 | 3,502,780 |
| 1909 | 3,023,845 | 1914 | 1,945,095 |

In 1905, Bessemer steel rails were made to the extent of 3,192,347 tons; in 1914 this class was represented by only 323,897 tons. On the other hand, open-hearth steel rails advanced from 183,264 tons in 1905 to 1,525,851 tons in 1914. The causes of the great contraction observable last year in American steel-rail making were due to the reduction of railroad construction and to a curtailment of renewals due to unsatisfactory internal conditions in the United States and to the adverse financial influence, of course, of the great European war. The external demand for American steel rails dwindled to small proportions last year, having amounted to only 174,680 tons, as compared with 460,553 tons in 1913, 446,473 tons in 1912, and 420,874 tons in 1911.

## THE RUSSIAN PETROLEUM INDUSTRY

The firm of Nobel Brothers has, according to *Engineering*, **99** (1915), 572, published a budget, for the current year which emphasizes the fact that, on account of the war, very special conditions and factors have to be reckoned with for 1915. On the one hand there will be higher expenses, such as excise, railway freights, and imperial taxation, and, further, necessary materials and plant have very materially risen in price. On the other hand must be considered the further large growth in the use of naphtha for fuel in the neighboring districts, a movement which is likely to continue on an increasing scale on account of the great shortage of coal and of several large railway concerns having decided to adopt naphtha firing in preference to coal. This movement, in its different phases, has been accelerated by the material increase in the production of naphtha in the Baku district, especially from the newly-opened springs. So as to be able to satisfy this growing demand, the company has been endeavoring to increase the stock of naphtha in its Volga tanks, and further purchases will have to be undertaken. The company estimates its sale of naphtha for 1915 at 2,930,800 tons, against 2,567,080 tons for 1914. The bulk of this increase is for liquid fuel. The sale of petroleum is calculated to yield an increase of $721,000. The sale of lubricating oil is likely to decrease, as the war has put a stop to the export. The budget for 1915 balances with $83,945,000, against $61,285,000 for 1914. Quotations at Baku are stated to have risen $0.86 per ton for petroleum and $0.50 per ton for naphtha residues.

## ALCOHOL IN GERMANY

At the annual meeting of the Association of German Alcohol Manufacturers, held in Berlin in the last week of February, it was stated that there was a strong demand, at the beginning of the war, for prohibiting the use of potatoes, which were wanted as food, as raw material for alcohol distillation [*Engineering*, **99** (1915), 517]. This is one of the chief resources of the large farmers, especially in the eastern parts of Prussia, where the soil is not suitable for raising much grain. The need of alcohol for chemicals and as substitute for benzol, lamp oil, etc., was too imperative, however, and the actual consumption of alcohol for technical purposes was higher in the last quarter of 1914 than it had been before. The production decreased, however. It was pointed out that a certain consumption of alcohol seemed to be indispensable in the interest of the economy of the industry, as long as the fermentation of the starch in the potato and the distillation could not be conducted in such a way as to yield a product of higher value than alcohol. A certain success has been realized in this respect. In his new works at Arnsdorf, near Frankfort, Böttinger gains one-third of the possible yield in alcohol as acetone. Scientific investigation has been pushed successfully in other directions also. One of the minor sources of waste stopped is that feeding of cattle with raw potatoes has been abandoned, because cattle cannot extract any nutriment from this food, while pigs can. Considerable success has also been realized in the cultivation of waste moorlands.

## COKE-BREEZE BRIQUETTES

An article in the *Journal für Gasbeleuchtung*, of the 6th of March, by Mr. Behr, the Manager of the Gas and Water Works at Kolberg, describes experiments made during the past six years on the briquetting of coke breeze, and the plant which, as the result of the experiments, has been installed at the Kolberg gas works for making briquettes.

The utilization of coke breeze in gas works for firing boilers, either with or without admixture with thick tar, necessitates the use of suitable grates, blowers, etc. The flues rapidly get choked, and much unconsumed breeze is lost, owing to the action of the blast. The use of coke breeze in specially constructed suction producers leaves little to be desired as regards economy and complete consumption, but there are not sufficient of these plants to utilize much of the breeze, and in many cases local conditions would preclude their use.

Having regard to these considerations, the author proceeded to study the manufacture of briquettes from coke breeze.

The process which gave the best results was the compression of the breeze after the addition of finely divided hard pitch and heating the mass to 300°–400° C. Experiments with other binders—such as both thin and thick tar, with an addition of sawdust and coal dust—all failed in respect of ease of ignition.

In regard to uses for the briquettes, a small $2^1/_2$ by $2^1/_2$ inch size may be used in all cases where the layer of fuel is not less than 8 to 10 inches. Good chimney draught is obviously desirable—*i. e.*, such as is required for ordinary 2-inch coke. The best results, however, are obtained in closed iron stoves, central heating plants, etc., in which 50 to 100 per cent of the fuel ordinarily used can be replaced by coke briquettes. Like any novelty, it has proved rather difficult to introduce the use of coke briquettes. It is necessary to show a small stove burning the briquettes to convince people that they burn well.

When the coke briquettes were introduced about six years ago they did not give great satisfaction, but these were a larger size, 4 inches diameter, and they were not as hard as the later ones. After the small $2^1/_2$-inch briquettes had been introduced, many householders took kindly to them, and now at times the output does not meet the demand. The result of the introduction of the briquetting plant at Kolberg has been not only to dispose entirely of coke breeze produced on the works, but coke breeze has been bought from other works to work up into briquettes.

## CANADIAN RAILWAYS

At the close of June, 1914, the length of railway completed in Canada was 30,795 miles, while 22,891 miles more were under construction, or had been planned [*Engineering*, **99** (1915), 471]. The increase of completed railway in 1913–14 was 1491 miles, in addition to which 309 miles of previously opened line were double-tracked. The capital embarked in completed Canadian railways amounted at the close of June, 1914, to $1,808,320,761; and if securities of lines under construction are taken into account, the aggregate is increased to $1,962,128,070. The gross earnings of Canadian railways in 1913–14 were $243,083,539, showing a decrease of $13,619,150 or $5^1/_2$ per cent as compared with 1912–13. The net earnings declined in 1913–14 to the extent of $10,582,723. Guarantees and subsidies granted by the Dominion Government and sundry provincial bodies amounted at the close of June, 1914, to $406,259,165.

### NICKELPLATING OF ALUMINUM

In a communication to the Académie des Sciences, M. Le Chatelier gives particulars of a new process for the nickelplating of aluminum. The aluminum is given a preliminary treatment in a bath of hydrochloric acid containing a certain portion of iron. The iron is precipitated on the surface of the aluminum forming a kind of network. When this is passed into a nickel bath the nickel becomes entangled in this network and adheres strongly to the aluminum. This process is based on a physical action, and appears to solve the problem hitherto considered impossible.—D. G. ANDERSON.

### PRODUCTION OF TUNGSTEN AND MOLYBDENUM IN ENGLAND

According to the *Times Engineering Supplement*, **1915**, 486, the outbreak of war found Great Britain very deficient in the supplies of many of the rarer metals employed in steel manufacture, and for a time much anxiety was felt respecting the possibilities of manufacturing in England certain of these metals hitherto obtained in large quantities from the Continent. Among these mention may be made of the compounds of chromium, tungsten and molybdenum.

In the case of tungsten, the best wolfram ores are brought from Portugal and India, while the molybdenite used in the preparation of ferro-molybdenum comes from Norway, Sweden, and Australia. The Australian ores cannot, in the most favorable circumstances, be conveyed from the mines to Britain in less than two months, and as they are extremely costly it would not pay the manufacturer to hold large quantities of ore in reserve.

One factory at Luton, in England, has now extended its plant so that it is capable of turning out nearly 1,000 tons of ferrotungsten and tungsten powder annually, and it is unlikely that the trade in tungsten powder will ever revert to Germany after the war. The process used at the Luton factory for the production of tungsten powder consists in boiling the finely ground wolfram with a soda solution. The tungstate of soda formed is settled in tanks and dried so as to produce coarse crystals. The compound is then treated with hydrochloric acid in wooden vats, by which means the tungstic acid is liberated as a yellow paste. In order to reduce the acid, it is mixed, after thorough drying, with charcoal in large crucibles and heated for 18 hours in a reverberatory furnace. The slaglike mass thus prepared is crushed and ground to a fine powder, which is finally passed through wire sieves with 120 meshes to the inch, and represents tungsten of 98 per cent purity.

In the manufacture of ferrotungsten large 3-ton electric furnaces, each with three suspended electrodes are used. The feeding of the furnaces takes place by hand in small charges of the mixed ore, with the requisite quantity of carbon-fuel, scrap iron and flux. The molten masses of ferrotungsten are drawn off from time to time and after cooling are hand-broken and sorted into various sizes. Owing to the great weight of the material, it is a matter of considerable difficulty to handle it in bulk. It is usually packed in steel casks, each of which contains 25 cwt.—A.

### PALM KERNEL CAKE AND MEAL

In a recent issue of the *Bulletin of the Imperial Institute*, it is stated that the chief center of the palm kernel industry was Hamburg, where, until recently, practically all the palm kernels extracted in Africa were shipped. This included very large quantities from British West African possessions, as, for some inexplicable reason, very little crushing of these kernels was done in England. This condition of affairs is likely to be altered in the near future, and as a matter of fact the change has already commenced, the first shipment ever received in Hall, consisting of 1,600 tons of kernels, having arrived, but since then over 100,000 tons of kernels have been imported into Great Britain.

Palm kernel oil is very similar in its properties to coconut oil, but has not such a marked taste and odor. It is quite neutral and can be used as an alimentary fat. It is easily saponified and forms a good hard soap, especially suitable for and largely used in the manufacture of dry soaps. The press cake or meal is quite suitable for cattle feeding, and it is well known and largely employed for this purpose in Germany, Holland, and Denmark, but it is practically unknown in England. Experimental feeding trials with this cake have been arranged at several agricultural colleges in England and in view of the fact that the import feeding cakes (linseed, cottonseed, and rapeseed) for the year 1913 totaled 406,700 tons, the results will be of considerable interest.—A.

### MARBLE FOR ELECTRIC LIGHT SHADES

It has been found that marble cut into thin sheets, 0.02 in. to 0.1 in. thick, is sufficiently transparent to be used instead of opal glass for electric light shades. The sheets are given a special treatment with oil at a high temperature and pressure, and give beautifully clear effects. Comparing the transparency and diffusive properties of such marble sheets and opal glass, it was found that the amount of light transmitted was approximately the same in both cases, but that the diffusive power of marble was distinctly better.—A.

### PRODUCTION OF PLATINUM IN RUSSIA

A Russian correspondent writing to the *Mining Journal*, **1915**, 4159, states that the production of platinum since the outbreak of the war has been on the decrease. The production for the year 1913 was 173,642 ozs., and for the year 1914 was 156,775 ozs., *i. e.*, a decrease of 16,642 ozs.

As soon as the war broke out the market for platinum—which is, of course, chiefly in France and Germany—being temporarily isolated from the producers, the outlook for the latter, especially the smaller ones, was extremely black. The Government, however, soon came to their assistance, offering $15.79 per oz. on platinum ore at an annual rate of interest of 7 per cent. These terms, however, were not good enough for some of the small producers, especially those working on placers by primitive methods. The Government and private banks eventually increased the terms to $21.90 per oz. at the same rate of interest of 7 per cent, half the year's interest being payable in advance. On the aforementioned terms about 46,240 ozs. of platinum have been deposited in the various banks at Ekaterinburg, some of it having been forwarded to their Petrograd agents. The output of platinum during the year 1915 is estimated as between 86,700 and 104,040 ozs. Although there is at present an embargo on the export of platinum, permission can be, and has been, obtained from the Minister of Trade and Commerce in the event of export to friendly countries.

From the month of July, 1915, however, there is to be an export duty on platinum ore which will probably be prohibitive (about 20 per cent) and which will necessitate the construction in Russia of refineries.—A.

### TANNING EXTRACT FOR SULFITE LYE

A British Consular report mentions that the Norwegian Farmand states an establishment for utilizing the waste lye from sulfite pulp production is now being built at Embretsfor, near Drammen.

The establishment will be ready to begin work in three months, and it is estimated that the production of tanning extract from the lye will be about 3000 barrels per year. A factory for producing alcohol from the lye is also likely to be erected in the near future and this latter enterprise will be under the control of a Norwegian cellulose mill.—A.

# NOTES AND CORRESPONDENCE

## THE SEATTLE MEETING OF THE A. C. S. AUGUST 31 TO SEPTEMBER 2

In addition to the announcements made in the last two issues of THIS JOURNAL (pages 545 and 633) several special features should be noted.

I—THE INDUSTRIAL DIVISION will hold two symposiums: One a continuation of the New Orleans symposium, especially devoted to the part the chemist has had in the progress of special lines of chemical industry. Papers will be presented as follows:

| | |
|---|---|
| IRON AND STEEL | GEO. W. SARGENT |
| IRON AND STEEL | A. S. CUSHMAN |
| PERFUMERY | ALOIS VON ISAKOVICS |
| PERFUMERY | E. T. BEISER |
| LEAD | G. W. THOMPSON |
| PAINTS AND VARNISHES | MAXIMILIAN TOCH |
| PETROLEUM | DAVID T. DAY |
| ILLUMINATING GAS | SIDNEY MASON |

A symposium will also be held on "The Distillation of Wood," papers being presented by the following experts:

| | | |
|---|---|---|
| J. R. WITHROW | MARC DARRIN | BAILEY TREMPER |
| J. E. TEEPLE | CHAS. H. HERTY | NEWTON CRITUS |

II—The convention will spend September 4th in Portland, Oregon, as guests of the Oregon Section.

III—On the evening of September 6th, a complimentary Smoker will be tendered the visiting members at Techu Tavern, in San Francisco.

IV—A special bulletin containing the itinerary and general information concerning the route of the special train from Chicago has been issued by the Passenger Departments of the Chicago & Northwestern Railway and the Great Northern Railway, from their Chicago offices.

C. L. PARSONS, *Secretary*

BOX 505, WASHINGTON, D. C.

## EXPOSITION OF CHEMICAL INDUSTRIES

Arrangements for the Exposition of Chemical Industries to be held at Grand Central Palace, New York, the week of September 20th, are progressing very favorably, and over fifty per cent of the entire main floor space has been reserved by manufacturers throughout the country.

There will be many working exhibits that will be unusually interesting and instructive.

Motion pictures of industrial processes will be a feature as will also lectures by men of prominence in the Chemical Industries.

Meetings of the chemical, chemical engineering and engineering societies are being arranged. The meeting of the American Electrochemical Society, New York Section, has been fixed for Tuesday, September 21st.

An Exposition with as many and as diversified interests has never before been held and a record attendance is expected.

For the benefit of all visitors to this Exposition a very elaborate entertainment program is being arranged for by an Entertainment Committee. Arrangements will also be made by a Ladies' Receiving Committee for the entertainment of all visiting ladies.

The Bureau of Foreign and Domestic Commerce at Washington is heartily in sympathy with the exposition and is contemplating an elaborate exhibit in conjunction with eight other Governmental Bureaus. A large section has been reserved to be known as the Canadian Section, in which a collective exhibit will be made by Canadian manufacturers.

By a special Act of Congress all foreign exhibits for this Exposition upon which there shall be a tariff or customs duty, shall be admitted free of payment of such duty, customs, fees or charges, provided same are not sold or disposed of during the Exposition. All such articles when sold or withdrawn for consumption or use in the United States, shall be subject to the duty, if any, imposed upon such articles by the revenue laws in force at the date of withdrawal, and on articles which shall have suffered diminution or deterioration from incidental handling and necessary exposure, the duty, if paid, shall be assessed according to the appraised value at the time of withdrawal for consumption or use.

The Exposition has been organized by Messrs. Nagelvoort and Roth, with offices at the Grand Central Palace, New York, with the coöperation of the International Exposition Company, who have developed many successful expositions in the past.

## PRIZES OFFERED BY THE TECHNICAL SECTION OF THE AMERICAN PAPER AND PULP ASSOCIATION

The Technical Section of the American Paper and Pulp Association is anxious to bring about advancements in methods of manufacture of paper and pulp and, with a view of concentrating attention on some of the more important problems before the American paper and pulp manufacturers, it offers a prize of one hundred dollars for the best paper on each subject in the list given below. It is expected to offer similar prizes each year. This competition is subject to the following rules:

1—The authors of the papers presented must be residents of the United States or Canada.

2—The papers are to reach the office of the Secretary of the Section on or before December 31, 1916.

3—Each paper must be typewritten and must not bear the author's name or address. Instead of the author's name the paper shall bear a number or other designating character or word. Accompanying the paper shall be a sealed envelope containing the author's name and address and the number or designating character by which the paper is characterized.

4—Papers presented in this competition must not previously have appeared in print.

5—The determination of the papers winning the prizes shall be made by a committee of three appointed by the chairman of the Technical Section. This committee shall publicly report its findings to the Section at the time of the Annual Meeting next after February 1, 1917.

6—All papers received shall be returned to their authors soon after the announcement of the winning paper.

7—The articles winning the prizes offered shall be published in the Report of the Organization and also in *Paper*, the official journal of the Section.

LIST OF SUBJECTS

I—The various causes for the deterioration of the Fourdrinier wires and steps to be taken in the prolongation of the life of the wires.

II—How can the pitch in sulfite pulp be eliminated?

III—The effect of the order and time of adding alum, rosin and color on the retention of color.

IV—The retention of the various mineral fillers used in papermaking and their effect on the life of the machine, clotting and the quality of the paper.

## PROGRESS OF BUREAU OF MINES RADIUM WORK

Secretary of the Interior Franklin K. Lane announced on July 27th that the production of radium from Colorado carnotite ores by the Bureau of Mines, in connection with the National Radium Institute, has passed the experimental stage in its new

process and is now on a successful manufacturing basis. He also declared that the statements made to congress concerning the ability of the Bureau of Mines to produce radium at a greatly decreased cost over other processes had actually been accomplished and that the costs were even less than predicted.

"The cost of one gram of radium metal produced in the form of bromide during March, April and May of the present year was $36,050, I am informed by Dr. Charles L. Parsons, in charge of the radium investigations of the bureau. This includes the cost of ore, insurance, repairs, amortization allowance for plant and equipment, cost of Bureau of Mines coöperation, and all expenses incident to the production of high-grade radium bromide. When you consider that radium has been selling for $120,000 and $160,000 a gram, you will see just what the Bureau of Mines has accomplished along these lines."

"The cost of producing radium in the small experimental plant during the first few months of the Bureau's activities was somewhat higher but not enough to seriously affect the final average."

"The public, however, should not infer that this low cost of production necessarily means an immediate drop in the selling price of radium. The National Radium Institute was fortunate in securing through the Crucible Steel Company the right to mine ten claims of carnotite ores belonging to them and this was practically the only ore available at the time. Since then new deposits have been opened but these are closely held and, according to the best judgment of the experts employed by the Bureau of Mines, the Colorado and Utah fields, which are much richer in radium-bearing ores than any others known, will supply ore for a few years only at the rate of production that obtained when the European war closed down the mines. The demand for radium will also increase rapidly, for the two or three surgeons who have a sufficient amount of this element to entitle them to speak from experience are obtaining results in the cure of cancer that are increasingly encouraging as their knowledge of its application improves. A few more reports like that presented to the American Medical Association at its recent San Francisco meeting and the medical profession as a whole will be convinced of its efficacy. Under all the circumstances that have come to my knowledge it does seem to me that it behooves the Government to make some arrangement whereby these deposits, so unique in their extent and their richness, may be conserved in the truest sense for our people, by extracting the radium from the ores where it now lies useless and putting it to work for the eradication of cancer in the hospitals of the Army and Navy and the Public Health Service."

"The ten carnotite claims being operated at Long Park, Colorado, by the National Radium Institute have already produced over 796 tons of ore averaging above two per cent uranium oxide. The cost of ore delivered at the radium plant in Denver has averaged $81.30 per ton. This included 15 per cent royalty, salary of Bureau of Mines employes, amortization of camp and equipment and all expenses incident to the mining, transportation, grinding and sampling of the ore."

"A concentrating plant for low-grade ores has been erected at the mines and is successfully recovering material formerly wasted. Grinding and sampling machinery has been installed at Denver and a radium extraction plant erected in the same city. The radium plant has now a capacity of three tons of ore per day, having been more than doubled in size since last February. Before that time the plant had been run more or less on an experimental scale although regularly producing radium since June, 1914. To July 1st, slightly over three grams of radium metal had been obtained in the form of radium barium sulfate containing over one milligram of radium to the kilogram of sulfates. The conversion of the sulfates into chlorides and the purification of the radium therefrom is easily accomplished and with very small loss of material. Unfortunately, however, special acid proof enamel ware, obtainable only in France, has not been delivered of sufficient capacity to handle the crystallization of the full plant production, so that a little less than half the output, or to be exact, 1304 milligrams of radium element have been delivered to the two hospitals connected with the National Radium Institute. The radium remaining can be crystallized at any time from neutral solution in apparatus already installed, but the greater rapidity and efficiency of production of this very valuable material by the methods used have decided the Bureau of Mines to await the completion of apparatus now being built before pushing the chloride crystallization to full capacity."

"The average radium extraction of all ore mined by the National Radium Institute has been over 85 per cent of the amount present in the ore as determined by actual measurement. The amount present in the ore has been found in fact to be essentially the same as the theoretical amount required by the uranium-radium ratio. The extraction figures for the last five carloads of carnotite treated have shown a recovery of over 90 per cent in each case."

"A bulletin giving details of mining, concentration and methods of extraction is being prepared by the Bureau of Mines and will be issued early in the fall."

## NOTES ON THE GALACTAN DETERMINATION

In the course of an extended investigation of the Pacific Coast kelps recently carried out in this laboratory,[1] it became desirable to determine the galactan in a number of the dried samples. On attempting to apply the provisional method as given in *Bull.* **107,** Bureau of Chemistry, it was found impossible to obtain satisfactory results. Efforts were then made to make this method workable but no success can be reported in that direction. It is the aim of this paper to point out several faults in the present method and to emphasize the necessity of improving it by more systematic study of the reaction upon which it depends.

Briefly stated, the method consists in evaporating a weighed portion of the material with dilute nitric acid whereby the galactans are converted into mucic acid. Under the prescribed conditions the mucic acid crystallizes out, together with organic impurities. To remove the latter, the residue is extracted with ammonium carbonate solution, dissolving the mucic acid as ammonium mucate. The filtered solution is decomposed by nitric acid, causing the mucic acid to again crystallize out, after which it is filtered, dried and weighed on a tared Gooch crucible.

On following out the directions of the provisional method the difficulty already noted by Lindsey[2] was encountered that the final residue often appeared to be not mucic acid at all but organic decomposition products incidental to the reaction. Some improvement was obtained by following the plan recently proposed by Miyake[3] in which the material was filtered immediately after evaporation and washed thoroughly with hot water thus retaining the mucic acid in solution. The filtrate was then evaporated to one-third of the volume of the nitric acid taken and the crystallization allowed to proceed as usual. It was found that the large amount of mineral salts present in the sea-weeds prevented crystallization of the mucic acid in some cases. Accordingly, the further modification was introduced of leaching the sea-weeds with cold water to a filtrate volume of 50 cc., thus removing most of the salts. The extracted residue was then oxidized according to Miyake's method.

Even with these improvements no crystallization of mucic

[1] J. S. Burd, *Bull.* **248,** Cal. Agr. Exp. Sta. and D. R. Hoagland, Journal of Agricultural Research **4,** p. 39.

[2] Lindsey, 14th Convention A. O. A. C., *Bull* **51,** p. 94.

[3] Miyake, *Chem. Abs.*, **6,** 2958, October 20, 1912.

acid was obtained from samples which we were satisfied contained galactans. This led to a series of experiments in which varying amounts of galactan and milk sugar were treated in the usual manner.

It was found that the percentage yield of mucic acid on the galactose taken varied greatly with the amount taken. (This fact has been recently reported by Miyake[1] but was discovered independently by the author.) When 2 grams of galactose were taken, the amount of galactose recovered, as calculated by multiplying the weight of mucic acid by the official factor (1.33), was 90 per cent. When 0.2 gram of galactose was taken 54–74 per cent of galactose was recovered. When 0.1 gram was taken, in one case 37 per cent of galactose was recovered and in a duplicate determination no mucic acid crystallized out. Smaller quantities of galactose failed to yield any mucic acid.

Browne[2] has pointed out that theoretically 180 parts of galactose produce 210 of mucic acid—a yield of 116$^2/_3$ per cent. The oxidation of galactose to mucic acid has been generally accepted as following in practice the yield of 75 per cent on the galactose. This figure is the result of the work of Tollens[3] and his associates and was based on experiments in which he oxidized milk sugar and galactose in quantities of 1.25 to 5 grams. There is no record of experiments on small quantities of galactose and it has been assumed that the same factor holds for all amounts. The results obtained in this laboratory indicate that the usually accepted factor does not apply at all to any but large percentages of galactose and that when the quantity becomes small (2–3 per cent) the method may fail to yield any mucic acid whatever and at best will give results far below the truth.

There appears to be no relief from this source of error in the determination until the reaction upon which it depends is better understood. Evidently the changes taking place cannot be described by a single simple equation, but must take into account one or more secondary products. Further study of this reaction might result in controlling the formation of the undesirable compounds and thus make the method workable.

W. H. DORE
DIVISION OF AGRICULTURAL CHEMISTRY
UNIVERSITY OF CALIFORNIA EXPERIMENT STATION
BERKELEY, February 1, 1915

## NOTE ON STARCH-FORMING ENZYME FROM MALT

*Editor of the Journal of Industrial and Engineering Chemistry:*

In the February number of THIS JOURNAL, p. 115, an article appeared by Charles B. Davis entitled "On a Starch-forming Enzyme from Malt: Its Action on Hemi-cellulose and Its Commercial Application to Brewing." We have carefully repeated the experimental work in this article and were unable to confirm any of it as far as the enzyme "hemi-cellutase" is concerned, or to verify any of the conclusions of the author. We repeated the experiments outlined on page 118, preparing Solution "A" exactly as described in this article, and using various samples of starch, like rice and potato-starch, but in no case were we able to obtain a blue reaction due to starch, although we tested both the solution and the *residue* very carefully with dilute iodine solution, checking the latter against very dilute solutions of starch. We also repeated the experimental work outlined in the last two paragraphs of the article, using four different types of malt separately, and each one of these malts again with grits or flakes, but in no case were we able to obtain the blue reaction mentioned by Mr. Davis.

In footnote (*b*) to Table IV it is stated that "when the hemicellulose is finely divided, the reaction takes place at 10 to 20° C." This latter statement is contrary to all our accepted ideas about enzymes. If an enzyme has an optimum temperature of 82.5° C. we certainly would not expect that a mere subdivision of the substrate should reduce its optimum temperature over 60°, that is, from 82.5° C. to 10 to 20° C. However, to check this point we tried the effects of coarse and fine grinding on the samples of malt mentioned above, but in no case could we obtain the starch reaction at 82.5° C.

In conclusion I would say that we were unable to confirm any of the experimental work in this article and could obtain no evidence of the presence of an enzyme which would decompose hemi-cellulose at 82.5° C. In my opinion the entire article is erroneous.

WM. J. LEMP BREWING COMPANY SIDNEY BORN
ST. LOUIS, June 18, 1915

[1] Miyake, *Chem. Abs.*, **8**, 2007, June 10, 1914.

[2] Browne, "Handbook of Sugar Analysis," 1st ed., p. 459.

[3] Tollens and Creydt, *Ann.*, 227–231; Tollens and Rischbiet, *Ber.*, **18** (1885), 2616; Tollens, Kent, Rischbiet and Creydt, *Landw. Vers. Sta.*, **39**, 401.

## COLUMBIA UNIVERSITY ESTABLISHES A SEPARATE DEPARTMENT OF CHEMICAL ENGINEERING

Courses leading to the degree of Chemical Engineer have been offered in the Department of Chemistry of Columbia University for the past ten years, but, in recognition of the rapidly increasing importance of those industries based upon the applications of chemistry and the consequent demand for men specially trained in the fundamental engineering practices as applied to the problems of industrial chemistry, the Trustees of Columbia University have established a separate Department of Chemical Engineering upon the same plane of importance in the Columbia Graduate Engineering School as Mining, Civil, Electrical and Mechanical Engineering.

The demand for graduates to fill important positions in the rapidly developing industries of the United States has brought an ever-increasing number of students to study Chemical Engineering at Columbia, the registration in this subject having reached a total of eighty-one during the past year.

The new chemical engineering laboratories, which were recently installed, where the students are taught to use engineering methods and engineering appliances in the study and development of chemical industry, will be provided with still further equipment during the present summer. These laboratories are equipped with apparatus to illustrate the various fundamental operations of chemical and electrochemical processes, and the student learns by actual contact to apply fundamental scientific principles to industrial problems. Here research may be conducted on such a scale as to establish the dependable engineering data necessary for intelligent and accurate process design.

The sudden demand for products previously secured from Europe has greatly stimulated activity among chemical manufacturers. In many cases it is necessary first to develop the raw material supplies, as for example for th manufacture of coal-tar dyes, where large quantities of benzol, phenol, toluol, etc., are required. The demand for these materials is being met rapidly by the installation of large plants for the recovery from coke oven gases of these heretofore waste products. Such concerns as the Lackawanna Steel Co., United States Steel Co. and other large coke producers both in the United States and Canada are now recovering these products. Similar activity obtains in other fields; for example, on account of large demands for explosives, the production of sulfuric and nitric acids is being enormously increased.

Entirely aside from these abnormal developments, forced upon us by the war, it should be noted that chemical processes are being established in other fields. For instance, within the last month two enormous installations, one at the Anaconda Smelter and another at Chuquicamata, Chile, have been started for the extraction of copper by chemical methods. Plants for the production of sulfuric acid as a by-product from the roasting of sulfide ores along the lines of the plant at Ducktown, Tenn., have also been established at Langloth, Pa., Cleveland, Ohio, and by the United States Steel Corporation.

## POSSIBLE STERILIZING PROPERTIES OF DENTAL CEMENTS

*Editor of the Journal of Industrial and Engineering Chemistry:*

In THIS JOURNAL, March, 1915, appeared an article by Paul Poetschke, entitled "The Germicidal Efficiency of Dental Cements." The concluding paragraph promised reports on the comparative strength and other properties. These reports would be, as Mr. Poetschke states, "of more immediate interest to the dental profession" and it will be by clinical experience in the hands of the dentist that this subject will receive its final analysis and probably be reported mainly in the dental literature.

Since Mr. Poetschke very pointedly refers to and criticizes my paper entitled "Possible Sterilizing Properties of Filling Materials," published in the *Dental Review*, June, 1914, it may be of interest "to chemists and bacteriologists" to have reproduced in THIS JOURNAL the one illustration criticized by Mr. Poetschke, the criticism being mostly that only comparative inhibition has been shown and that there had been no bacterial count.

In my paper under criticism there is the statement: "Subjection of hardened pellets to media has been of interest, but it is by the application of freshly mixed cement to inoculated agar that we closely duplicate the placing of cement into a tooth cavity." This referred to a cavity from which all infected material had not been removed, there being, for this reason, a need of a sterilizing filling. It is well known by the dental

profession that a real copper oxid cement will furnish the means of sterilization of such an infected area, and yet furnish a mass, after proper setting, which is so highly insoluble that it would only show potency *in the hardened state* equal to the best of the so-called copper cements tested by Mr. Poetschke, including that made by the L. D. Caulk Company, the employers of Mr. Poetschke. The question of whether the testing of cements in the freshly mixed or the hardened state has most clinical significance is being logically considered by all interested.

In some attempts by the author, looking to an improvement of the integrity of dental cements, and an imparting of sterilizing properties thereto, the incorporation of precipitated copper with so-called oxyphosphates of zinc available, was one of the means employed.

In this employment of precipitated copper, it was incidentally observed that the film of oxid on the surface of the particles tended to make cement when the precipitate was mixed with an acid phosphate solution. This seems to have been the first suggestion of the cement-making power of the copper oxids.

Before dental societies and in the dental literature as early as 1894, attention was called to the cement-making property of the cuprous and cupric oxids, and the statement was then offered that the cupric furnished the better cement, all properties considered. There has been much clinical advantage taken of the germicidal efficiency of the combination and there has naturally been a general desire that an equally efficient material might exist of a color not limiting its use.

The difference in germicidal efficiency between a real copper oxid cement and an oxyphosphate of zinc cement, more or less modified by a copper compound, each in a freshly mixed state, is so great that results may be shown which appeal to the naked eye instead of needing microscopical count. For this reason in the presentation of the paper referred to, many such results were shown.

In the illustration here shown, the inoculation of the agar was such as would be termed overwhelming in testing hardened pellets. With this inoculation there would need to be extreme dilution to enable a count.

Fig. I shows the consistent inhibition by a real copper oxid cement. On the agar of the Petri dish No. 2 was placed mixture No. 1, a real copper oxid cement, No. 2, a zinc oxid cement carrying a small percentage of oxid of mercury (yellow), and No. 3, a pellet of the "white copper" cement manufactured by Mr. Poetschke's employers. Whether this method carries proper clinical significance, is, as we have said, being logically considered by those most intimately interested.

THE W. V.-B. AMES COMPANY
CHICAGO, July 9, 1915 W. V-B. AMES

## NOTES ON THE DETERMINATION OF HYDROCARBONS AND HYDROGEN IN GAS

*Editor of the Journal of Industrial and Engineering Chemistry:*

Every one who has determined the hydrocarbons in gases by combustion knows how irritating it is when the platinum spiral becomes overheated during combustion and melts, thus spoiling the analysis. If the combustion pipette contains three electric leads instead of two, there can be two different circuits with two different platinum spirals, so that, if one should be melted, it would be merely necessary to turn the current through the other, and thus the sample can be saved, and the determination finished. This has saved many a determination for me.

When hydrogen is determined by the Palladiumized Asbestos Method, trouble is often encountered owing to a film of liquid passing into the capillary tube, moistening the palladium and destroying its power of catalyzing the oxidation of hydrogen. If near each end of the palladium tube a small enlargement is blown, the films of liquid will be stopped, and the palladium will not become wet. Since using the palladium tube enlarged in this way, all of my troubles, due to the palladium becoming "poisoned," have ceased.

OHIO STATE UNIVERSITY
COLUMBUS, April 21, 1915 D. J. DEMOREST

## NOTE ON THE DETERMINATION OF FAT IN MOLASSES FEEDING STUFFS

When making fat determinations on molasses feeding stuffs (the ordinary feeds mixed with molasses) the writer has found that the official method gives low results, as the molasses covering the grains prevents thorough action of the ether. The method now followed for this class of feeds is to extract with ether as usual, drive off the ether from the thimble and suspend the thimble in a liter of water to dissolve out molasses, using two portions of water. The thimble and their contents are then dried and re-extracted with ether which now takes out all the fat.

| Extraction | I | II (after removing molasses) |
|---|---|---|
| Sample No. 1 | 0.91 per cent fat | 2.90 per cent fat |
| Sample No. 2 | 0.60 per cent fat | 2.24 per cent fat |

Maximum differences are shown above; the determinations were made on two samples which contained a large percentage of molasses.

PAUL-GALE-GREENWOOD BUILDING
NORFOLK, VIRGINIA, May 1, 1915 E. O. THOMAS

# PERSONAL NOTES

Dr. Clifford Richardson, of New York, was elected *President* of the Association of Harvard Chemists at the fourth annual dinner, held recently at Young's Hotel, Boston. Other officers are: *Vice-Presidents*, Professor W. D. Bancroft, of Cornell University, and Dr. F. W. Clark, of Washington; *Secretary and Treasurer*, Professor S. B. Forbes.

Prof. S. C. Lind has resigned the chair of general and physical chemistry in the University of Michigan. He has already been absent from the university for two years on leave as a member of the Denver U. S. Bureau of Mines Experiment Station, where he will continue his work on radium.

The Pittsburgh Section of the A. C. S. has recently issued a 32-page pamphlet containing its history, its by-laws and membership directory. The directory includes the full name, home address, position and specialty of each individual.

Prof. Charles Lee Crandall, of the college of civil engineering, Cornell University, has retired from the faculty after a service of forty-two years, and has been elected a professor emeritus.

The Bureau of Standards has completed the plans for its new chemical laboratory building, the cost not to exceed $200,000, for which appropriation was made by congress last winter. The laboratory will be situated on Pierce Mill Road near Connecticut Avenue, in the northwest suburbs of Washington, D. C., and will form the seventh of the group of special laboratory buildings erected for the bureau.

Prévost Hubbard has recently accepted the position of Chief of the Division of Road Material Tests and Research in the U. S. Office of Public Roads and Rural Engineering, and has resigned as Chemical Engineer in charge of the division of Roads and Pavements of the Institute of Industrial Research.

The preliminary list of awards by the Panama-Pacific International Exposition gives the Department of the Interior collective exhibit one grand prize. The exhibit of the Geological Survey receives one grand prize, four medals of honor, five gold medals, six silver medals, and two bronze medals. The Bureau of Mines receives one grand prize, six medals of honor, three gold medals, and three silver medals.

The Trustees of the Colorado School of Mines announce the election of Dr. W. B. Phillips as President of that institution.

Dr. Arthur A. Noyes, of the Massachusetts Institute of Technology, is to become a member of the faculty of the Throop College of Technology, Pasadena, Cal., for a portion of the coming academic year, and for one-half of the time in succeeding years, beginning with 1916–1917. This arrangement has been made possible by a gift of $10,000 for the equipment of a physical chemistry laboratory, and the endowment of this laboratory in a sum yielding $10,000 annually for its support. This laboratory is to be located in a new chemistry building, which is expected to be built during the coming academic year.

Arrangements for an exchange of professors between the University of Washington and the University of the Philippines have progressed to the stage where it is probable that Dr. Horace G. Byers, professor of chemistry in the University of Washington, will spend the next year in Manila. In the event of his going, Prof. Horace G. Deming, a graduate of the University of Washington, head of the department of chemistry in the University of the Philippines, will go to the University of Washington for the year.

Gail Mersereau died at his home in Cayuga, N. Y., on Wednesday, July 14th, of cerebral meningitis, superinduced by poisoning by noxious gases. Mr. Mersereau was a graduate of Columbia University, in the class of 1903, member of the American Chemical Society, the New York Section of the Society of Chemical Industry, the Chemists' Club and the Verein Deutscher Chemiker. For two years he was chemist to the Susquehanna Dye and Silk Works, at Williamsport, Pa. He was successively silk chemist, consulting chemist to the Panama Canal Commission, chemist for the Standard Oil Co. of New York, and consulting chemist and chemical engineer. At the time of his death Mr. Mersereau was engaged in the manufacture of explosives.

Frederick W. Spanutius died in Hastings-on-Hudson, on June 20th, at the age of forty-seven years. He was formerly an instructor in chemistry in the Pennsylvania State College, the Iowa State University and Lehigh University. Later he engaged in industrial work and owned works at Hastings called the Pan Chemical Company.

The Pfaudler Company announce that they have contracted for space No. 93 for an exhibit of their equipment at the National Exposition of Chemical Industries to be held at the Grand Central Palace, New York City, during the week of September 20th.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### SUPERINTENDENT OF DOCUMENTS

**Publications on Animal Industry.** Price List 38, 6th Edition. 36 pp. This is a list of the United States Public Documents relating to various phases of animal husbandry, including poultry and dairy industries, which are for sale by the Superintendent of Documents.

**Health, Disease, and Sanitation.** Price List 51, 6th Edition. 58 pp. A list of the Government publications which are for sale by the Superintendent of Documents.

### BUREAU OF MINES

**The Radium-Uranium Ratio in Carnotites.** S. C. Lind and C. F. Whittemore. Technical Paper 88. 28 pp. Paper, 5 cents. This is a report on an investigation of the physical and chemical properties of certain carnotites with a discussion of the radium-uranium ratio as determined by various methods. The problem is discussed in its theoretical aspects and the practical application of the ratio as affecting the basis of purchase and sale of carnotites is pointed out. It is stated that "Radium may be easily determined in one operation by the emanation method, either by solution or by ignition from tubes in which it has been sealed for one month to reach equilibrium.

"In contrast with the success of the solution and the ignition methods for de-emanating carnotite, the method of fusion with sodium and potassium carbonates and the fusion-and-solution method both gave low results and were abandoned."

These conclusions are drawn from the analyses of twenty-four lots of the ore from which an average ratio was found identical with that of pitchblende ($3.33 \times 10^{-7}$). The range in value was from $2.48$ to $4.6 \times 10^{-7}$.

### UNITED STATES NATIONAL MUSEUM

**The Fisher, Polk County, Minnesota, Meteorite.** GEORGE P. MERRILL. Reprint No. 2084. From the Proceedings of the Museum, 48 (1915), 503–6. This gives detailed description with analyses of the portion of the meteorite which is owned by the Museum and the portion owned by the University of Minnesota.

### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Some Aspects of the Iron and Steel Industry in Europe.** Special Consular Report No. 71. 48 pp. Paper, 5 cents. This is a compilation of Consular correspondence on the subject covering the questions of interest regarding the industry in France, Germany, Italy, Switzerland, Sweden and Great Britain. The production data which are of greatest interest are as follows: "The total production (French) of finished iron goods during that year was 524,907 metric tons of 2,204.6 pounds, to which the Paris district contributed 16,311 metric tons, made entirely from scrap iron. The production of finished steel products in the same year reached 3,250,278 metric tons, of which only 111,871 metric tons were made in this district.

"A detailed list of iron and steel products manufactured in 1912 in the Paris district is given below, in metric tons of 2,204.6 pounds each: Iron—merchant iron, 10,492 tons; beams and structural shapes, 4,867 tons; forgings, 82 tons; metal tires, 870 tons; total, 16,311 tons. Steel—merchant steel, 36,957 tons; beams, 12,288 tons; sheets and plates, 28,093 tons; castings, 125 tons; tin plate, 3,694 tons; structural shapes other than beams, 3,134 tons; wire, 23,300 tons; forgings, 4,280 tons; total, 111,871 tons." .....

"The production of iron and steel in the whole of Sweden in 1912, according to the statistics of the Swedish Government, amounted to 699,816 metric tons of pig iron and cast goods direct from blast furnaces, valued at $14,308,213; 664,141 metric tons of blooms and rough bars; Bessemer and Martin ingots, scrapped and cast goods, valued at $19,677,099; 3,979 metric tons of 'iron sponge,' valued at $65,049; 425 metric tons of blister steel, valued at $29,753; and 509,224 metric tons of 'certain manufactures of iron and steel,' such as bars, wire rods, nails, etc., valued at $21,558,749.

"The exports of iron and steel from Sweden in 1912 were valued at $10,812,500, and of manufactures of iron and steel at $13,129,623. The imports of iron and steel were valued at $4,040,000, and of manufactures of iron and steel at $7,492,300; a total of $11,532,300."

"The largest importers of Swedish iron are Germany and Great Britain. The declared exports of iron and steel from this consular district (Goteborg) to the United States, according to invoices certified at this consulate in 1913, amounted to $520,235, including the following items: Bars and bundles, $159,592; blooms, $115,660; ferrosilicon, $20,286; pig iron, $12,133; steel and iron strips, $157,294; wire rods, $54,865; other kinds, $414.

"Charcoal is used as fuel in the manufacture of Swedish iron and steel, as Sweden does not produce sufficient coke, and it would not be economical to import it for that purpose. Sweden can compete for the world market by producing iron and steel of high quality."

"Despite Sweden's heavy production and exportation of iron and steel, the importation of iron, steel, and certain products of iron and steel amounted in 1912, the last year for which complete statistics are available, to $11,532,400. While the imports of most of the items are very small and may be regarded as mere incidents in the trade, the demand for certain forms of iron and steel from abroad is regular, and, it appears, of sufficient importance to be of interest to American exporters."

The more important items in the list of iron and steel imports for 1912, and the countries from which they were imported, are also listed.

### BUREAU OF STANDARDS

**The Emissivity of Metals and Oxides. IV. Iron Ore.** GEORGE K. BURGESS AND PAUL D. FOOTE. Scientific paper 249. 7 pp. "The present paper is a continuation of the study of the radiometric properties of metals and oxides. The experimental methods and bibliography of the subject have been given in the preceding three numbers of the series.

"The object of this investigation has been the determination of the monochromatic emissivity for a wave length $\lambda = 0.65\ \mu$ and the total emissivity of the oxide of iron formed by heating iron in air."

**Electrical Measuring Instruments.** Circular No. 20. 2nd Edition. 57 pp. "The object of this circular is to present briefly the fundamental principles underlying the construction and operation of commercial electrical measuring instruments, together with such information concerning the advantages and limitations of the various types of instruments as will assist the user in the determination of the general type best suited to a given purpose.

"The question of sources of error has been treated in some detail, with a threefold purpose: First, to suggest how some errors may be avoided; second, how corrections may be made for known sources of error; and third, to furnish suggestions which will assist those who have to specify instrument performance or to select instruments."

The discussion includes direct current and alternating current ammeters, voltmeters, wattmeters, ampere-hour and watt-hour meters, recording electrical instruments, instrument transformers, and other apparatus of similar character.

### UNITED STATES GEOLOGICAL SURVEY

**Geology and Coal Resources of North Park, Colorado.** A. L. BEEKLY. Bulletin 596. 118 pp. The greater part of this report is of geologic and mineralogic interest only, but there are included sections on the mineral resources, particularly the coal deposits, the ores of copper, gold, and silver and the gilsonite deposits of the districts.

**Geology and Ore Deposits of Copper Mountain and Kasaan Peninsula, Alaska.** C. W. WRIGHT. Professional Paper 87. 110 pp. and 22 plates. "A detailed description of the geology of the two most important copper-bearing areas in southwestern Alaska, prefaced by a general account of the geology of the Ketchikan district, within which these areas lie. The mining development is only briefly discussed, because it is not of permanent interest and is fully treated in the Survey's annual bulletins showing the progress of investigations of mineral resources in Alaska. The genesis and occurrence of the copper ores are discussed, and special attention is paid to contact deposits, which are well exemplified in this region. The illustrations include a geologic map of the Ketchikan district, topographic and geologic map of Copper Mountain and Kasaan Peninsula, plans and sections of mines, and halftone views of rocks and minerals from the areas discussed."

**Shorter Contributions to General Geology, 1914.** DAVID WHITE, and Others. Professional Paper 90. 199 pp. and 7 plates. Paper, 50 cents. The separate articles of particular interest have already been reviewed in THIS JOURNAL.

**Contributions to Economic Geology. Part I. Metals and Nonmetals Except Fuels.** F. L. RANSOME, HOYT S. GALE, and Others. Bulletin 580. 462 pp. Paper, 40 cents. The combined report, separate parts of which have already been reviewed in THIS JOURNAL

**Some Mining Districts in Northeastern California and Northwestern Nevada.** J. M. HILL. Bulletin 594. 200 pp. and 19 plates. "A general outline of the geology of a part of northern California and northwestern Nevada, with a brief statement of the nature and occurrence of the ore deposits as a whole and

detailed descriptions of individual mining districts. In these descriptions the following points concerning the districts are considered: Location, accessibility, history, production, climate and vegetation, topography, geology, type and origin of the ore deposits, and origin and character of the veins. Sketch maps of the districts, structure sections of the mountain ranges, and halftone plates showing geologic features make up the illustrations."

**Mineral Deposits of Santa Rita and Patagonia Mountains, Arizona.** FRANK C. SCHRADER AND JAMES M. HILL. Bulletin 582. 370 pp. The geographic, climatic and physiographic conditions of the district are discussed and detailed information is given of the geography of these ranges. The building materials available are described and the coal and lignite deposits indicated. It is believed that the onyx deposits "are too calcareous to be of commercial value." It is also doubtful whether the deposits of opal will prove commercially worth development. Several pages are devoted to the discussion of the alunite deposits of the district and the water resources.

**The Production of Chromic Iron Ore in 1914.** J. S. DILLER. Separate Mineral Resources of the United States, 1914. Part I. 15 pp. "The increased marketed production of chromic iron ore in 1914 is noteworthy. The output sold was 591 long tons in 1914, valued at $8,715, as compared with 255 long tons in 1913, valued at $2,854, a gain in 1914 of nearly 132 per cent in quantity and of more than 205 per cent in value. The great increase in value in 1914 was due in part to the rise in price per ton.

"Almost the entire annual output has come from Shasta County, California."

"The large supplies of foreign chromic iron ore permit its delivery in American ports at low rates. It is sold on the basis of 50 per cent content of chromic oxide, and a fair price prior to 1914 for cargo purchases was from $14.50 to $15.50 a ton. Chromic oxide in excess of 50 per cent is sold at the rate of 50 to 60 cents per additional unit.

"In California the price is said to vary from $10 to $17 a long ton, with recent quotations at $15 a ton f. o. b. at shipping point. The average price per long ton of the marketed production of the United States in 1913 was $11.19, but in 1914 the average selling price increased to $14.75. Under this average price is included also the chrome sand of Baltimore, which is used abroad for making special colors and which commands a higher price than any other chromic iron ore because of its cost of production.

"The price of the chromate and bichromate of potash imported in 1913 averaged 8.1 cents a pound and that of chromic acid 14.9 cents a pound. Early in 1915 American manufacturers quoted bichromate of potash at 15–15¼ cents a pound and bichromate of soda 4¾–5½ cents a pound. The restrictions on the importation of chrome ore has not yet materially affected the price of bichromates, but it may be expected to do so if long continued. The abnormally high price of bichromate of potash is due to the great advance in the price of muriate of potash. Chromate of soda is quoted at 6 cents a pound.

"The market price of chrome brick, standard sizes, in carload lots, January 1, 1914, was, on the Atlantic seaboard, $135 a thousand; but at the close of the year the price had greatly advanced on account of the difficulty in importing the chromic ore necessary for the manufacture of the brick."

"In 1914 the imports of chromic iron ore amounted to 80,736 long tons, valued at $695,645, an increase of 15,556 tons in quantity and of $72,824 in value. The imports of chromic acid and of chromates were much greater in quantity and value than in 1913, notwithstanding the restrictions on exports of chromite from Rhodesia, New Caledonia, and some other foreign sources."

The means and uses of chromite and chromic ore deposits of North America are described. There is also included a number of new analyses of chromic iron ores from different districts in this country.

**The Recovery of Secondary Metals in 1914.** J. P. DUNLOP. Separate from Mineral Resources of the U. S., 1914. Part I. 9 pp. There is included a general discussion of the scope and character of the industry devoted to the recovery of secondary metals from scrap, sweepings, skimmings, and dross. The standard classification for old metals which was adopted by the National Association of Waste Metal Dealers and which took effect January 2, 1915, is reprinted. This indicates the specifications which must be met by waste metals in order to classify in the different grades. The following table shows the recovery of secondary metals in the United States in 1914:

| Metals | Quantity Short tons | Value |
|---|---|---|
| Secondary copper, including that in alloys other than brass | 58,556 | $15,435,362 |
| Remelted brass | 99,038 | 21,054,300 |
| Secondary lead | 29,337 | 4,762,836 |
| Recovered lead in alloys | 31,725 | |
| Secondary spelter | 42,969 | 4,782,066 |
| Secondary zinc in alloys other than brass | 3,914 | |
| Secondary tin | 4,535 | 8,887,158 |
| Recovered tin in alloys | 7,912 | |
| Secondary antimony | 1 | 444,844 |
| Recovered antimony in alloys | 2,645 | |
| Secondary aluminum | 2,291 | 1,673,140 |
| Recovered aluminum in alloys | 1,783 | |
| TOTAL | | $57,039,706 |

**Potash Salts, 1914.** W. C. PHALEN. Separate from Mineral Resources of the United States, 1914. Part II. 25 pp. The importance of the potash industry to the soap, match, glass-making, photographic, pharmaceutical and general chemical industries makes this report of particular value to many chemists. The following tables include the most important data given in the report:

POTASH SALTS IMPORTED FOR CONSUMPTION INTO THE UNITED STATES, IN POUNDS

| Potash | 1913 Quantity | 1913 Value | 1914 Quantity | 1914 Value | Fourth quarter, 1914 Quantity | Fourth quarter, 1914 Value |
|---|---|---|---|---|---|---|
| Carbonate of crude | 9,715,878 | $272,973 | 9,326,899 | $265,158 | 2,018,452 | $67,821 |
| Caustic, including refined | 8,648,253 | 342,056 | 7,284,176 | 285,739 | 2,052,432 | 89,510 |
| Cyanide of | 1,470,987 | 216,844 | 417,139 | 59,278 | 71,158 | 10,602 |
| Chloride of | 475,261,595 | 7,075,745 | 371,521,920 | 5,745,385 | 32,374,720 | 527,206 |
| Nitrate of saltpeter, crude | 9,652,366 | 261,078 | 2,230,528 | 74,869 | | |
| Sulfate of | 88,698,193 | 1,677,429 | 80,447,360 | 1,557,224 | 10,053,120 | 208,890 |
| All other | 19,067,144 | 959,595 | 14,590,437 | 756,320 | 2,339,009 | 148,896 |
| TOTAL | 612,514,916 | 10,805,720 | 485,818,459 | 8,743,973 | 48,908,891 | 1,052,925 |

NOTE—The data for the Fourth Quarter of 1914 show the marked influence of the war

IMPORTS OF POTASH SALTS IN THE MONTH OF FEBRUARY, 1914 AND 1915

| | February, 1914 Quantity Long tons | February, 1914 Value | February, 1914 Av. price Per ton | February, 1915 Quantity Long tons | February, 1915 Value | February, 1915 Av. price Per ton |
|---|---|---|---|---|---|---|
| FERTILIZER SALTS: | | | | | | |
| Kainite | 72,008 | $321,723 | $ 4.47 | 1,852 | $18,445 | $ 9.95 |
| Manure salts | 12,451 | 124,422 | 9.90 | 900 | 14,748 | 16.39 |
| Sulfate of potash | 5,098 | 210,327 | 41.26 | 1,378 | 59,804 | 43.40 |
| Chloride of potash | 13,172 | 431,820 | 32.78 | 22,818 | 836,868 | 36.65 |
| OTHER POTASH SALTS: | Pounds | | Per lb. | Pounds | | Per lb. |
| Carbonate of potash | 1,674,685 | 49,110 | $ 0.30 | 1,317,849 | 46,015 | $ 0.30 |
| Caustic potash | 520,166 | 19,607 | 0.04 | 308,805 | 17,508 | 0.06 |
| Nitrate of potash | 22,699 | 978 | 0.04 | | | |
| Cyanide of potash | 5,641 | 890 | 0.16 | 266,634 | 39,527 | 0.15 |
| Other potash salts | 638,112 | 52,119 | 0.08 | 486,011 | 43,429 | 0.09 |

FERTILIZERS IMPORTED AND ENTERED FOR CONSUMPTION IN THE UNITED STATES, 1913–1914, IN LONG TONS

| Fertilizer | 1913 Quantity | 1913 Value | 1914 Quantity | 1914 Value |
|---|---|---|---|---|
| Apatite | 2,962 | $22,471 | 20 | $300 |
| Bone dust or animal carbon, and bone ash, fit only for fertilizing purposes | 35,012 | 851,136 | 36,000 | 892,529 |
| Calcium cyanamid or lime nitrogen | 26,729 | 1,410,248 | 21,793 | 1,119,785 |
| Guano | 16,674 | 518,429 | 25,335 | 761,562 |
| Kainite | 465,336 | 2,201,730 | 313,898 | 1,551,115 |
| Manure salts, including double manure salts | 223,687 | 2,245,509 | 168,969 | 1,846,475 |
| Phosphates, crude | 17,121 | 124,815 | 15,079 | 136,526 |
| Slag, basic, ground or unground | 13,186 | 130,455 | 9,199 | 105,272 |
| All other substances used only for manure | 154,729 | 3,314,460 | 171,603 | 3,507,875 |
| TOTAL | 955,436 | 10,819,253 | 761,896 | 9,921,439 |

MATERIALS ENTERING LARGELY INTO THE FERTILIZER INDUSTRY, FOR THE YEAR 1914, IN LONG TONS

| | Quantity | Value |
|---|---|---|
| Imported[1] | | |
| Fertilizers | 761,896 | $ 9,921,439 |
| Potassium chloride | 165,858 | 5,745,385 |
| Potassium sulfate | 35,914 | 1,557,224 |
| Sodium nitrate | 545,730 | 15,204,539 |
| Domestic phosphate rock | 2,734,043 | 9,608,041 |
| TOTAL | ..... | $42,036,628 |

[1] Bibliography of recent articles on the subject is also included.

There is also given in this report a long discussion of the progress of the searches made by the Geological Survey and the investigation by the Bureau of Soils looking for potash resources in this country; bibliography of recent articles on the subject is also included.

### DEPARTMENT OF AGRICULTURE

**Antagonism between Anions as Affecting Barley Yields on a Clay-Adobe Soil.** CHARLES B. LIPMAN AND W. F. GERICKE. "Journal of Agricultural Research," **4**, 201–18. This is a report on tests of pot and field experiments as to the influence of sodium chloride, sulfate and carbonate, and calcium sulfate.

**Methods Followed in the Commercial Canning of Foods.** A. W. BITTING. Department Bulletin 196. Contribution from the Bureau of Chemistry. 79 pp. Paper, 10 cents. (This is a revision of Bureau of Chemistry Bulletin 151.) The discussion includes a description of modern factory equipment and methods of canning and does not deal with subjects of interest in connection with home canning of food.

**The Production of Lumber in 1913.** Department Bulletin 232. Contribution from the Forest Service, Office of Industrial Investigations. 32 pp. Paper, 5 cents.

**Studies on Fruit Juices.** H. C. GORE. Department Bulletin 241. Contribution from the Bureau of Chemistry. 19 pp. Paper, 5 cents. "This bulletin will be of interest only to those concerned with the commercial manufacture of fruit juices. The methods given call for cold storage, sterilization in carbon dioxide, and other processes not commonly available to the house-wife."

**Native Pasture Grasses of the United States.** DAVID GRIFFITHS, GEORGE L. BIDWELL AND CHARLES E. GOODRICH. Department Bulletin 201. Contribution from the Bureau of Plant Industry. 52 pp. Paper, 15 cents. This bulletin reports the results of investigations and of compilations, mainly of experiment station literature, relating to a large variety (more than 140 species) of native grasses. In almost every case, analyses are given of samples taken by the Department as well as summaries of analyses recorded in the literature.

**The Alcohol Test in Relation to Milk.** S. HENRY AYERS. Department Bulletin 202. Contribution from the Bureau of Animal Industry. 35 pp. Paper, 5 cents. The object of the work is stated as follows: "The principal object of this work was to determine the practical value of the alcohol test as a test for the quality of market milk. As incidental to our primary object, it was our purpose to determine some of the causes for the precipitation or coagulation of milk by alcohol."

The general effect of the test is indicated as follows: "The test is considered positive when a precipitate is formed, or in other terms, when a coagulum is produced. When a positive test is obtained with fresh milk from a single cow or small herd, it is generally believed that it indicates an abnormal milk, due to physiological or pathological conditions in the cow. A positive test with market milk is supposed to indicate that changes have been produced in the milk as a result of bacterial fermentations."

**Composition of Corn (Maize) Meal Manufactured by Different Processes and the Influence of Composition on the Keeping Qualities.** A. L. WINTON, W. C. BURNET AND J. H. BORNMANN. Department Bulletin 215. Contribution from the Bureau of Chemistry. 31 pp. Paper, 5 cents. "The main purpose of this paper is to show the general composition of American table meal milled by different processes, and especially the keeping qualities of the extreme types dried to different degrees and stored in different localities. Incidentally the composition of grits and the by-products are considered."

The most general conclusions that are drawn from a study of the products from 41 mills are given as follows: "A study of all the results leads to the conclusion that degerminated, bolted meal containing not over 14 per cent of moisture and 1 per cent of fat, as determined by the method of the Association of Official Chemists, properly stored, should keep for 6 months; with a moisture content of 15 per cent it should keep 3 months. Schindler's limit for moisture, namely 13½ per cent, obtained by drying in an open dish, corresponds to about 14½ per cent by the method of the Association of Official Agricultural Chemists.

"Whole-kernel meal, like cream, should be produced locally and consumed soon after grinding; properly dried, degerminated meal, like butter, keeps well during transportation and long storage."

The bulletin contains the results of a large number of analyses of the various products.

**Drug Plants under Cultivation.** W. W. STOCKBERGER. Farmers' Bulletin 663. Contribution from the Bureau of Plant Industry. 39 pp. Paper, 5 cents. This bulletin gives general cultural discussions and suggestions regarding harvesting, distillation, and marketing with a description of the more important drug plants; it is "suitable for general distribution."

**Citrus Fertilization Experiments in Porto Rico.** C. F. KINMAN. Bulletin 18. Porto Rico Agricultural Experiment Station. 33 pp. Paper, 10 cents. "To determine the comparative effects of the three fertilizer constituents—nitrogen, phosphoric acid, and potash—or to prove which is the limiting factor in fruit production on those soils, there was given to each of three plats an incomplete fertilizer, or a mixture containing but two of these elements. Each plat was given one of the three possible combinations. To compare the results from complete and incomplete mixtures and to determine the relative values of nitrate of soda, sulfate of ammonia, and dried blood, of muriate and sulfate of potash, a number of plats to be given a complete fertilizer were arranged. The tables give in detail the materials applied to the individual plats in each orchard."

### PUBLIC HEALTH SERVICE

**Public Health Administration in Toledo.** CARROLL FOX. Public Health Reports, **30**, 1873–1930. This report includes a discussion of a number of matters of chemical and municipal engineering interest. A description of the sewage disposals, water supply and garbage and rubbish handling systems of the city are given as well as a discussion of the general foot inspections and other testing and laboratory work done by the Board of Health of this city.

### COMMERCE REPORTS—MAY 22 TO JUNE 30, 1915

A German patent has been granted to H. Stefferis for making a lubricant from **beet sugar molasses.** (P. 864.)

It is proposed to organize a nitrate holding company in Chile, with a capital of nearly $10,000,000, to regulate the price of

nitrate, and to increase the production and export. (P. 874.)

American interests are about to erect factories in China for the manufacture of **dried and desiccated eggs.** (P. 891.)

The Krupp works are making a burglar-proof safe, constructed of **steel** which required $1^1/_2$ hrs. with an oxyacetylene flame, to produce a hole 2 in. in diameter in a plate 1.5 in. thick.

A yellow **dye,** suitable for silks, is being made from the berries of the bush *Phamnus Tinctoria* which grows in Asia Minor. (P. 898.)

New by-product **coke ovens** have been erected in Monmouthshire, England. (P. 918.)

The Government **oil fields** of Chubut, Argentina, produced, in 1914, over 275,000,000 bbls. of oil, which is refined there. (P. 920.)

Importations of **potash salts** into the United States, from January 1 to April 30, 1915, show a marked decrease from the amount in the corresponding period of 1914. (P. 922.)

The world's **coffee** production in 1914 was 893,000 tons, a decrease of 92,000 tons from 1913. (P. 955.)

The Bureau of Standards is engaged in a study of the **spectroscopic analysis of steels,** which has shown the presence of Mo, Co, V, Ni, and Cr in regular irons and steels. (P. 967.)

The mineral products of Canada include **copper, gold, iron, lead, nickel, silver, asbestos, coal, gypsum, natural gas, petroleum, pyrites, salt, cement, clay, lime, and stone.** (Supplement 23c

The Philippine Bureau of Science has just completed a survey of the deposits of **iron ore** in Surigao Province, P. I. The deposit is a surface blanket of iron-bearing clay, resulting from the weathering of serpentine. (P. 979.)

**A vanilla**-producing plant (*Vanilla ovolis*) has been found in the Philippines. (P. 994.)

Activity is shown in the Philippine **sugar industry.** Hawaiian sugar cane has been introduced and found preferable to the local cane. (P. 995.)

The annual **gold** output of Nicaragua is about $2,500,000. The high-grade deposits have been exhausted, and the low-grade ores can be operated only on a large scale, preferably by cyaniding, of which considerable development is expected. (P. 1000.)

The water hyacinth removed from rivers in French Indo China to aid navigation, is now burned and the ashes used as a **fertilizer** for rice. (P. 1006.)

The **coal** output of Chile is increasing. (P. 1012.)

Efforts are being made to utilize the present surplus of bananas in Jamaica, by converting them into **banana flour,** which is used together with wheat flour. (P. 1019.)

A preliminary report of the Philippine Bureau of Science on the **gold** deposits near Iligan, Mindanao, states that the ore is a conglomerate and contains variable amounts of gold, up to $25 per ton. (P. 1034.)

An abstract is given of the methods of dyeing and bleaching **cocoanut fiber,** described in a paper by S. G. Bailey. (P. 1047.)

Tachienlu, China, is one of the world's principal musk markets, the **musk** being obtained from a gland of a male deer, of a species likley to become extinct. The musk is said to be radioactive. (P. 1053.)

Among the important products of Siam are **soya beans, kapok** (tree fiber), **stick lac, gum dammar** and **catechu.** (P. 1055.)

In an improved Philippine **copra** drier 850 cocoanuts can be dried in $3^1/_2$ hrs.

The **copra** industry of the Philippines is increasing, although the price is below normal. (P. 1082.)

A new **steel plant** has just been started at Newcastle, Australia, with a 350 ton blast furnace, three open hearth furnaces, a structural steel and rail mill, and sixty by-product coke ovens. Most of the expert steel workers were brought from the United States. (P. 1091.)

Efforts are being made to develop new markets for the following products from Chile: **sodium nitrate, copper, borax, sodium sulfate, tin, iodine, iron, and sulfur.** (P. 1098.)

A rubber **goods** factory is to be erected at Bandoeng, Java. (P. 1126.)

There is a marked decrease in **sugar beet** cultivations in all European countries except Italy and Russia, which show an increase. (P. 1145.)

The **coal** industry of Nottingham, England, is increasing, both domestic and steam coal being obtained. A large number of **by-product coke ovens** have been installed. (P. 1160–4.)

The **coal exports** of the United States, both anthracite and bituminous, fell off in the early part of the war, but are now above normal. (P. 1164.)

In a report by Thomas H. Norton on the **potash** situation, it is stated that owing to the greatly decreased imports into the United States, the price of potash salts has advanced from $38 to $160 or $175 per ton. Over 20,000 tons of potash salts purchased by American firms are still interned in German ports. Efforts to develop the American potash industry are promising. The American Trona Company, operating at Searles Lake, California, expects soon to market **potash, borax,** and **sodium chloride, sulfate,** and **carbonate.** Development in the Imperial Valley, California, awaits railroad facilities. A plant is being erected at Marysville, Utah to extract the potash from the **alunite** deposits. The utilization of **kelp** on the Pacific is progressing. One company has an output of one ton per day of nearly pure potassium chloride. Much of the kelp is being used wet as a fertilizer, and a large part is dried and pulverized, *e. g.,* for use in mixed fertilizers. The various processes of extracting the potash from kelp are briefly considered. (Pp. 1166–9.)

A new Brazilian **oil nut,** the product of *Ostesphorum platysperinum* (myristica platysperma) has been examined at the Kew Gardens, Liverpool, and found to contain 55.2 per cent of a white crystalline fat with a slight odor and the following constants: Melting point, 43° C.; solidifying point, 39° C.; saponification value, 240.2; iodine number, 6.3; refractometer reading at 40°, 36.9; free fatty acids (calculated as oleic), 5.3. It will probably prove suitable for alimentary purposes. (P. 1187.)

Shipments of **antimony ore** and **regulus** from Hankow, China, are increasing, the price being four times the normal. (P. 1188.)

A new **zinc factory** is to be erected in Japan, to use Siberian ores, formerly shipped to Germany and Belgium. (P. 1191.)

In an effort to promote the development of **platinum** refineries in Russia, the exportation of any large quantities of crude platinum was prohibited. No refineries were opened, however, and now efforts are being made to increase the export of platinum to the United States. (P. 1211.)

The manufacture of **cocoanut oil** in the Philippines is increasing, most of the output being sent to the United States. (P. 1227.)

Exports of **rubber** from the Malaysian States show an increase over last year. (P. 1239.)

The consumption of Chilean **nitrate** in the United States is increasing. (P. 1247.)

Owing to the scarcity of **coal** in Holland, the street lights are burning at only half strength. (P. 1254.)

Balata, from Guiana and Venezuela, a plant with a milky latex similar to **rubber,** is finding increasing use in the manufacture of belting. (P. 1283.)

In spite of the demand for Swedish **wood pulp,** the output is restricted by lack of fuel and shipping facilities. (P. 1292.)

The price of **tungsten** and **ferrotungsten** in England is still increasing. (P. 1297.)

The output of the Hanyang Iron Works, China, in 1914, was 135,000 tons of **pig iron** and 98,500 tons of **steel.** (P. 1324.)

The entire **coal** output of China in 1914 was 9,272,000 tons. (P. 1324.)

The Canadian Government proposes to open new timber lands in Ontario for the manufacture of **paper pulp,** under terms requiring the contractor to erect pulp and paper mills costing not less than $1,750,000. (P. 1338)

Owing to a shortage of **gas coal,** the price of gas in Nottingham, England, has been advanced 12.5 per cent; and in other localities still more. (P. 1341.)

The price of **spelter** in Birmingham, England, has advanced from $105 to $525 per ton. (P. 1341.)

A new **tin** mining district has been opened on the east coast of Johore, Federated Malay States. (P. 1364.)

Considerable amounts of **manjack,** a bituminous substance used in the manufacture of insulating **varnishes,** protective **paint,** etc., are being shipped from Trinidad to the United States. (P. 1408.)

The use of **carbide slime** from acetylene generators, in the preparation of building mortar is suggested in Germany. (P. 1417.)

Efforts are being made to develop the **tanning industry** in the Philippines to utilize large amounts of hides now almost wasted. (P. 1432.)

A monograph (Special Agents' Series No. 99) upon the **"Cotton-seed Industry** in Foreign Lands," by Dr. Thomas H. Norton, discusses the foreign conditions and the field for American products. (P. 1442.)

Efforts are being made to develop the **paper** industry of India. In a report by the Indian Director General of Commercial Intelligence, the nature of the foreign competition, and the available resources of India are described. The raw materials emphasized are bamboo and savannah grass. (Pp. 1444–6.)

Imports of **potash salts** into the United States show still further decreases. (P. 1447.)

The total output of the German **amber** industry in 1914 amounted to $1,250,000. (P. 1447.)

The ash of seaweed collected in Manila Bay contains 5 per cent of **potash.** (P. 1457.)

Special supplements were published during the month as follows: In general they contain discussions of the manufacturing an trade conditions and in most cases import and export statistics.

Bulgaria—*3a*
France, Havre—*5c*
Marseille—*5d*
Greece, Athens—*7b*
Italy, Florence—*8a*
Netherlands, Amsterdam—*9a*
Norway, Bergen—*10a*
Spain, Madrid—*15b*
Turkey, Smyrna—*18b*
Abyssinia—*79b*

United Kingdom, Ireland—*19j*
Bradford—*19k*
Hull—*19l*
Costa Rica—*24a*
Dominican Republic, Puerto Plata—*26a*
Dutch West Indies—*27a*
Haiti—*30a*
Colombia—*42a*

China, Manchuria—*52b*
Shanghai—*52c*
Canton—*52d*
Japan, Jauvan (Formosa)—*55b*
Korea, Chosen—*55c*
British North Borneo—*59a*
British South Africa—*66b*

DEMANDS FOR AMERICAN PRODUCTS (PP.)

BRAZIL—1121
Dyestuffs
Drugs
Chemicals
Refrigeration supplies
Enameled ware
Hardware
Porcelain
Crockery
Cement (1380)

RUSSIA—1430
Borax
Yellow wax
White wax
Resin
Gum tragacanth
Dextrin
Nitric acid
Castor oil
Cottonseed oil

Cocoanut oil
Ammonia

CHINA—1179
Sheet glass

Holland—1254,
Sweden—1258
France—1366, and
Argentina—1381
Coal

STATISTICS OF EXPORTS TO THE UNITED STATES

NORWAY—Sup. *10a*
Aluminum
Ferrochrome
Guano
Hides
Codliver oil
Paints

SPAIN—Sup. *15b*
Ergotin
Licorice root
Castile soap
Fusel oil
Soap stock
Sulfur oils
Olive oil
Almond oil
Iron oil
Garnets
Sugar beet pulp
Glycerine
Peanuts
Saffron
Calcium tartrate
Beeswax

DOMINICAN REPUBLIC—Sup. *26a*
Beeswax
Hides
Sugar
Cottonseed

DUTCH WEST INDIES—Sup. *27a*
Aloes
Bones
Castor beans
Divi divi
Guano
Hides
Resin
Salt

HAITI—Sup. *30a*
Fustic
Hides
Logwood
Wax
Shellac
Copra

SHANGHAI—Sup. *52c*
Antimony
Beeswax
Chemicals
Earthenware
Gold
Grease
Hides
Pig iron
Vegetable oils
Paper
Tin
Zinc ore

HANKOW, CHINA—Sup. *52c*
Albumen
Antimony
Gall nuts
Hides
Pig iron
Wood oil
Cottonseed oil
Sesame seed
Vegetable tallow

STATISTICS OF EXPORTS TO THE UNITED STATES

MEXICO—Sup. *32a*
Bones
Glycerine
Hides
Ixtle fiber
Mercury
Guayule rubber
Beeswax
Chicle
Sarsaparilla
Vanilla
Calamine
Turpentine
Vegetable wax
Gold
Lead
Silver
Copper
Tin ore
Arsenious acid
Resin

PANAMA—Sup. *35a*
Balata gum
Cocobolo
Hides
Ipecac
Rubber
Jagua (Ivory) nuts

BRAZIL—Sup. *40a*
Brazil nuts
Carnauba wax
Gold
Hides
Manganese ore
Monazite
Rubber
Sugar
Precious stones

BRITISH GUIANA—Sup. *44a*
Balata gum
Cocoanuts
Diamonds
Gold
Hides
Rum
Sugar

HONGKONG, CHINA—Sup. *52a*
Aniseed
Aniseed oil
Camphor
Cassia
Cassia oil
Earthenware
Glassware
Paper
Peanuts
Peanut oil
Sugar
Tin

AUSTRALIA—Sup. *60b*
Butter
Coal
Coke
Tin
Stearin
Eucalyptus oil
Copper
Glue stock
Hides
Nickel matte
Cocoanut oil

BRAZIL—994
Rubber

PHILIPPINES—1092
Hemp
Sugar
Vegetable oils
Copra

HAVRE, FRANCE—Sup. *5c*
Aluminum
Animal charcoal
Antimony
Bronze
Brass
Casein
Copper
Drugs
Dyewood extracts
Glue
Glycerine
Hides
Indigo
Cola oil
Oleostearin
Flint pebbles
Prussiate of potash
Rubber
Tin
Porcelain
Vanilla
Kaolin
Linseed oil
Rapeseed oil
Paper
Tallow
Zinc oxide

CANADA—Sup. *23c*
Coal
Coke
Drugs
Chemicals
Hides
Leather
Metals
Minerals
Paper

CUBA—Sup. *25a*
Asphalt
Cocoanuts
Copper ore
Hides
Bones
Iron ore
Molasses
Sugar
Beeswax

ARGENTINE—1173
Bone meal
Bones
Casein
Fertilizer
Glue stock
Glycerin
Hides
Linseed
Neat's-foot oil
Quebracho extract
Stearin
Tallow
Copper

MARSEILLES, FRANCE—Sup. *5d*
Ferro tungsten, etc.
Cochineal
Gall nuts
Gums
Bauxite
Glue stock
Sulfur oil
Crude olive oil
Vegetable tallow
Hides
Rubber
Nickel matte
Paper stock
Graphite
Tin
Aluminum
Tartaric acid
Glycerine
Prussiate of potash
Licorice
Vanilla
Glue
Coco butter
Copra oil
Peanut oil
Sesame oil
Ocher
Zinc oxide
Parchment paper
Castile soap
Wines
Emery

GREECE—Sup. *7b*
Gum mastic
Marble
Chrome ore
Magnesite ore
Pumice
Hides
Wines, etc.
Amyl alcohol
Olive oil
Opium
Saffron

ITALY—Sup. *8a*
Hemp
Porcelain
Marble
Terra cotta
Hides
Drugs and chemicals
Dyeing and tanning extracts
Glue stock
Artificial silk
Crude tartar
Beet pulp
Glycerine

BRADFORD, ENGLAND—Sup. *19k*
Emery
Formic acid
Antimony compounds
Dyes
Isinglass
Potassium carbonate
Grease and oils
Hides
Iron and steel
Paper stock
Artificial silk

TURKEY—Sup. *18b*
Chrome ore
Emery
Gum mastic
Gum tragacanth
Licorice root
Olive oil
Sesame oil
Opium
Soap
Valonia
Galls

HULL, ENGLAND—Sup. *19l*
Cement
Carbolic acid
Ammonium sulfate
Barium peroxide
Creosote
Creosote oil
Creosote, saponified
Cresol
Fish glue
Glycerine
Fertilizer
Glue stock
Oleine
Castor oil
Colza oil
Linseed oil
Rape oil
Rice oil
Soya bean oil
Sunflower oil
Washing blue
Oxide of iron
Ultramarine
Paper stock

COSTA RICA—Sup. *24a*
Hides
Gold
Rubber
Silver
Sugar

COLUMBIA—Sup. *42a*
Silver
Hides
Ivory nuts
Rubber
Cottonseed
Balsam copaiba
Balsam Tolu
Gold
Ipecac
Platinum
Mangrove extract

MANCHURIA—Sup. *52b*
Soya bean oil
Hides
Talcum

CANTON, CHINA—Sup. *52d*
Antimony
Aniseed oil
Hides
Cassia

KOREA, CHOSEN—Sup. *55c*
Gold
Graphite

BRITISH NORTH BORNEO—Sup. *59a*
Rubber
Cutch (mangrove extract)

BRITISH SOUTH AFRICA—Sup. *66b*
Aloes
Argol
Buchu leaves
Hides
Chrome ore

TAIWAN, FORMOSA—Sup. *55b*
Camphor

NETHERLANDS—Sup. *9a*
Cinchona bark
Copal gum
Condensed milk
Drugs and chemicals
Earthenware
Hides
Kapok
Linoleum
Magnesite
Milk sugar
Milk powder
Oils
Paper
Quinine
Rags
Rubber
Straw pulp
Paraffin wax
Tin

IRELAND—Sup. *19j*
Fusel oil
Paper stock
Whiskey

# BOOK REVIEWS

**Chemistry of Common Things.** By BROWNLEE-FULLER-HANCOCK-WHITSIT. Teachers of Chemistry in New York High Schools. Allyn and Bacon, New York. 1914. 12mo., viii and 616 p. Price, $1.50

This book is a decided departure from the traditional elementary text. Quoting from the preface: "As the title indicates, this book deals with the chemistry of every-day affairs. It is designed to meet the growing demand that high-school courses should prepare the pupil for citizenship. In other words, the book is planned for that large number of students who are limited to a single course in chemistry. The facts and principles of such a course should be of practical use throughout life."

"In an endeavor to meet the varying needs of such students, a wide range of topics has been treated. This will enable the teacher to select a course best suited to the requirements of his community. To this end, particular attention has been given to the chemistry needed for the first courses in industrial, technical, and agricultural schools, as well as in those teaching domestic science....."

The book is divided into two parts: Part I discusses the fundamental ideas and practical topics of universal interest under the following chapters: Chemical Action; Direct Combination; Acids, Bases, Salts; Weight Relations; Nomenclature and Valence; Writing of Chemical Equations; Solutions; Burning and Oxidation; Fuels, Fireplaces and Stoves; Gas and Gasoline Stoves; Oil and Gas Lights; Air and Ventilation; Chemical Purification; Water; Typical Properties of Metals; Carbon Compounds (Hydrocarbons, Substitution Products, and Alcohols); Carbon Compounds (Aldehydes, Acids, Esters, and Carbohydrates); Foods.

In Part II, "The authors have striven to group a large amount of interesting information around scientific principles and to make it both usable and scientifically accurate." The chapters are: The Cooking and the Adulteration of Foods; Bread Making; Milk; Cream, Ice Cream, Butter and Cheese; Cleaning and Laundering; Ink; Textile Materials; Dyes and Dyeing; Photography; Paints, Oils, and Pigments; Distillation of Petroleum, Wood, and Coal; Blast Lamps and Blowpipes; Gas Engines; Extraction of Metals; Electric Furnaces; Electrochemistry; Corrosion of Metals; Cleaning of Metals; Iron and Steel; Lime, Cement, and Building Materials; Brick and Pottery; Glass; Commercial Chemicals; Agriculture; Chemical Calculation.

Each chapter is taken up in a very systematic manner, each topic being assigned a number, making references very accessible. The illustrations are aptly chosen and the descriptions and explanations clearly stated. At the end of each chapter is a clear, brief summary of every topic treated, followed by a list of well selected questions bearing on the chapter. The many drawings and illustrations add greatly to the worth of the text.

The book contains quite a few scientific inaccuracies. "The change of one substance into another is called *chemical change*" (p. 1). From this definition the change of ice into water is chemical. "Boric acid and its salts are largely employed as food preservatives" (p. 19). Valence is spoken of (pp. 55 and 205) as the combining power of an atom instead of a property of an atom. Throughout the book the word nascent is used as it is on page 67: "Nascent oxygen is considered to be atomic oxygen (oxygen as it occurs at the instant it is liberated from a chemical compound)." The definition given for saturated solution (p. 87) is a better definition for supersaturation, but since supersaturation is not touched on in the chapter it will answer. The explosive range of acetylene in air is not 3–30 per cent as given on page 134, but 3–52 per cent, and under some conditions as high as 75 per cent (Butterfield). In the manufacture of Welsbach mantles the cotton threads are never impregnated before weaving (p. 136), but always after weaving the mantle. The pressure of Blau gas (p. 139) is 80 to 100 atmospheres, not 20.

The germicidal action of bleaching powder in water purification (p. 181) is credited to the nascent chlorine and not to the hypochlorite or hypochlorous acid; and on page 232, "The hypochlorous acid is itself an oxidizing agent and the chlorine liberates oxygen from the water in the fiber." Also on page 555, "The active agent of bleaching powder is believed to be nascent oxygen." $Cl_2 + H_2O \longrightarrow 2HCl + O$ (nascent oxygen). In the description of the manufacture of sugar (p. 236), "The purified syrup is then concentrated in vacuum pans, run out into tanks, and allowed to crystallize, forming the granulated sugar of commerce." In the manufacture of American Cheese (p. 298), "The process may be briefly outlined as follows: Sweet skimmed milk is heated to about 86° F. and the rennet added." Unskimmed is what is intended. In the Hall Process for Aluminum (p. 406), "An artificial mixture of fluorides, containing the fluorides of sodium, calcium and aluminum....., and the aluminum collects in the lower part of the box, from which it is drawn from time to time by removing a wooden plug from the taphole." The natural fluoride cryolite is used and since aluminum has a melting point of 657° C. a wooden plug would hardly be suitable. In the sentence, "Soda should never be allowed to come in contact with aluminum for it will turn it black" (p. 466), the last four words should be changed to "dissolves it." In the description of the blast furnace (a very clear description for an elementary text) the statement is made (p. 470) that "ferric oxide is reduced by the carbon;" this should read reduced by the carbon monoxide, etc. The topic Minor Sources of Nitrogen (p. 570) has the statement, "Leather and hair are subjected to the fumes of hydrofluoric acid in order to render available the nitrogen they contain."

The authors, who by the way are the authors of an admirable text on Elementary Chemistry used extensively in the high schools, fulfilling the requirements of the Board of Regents and the College Entrance Board, are undoubtedly sincere in their conviction that their most recent production is the kind of chemistry best suited to the majority of the students passing through their hands. The book is exceedingly practical, especially the first part, and many of the chapters are well selected to prepare the student for citizenship. It should have a tendency to stimulate the young mind to scientific study, especially chemistry, and if so then the systematic study of chemistry could, to added advantage, begin in the college, the engineering, or the technical schools. The authors deserve credit for being the pioneers in this field and the work will undoubtedly meet with favor.

ARTHUR C NEISH

**American Fertilizer Hand Book.** Eighth Edition, 1915. 400 pages. Price, $1.00. Ware Bros. Company, Philadelphia.

This book follows the form of the previous editions and covers the standard reference statistics and directory features of the fertilizer and allied trades. An adequate idea of the scope of this work may be obtained from the following list of subjects treated: The National Fertilizer Association, Fertilizer Materials Statistics, American Potash, Agricultural Experiment Stations, State Fertilizer Officials, Conversion Tables, German and Other Sources of Potash Supply, Sulfate of Ammonia and Nitrate of Soda, Tankage and Blood, Sulfate of Ammonia Statistics, Middle West Soil Improvement Committee, Sulfuric Acid Industry, World Movement of Fertilizer Materials, Southern Soil Improvement Committee, Net Returns per Acre of Cultivated Lands of the United States, Use of Concrete in Fertilizer Plants, Dictionary of Fertilizer Materials, Five Years of Cyanamid in America, Fertilizer Tonnage, Reference Index, Reference Library, State Fertilizer Tonnage, Phosphate Rock Section, Cottonseed Section, Packers and Renderers Section.

M. C. WHITAKER

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Agricultural Chemistry: Chimie agricole.** By E CHANCRIN 5th Ed. 16mo. 251 pp. Price, $2.00. Hachette et Cie, Paris

**Alternating Currents: A Treatise on the Theory of Alternating Currents.** By ALEX. RUSSELL. New Ed. 8vo. Price, $3.75. G P. Putnam's Sons, New York.

**Analysis: Cours d'analyse mathematique.** Vol 3. By EDOUARD GOURSAT. 2nd Ed. 674 pp. Price, $5.00. Gauthier Villars, Paris.

**Atoms: Principien der Atomdynamik.** By J. STARK 8vo 280 pp Price, $2.25. S. Hirzel, Leipzig.

**Concrete: Reinforced Concrete Field Handbook.** By JEROME COCHRAN. 12mo. 133 pp. Price, $1.00. Concrete-Cement Age Publishing Co., Detroit.

**Concrete Stone Manufacture.** By H WHIPPLE. 8vo Price, $1.00. Concrete-Cement Age Publishing Co., Detroit.

**Copper: Kupfer.** By WILHELM BORCHERS. 8vo. 450 pp Price, $7.00. W. Knapp, Halle.

**Dielectric Phenomena in High Voltage Engineering.** By F W PEEK, JR. 8vo. 265 pp. Price, $3.00. McGraw-Hill Book Co., New York.

**Diesel Engine: Ueber den Dieselmotor, seine Erprobung und seine Treibmittel.** By MAX BARTH. 4th Ed. 8vo 32 pp. Lipsius & Tischer, Kiel.

**Dyestuffs: The Analysis of Dyestuffs and Their Identification in Dyed and Colored Materials, Lake-Pigments, Foodstuffs, Etc.** By ARTHUR G. GREEN 8vo. 154 pp. Price, $2.25 C Griffin & Co., London

**Electrochemistry: Elektrochemie waesserige Loesungen.** By FRITZ FOERSTER. 2nd Ed. 8vo. 804 pp. Price, $8.00. J. A. Barth, Leipzig.

**Electrochemistry: Lehrbuch der Elektrochemie.** By SVANTE ARRHENIUS. 8vo. 305 pp. Price, $2.00. J. A. Barth, Leipzig.

**Engineering.** By G. D. KNOX. 8vo. 288 pp. Price, $1.00. T. C. & E. C. Jack, Edinburgh.

**Engineering Index Annual.** 1914. 8vo. Price, $3.50. A. F. Bird, London.

**Grinding Machinery.** By J. J. GUEST. 8vo. 456 pp. Price, $3.75. E. Arnold, London.

**Internal-Combustion Engine.** By H. E. WIMPERIS. 2nd Ed. 8vo. 336 pp. Price, $1.50. Constable & Co., London.

**Lifting Apparatus. Die Hebezeuge, Berechnung und Konstruktion der Elemente, Flaschenzuege, Winden und Krane.** By HUGO BETHMANN. 3rd Ed. 8vo. 790 pp. Price, $5.50 Vieweg & Sohn, Braunschweig.

**Lignite: Handbuch fuer den deutschen Braunkohlenbergbau.** 2nd Ed. 8vo. 880 pp. Price, $11.00. W. Knapp, Halle.

**Masonry as Applied to Civil Engineering.** By F. N. TAYLOR. 8vo 230 pp Price, $2.50. D Van Nostrand Co., New York

**Mechanical Engineers' Pocketbook of Tables, Formulae, Rules and Data.** By D KINNEAR CLARK. 12mo. 742 pp. Price, $1.25 C. Lockwood, London.

**Micrometers, Slide Gauges and Calipers.** By A. W. MARSHALL. 8vo. 78 pp. P. Marshall, London.

**Milk: Analysis of Milk and Milk Products.** By H LEFFMANN 4th Ed. 12mo. Price, $1.25. P. Blakiston's Son & Co., Philadelphia.

**Petroleum Technologist's Pocketbook 1915.** By SIR BOVERTON REDWOOD AND A. W. EASTLAKE 16mo Price, $2.25 C Griffin & Co., London.

**Platinum: Fusion du platine et dissociation.** Prepared by HENRY LE CHATELIER 8vo 120 pp Armand Colin, Paris

**Radioactivity: The Electrical Nature of Matter and Radioactivity.** By H C. JONES. 3rd Ed. 8vo. 212 pp. Price, $2.00 D Van Nostrand Co., New York.

**Railroad Field Manual for Civil Engineers.** By W. G. RAYMOND 8vo. Price, $3.00. Chapman & Hall, London.

**Statics: A Treatise on Statics.** Vol. 2. By G. MINCHIN. 5th Ed 8vo. 369 pp Price, $2.60 Oxford University Press, New York

**Steam Engine: A Manual of the High-Speed Steam Engine.** By H. K PRATT 8vo 270 pp Price, $2.00 D Van Nostrand Co., New York

**Steam Generators. Dampfkesselschaeden.** By GEORG FRANTZ. 8vo. Price, $0.75 Gebrueder Boehm, Kattowitz

**Surface Tension and Surface Energy and Their Influence on Chemical Phenomena.** By R S WILLOWS AND E HAVINCHEK 8vo 88 pp. Price, $0.75. Churchill, London

**Wastes: Utilisation des débris des animaux et déchets de la boucherie.** By R. LEZÉ 2nd Ed. 12mo 297 pp Charles Amat, Paris.

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## RECENT JOURNAL ARTICLES

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**Copper: Absorption of Gases by Refined Copper.** *Engineering and Mining Journal*, Vol. 100 (1915), No. 2, p. 52.

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**Metallurgical and Chemical Engineering in Great Britain.** *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 7, pp. 443 446.

**Mineral Oils: Ueber Neurungen auf dem Gebiete der Mineraloelanalyse und Mineraloelindustrie im Jahre 1914.** By LEOPOLD SINGER. *Chemische Revue ueber die Fett- und Harz-Industrie*, Vol. 22 (1915), No. 6, pp. 51–53.

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**Phenol: Bromine Method of Estimating Phenol.** By W. VERSFELD. *The Analyst*, Vol 40 (1915), No 471, pp 381 383

**Plating: The Successful Nickel Plating of Die Castings or Articles Made from Sheet Zinc.** By C H PROCTOR *The Metal Industry*, Vol 13 (1915), No 7, p 274

**Rubber: What the Rubber Chemists are Doing.** *The India Rubber World*, Vol. 52 (1915), No. 4, pp. 536 538.

**Soya Bean Oil: Die Oxydation und Polymerisation des Sojabohnoels.** By N J A. TAVERNE *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 28 (1915), No. 42, pp. 249–251.

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**Steel: Surface Decarburization of Steel.** By J. G. AYERS, JR. *Iron Trade Review*, Vol. 56 (1915), No. 25, pp 1305 1306

**Sulfur: The Estimation of Sulfide and Sulfate Sulfur, and the Action of Solvents on Vulcanized Rubber.** By H P STEVENS. *The Analyst*, Vol. 40 (1915), No. 471, pp. 275–281.

# RECENT INVENTIONS

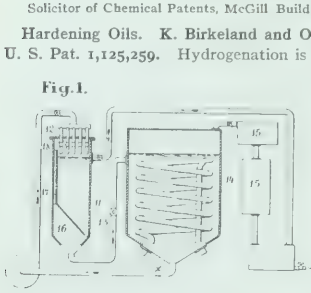
## UNITED STATES PATENTS

By C. L. Parker

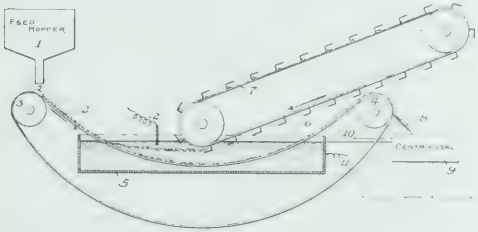
Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Hardening Oils. K. Birkeland and O. Devik, Jan. 19, 1915. U. S. Pat. 1,125,259.** Hydrogenation is effected by forming an unconfined jet of a mixture of oil and a catalyzer and causing the jet to pass first through an atmosphere of hydrogen and then onto a body of oil whereby hydrogen is carried down into the body of oil and is absorbed as it rises through the latter.

Fig. 1.



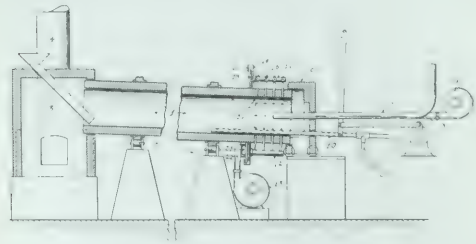
**Treating Ores. J. W. Emerson, Feb. 2, 1915. U. S. Pat. 1,126,965.** The blende is separated from concentrates containing it, by passing a shallow traveling layer of the concentrates into and through a bath which causes a preferential gas-evolving attack upon the blende to an extent only sufficient to lift the blende particles slightly above the surface of the




layer and mechanically removing the thus lifted blende aggregates from the mass.

The bath may consist of a ten per cent aqueous solution of sulfuric acid, hydrochloric acid or nitric acid; or, it may consist of salt or sulfate of soda, in which case an electric current is passed through the liquid from suitable insoluble electrodes to cause an evolution of acid or chlorine which produces a preferential attack upon the blende particles, sufficient to cause their separation from the other particles of the concentrates.

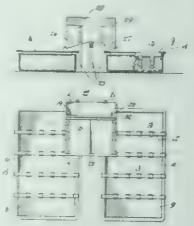
**Recovery of Metallic Oxids from Flue-Dust. G. F. Downs, Feb. 2, 1915. U. S. Pat. 1,127,209.** Flue-dust is passed in a continuous mass through a rotative cylindrical kiln or furnace slightly inclined from the horizontal and subjected to blasts



of air through numerous tuyeres so regulated that the air is admitted underneath the flue-dust and not only violently agitates it, but creates sufficient heat through the combustion of the carbon contained in the flue dust with the oxygen contained in the air to sinter or nodulize the flue dust.

**Improving Oils. A. McD. McAfee, Feb. 9, 1915. U. S. Pat. 1,127,465.** This is a process of converting a portion of the high boiling petroleum oils into lower boiling oils by heating the higher boiling oils with aluminum chlorid and distilling off the lower boiling oils formed. The heated oil is cooled while a substantial amount of higher boiling oils remain therein and the aluminum chlorid is separated from the higher boiling oil

**Sodium-Carbonate Crystals. M. Spazier, Feb. 9, 1915. U. S. Pat. 1,127,691.** The apparatus consists of two adjacent tanks 8 and 9, a third tank 10, adapted to discharge into either tank 8 or 9 and a drain receptacle 11, located above tanks 8 and 9.



In the use of this apparatus the crystals start their formation about the hangers 13 which are evenly distributed in the tanks 8 and 9 and at such a distance apart that they do not prevent the crystals falling to the bottom, when, in the process of crystallization, a sheet of crystals has formed. After crystals have formed in one tank the cróss-bars 12 and hangers 13 are removed and any solution which is not crystallized is taken out of the tank and placed in tank 10. The crystals are then placed in the draining receptacle 11 and the excess or remaining solution is allowed to drain into tanks 8 and 9.

**Recovery of Formic Esters Used as Solvents of Cellulose Compounds. J. Duclaux, Feb. 9, 1915. U. S. Pat. 1,127,871.** The vapors of the solvent are absorbed in water containing an alkaline agent. A strong acid and a large excess of methyl or methyl alcohol is then added to the dilute solution and the resultant formic ester recovered by distillation.

**Deposition of Iron. S. O. Cowper-Coles, Feb. 9, 1915. U. S. Pat. 1,127,966.** Iron sponge is added to an electrolyte maintained in suspension and distribution by agitation whereby the acid which is formed is neutralized as rapidly as possible.

**Fuse-Igniting Powder. S. Lilley, Sr., Feb. 9, 1915. U. S. Pat. 1,128,158.** The powder is composed of chlorate of potash, sugar, sulfur, and cobalt.

**Explosive. F. Sparre, Feb. 16, 1915. U. S. Pat. 1,128,380.** The composition comprises an oxidizing agent and a polysulfide of an alkaline earth metal.

**Gas. G. M. S. Tait, Feb. 16, 1915. U. S. Pat. 1,128,549.** A fixed gas is produced from hydrocarbon oils without material deposition of carbon, tar or the like, by passing them through the pores of a heated porous non-metallic decomposing substance maintained at a temperature of between 1000° F. and 1600° F.

**Hydrogen-Peroxid Solution. J. A. Trimble, Feb. 16, 1915. U. S. Pat. 1,128,637.** This is a 3 per cent aqueous solution of hydrogen peroxid containing one part of cinchonidin to approximately 20,000 parts of hydrogen peroxid solution.

## BRITISH PATENTS

By D. Geddes Anderson

Chemical Engineer and Patent Chemist, Glasgow, Scotland

The following abstracts are taken direct from the patent specifications as soon as these are published by the British Patent Office. The date given at the end of the abstract is date of acceptance.

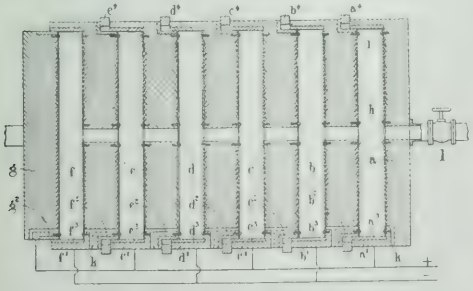
**Treatment of Fabrics Used in Conjunction with India Rubber. W. E. Muntz. Feb. 25, 1913. Brit. Pat. 4910.** Fabrics to be subsequently used in the manufacture of rubber goods are treated in an evacuated vessel, with a 3 per cent solution of barium hydroxide and then with a 3 per cent solution of ammonium carbonate. The insoluble barium carbonate precipitated in the fibers neutralizes the sulfuric and sulfurous acids formed after the vulcanization of the rubber.—April 1, 1915.

**Dyeing or Softening Wood at High Temperatures. L. Petersen-Hviid, Dec. 23, 1913. Brit. Pat. 29,614.** The wood, either in its natural condition or impregnated with liquids which will soften or color it, is heated in a closed vessel to a suitable temperature. When the temperature reaches about 135° C. a stream of gaseous ammonia under pressure is introduced. This treatment prevents the acids which are liberated from the wood at this temperature from injuring the wood fiber.—March 25, 1915.

**Manufacture of Casein Binding Material. L. Petersen-Hviid, Jan. 14, 1914. Brit. Pat. 1016.** Infusorial earth is added to the freshly precipitated curd. This addition gives a uniform drying and oxidation of the casein products and makes it very easily soluble in alkali.—April 14, 1915.

**Improved Rubber Substance. P. Schidrowitz and H. A. Goldsbrough, Jan. 15, 1914. Brit. Pat. 1111.** This relates to a process for obtaining a porous or spongy rubber substance direct from rubber latex. The latter is coagulated under conditions producing a spongy coagulum, and the pores so produced fixed by vulcanization. The coagulum is vulcanized in a wet state. One example quoted is: Equal quantities of latex, and a saturated solution of ammonium carbonate are heated on a water bath and 1 per cent of sulfur stirred in. Coagulation is induced by adding acetic acid and the mixture then vulcanized for one hour at 286° F.—April 15, 1915.

**Utilization of Peat. M. A. Adam and Wetcarbonizing, Ltd., Feb. 14, 1914. Brit. Pat. 3888.** Wet peat is subjected to heat treatment and dewatered to the condition of a solid or semi-solid mass. It is then subjected to an electric current under conditions adapted to secure electrosmose, and to pressure in a space of gradually decreased volume. The drawing shows the new type of filter press, which has collapsible chambers and is provided with electrodes in each chamber to pass current through the cakes of peat when formed.—April 14, 1915.



**Agglomerated Combustibles. L. Martel, March 26, 1914. Brit. Pat. 7664.** This invention relates to the manufacture of agglomerated combustibles made with cool, ground pitch, and tar. The improvement consists of atomizing the tar by compressed air or steam before adding it to the coal and pitch. When the tar is added in this fashion less than 1 per cent is required.—March 25, 1915.

**Extraction of Metal from Metal Bearing Material. W. H. James, April 21, 1914. Brit. Pat. 9846.** A solution of a salt, such as sodium chloride, is electrolyzed in a separate electrolyzer. The respective electrolyzed solutions in the vicinities of the electrodes are withdrawn and the anode product is passed to a receptacle containing the metal-bearing material. The solution, after dissolving the base metal, is withdrawn from the material and is mixed with the solution from the cathode of the electrolyzer and the metal content is precipitated: 1 is a vat provided with filter flour 2; 3 is the electrolyzer with electrodes 7 and 8, which are surrounded by pipes 9 and 10 for withdrawing the solutions.—April 15, 1915.

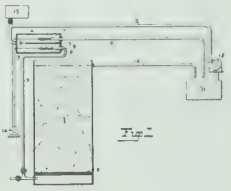
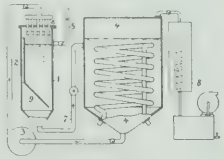


Fig. 1

**Alloys of Iron and Steel. B. Talbot, April 29, 1914. Brit. Pat. 10,582 and 10,877.** Copper, 0.3 per cent to 3 per cent, is added to soft steel or ingot iron. The metal is then rolled down to a suitable sized flat, cut up and piled. The piles are heated in a furnace to a welding temperature and are then cogged or hammered and rolled into sheets. The alloy is said to possess great powers of resisting corrosion.—April 15, 1915.

**Composite Briquette Fuel. E. Eaton. May 8, 1914. Brit. Pat. 11,345.** The material consists of: chalk 88 per cent, solidified tar 12 per cent. This mixture is ground, and during the grinding process is subjected to steam impregnated with petroleum oil vapor obtained by passing the steam through a closed tank containing oil.—March 25, 1915.

**Refining and Distillation of Oils. K. Birkeland and O. Devik, May 14, 1914. Brit. Pat. 11,588.** A mixture of oil and water vapor is produced by forming a jet of the oil and causing this jet to pass first through an atmosphere of water vapor and then into a body of oil. In this manner the water vapor forms an emulsion with the oil and the emulsion is passed into a low pressure receptacle where the vapor is allowed to escape and become condensed. An autoclave 1 is connected with a receptacle 4, which communicates with a vacuum pump. Water vapor is led through 5 and oil through injectors 6. The emulsion is conveyed through 7 to the low pressure chamber 4.—April 8, 1915.



**Cellulose Compounds. Courtaulds Ltd. W. H. Glover and L. P. Wilson, May 27, 1914. Brit. Pat. 13,055.** Refers in particular to the manufacture of viscose. The oxidation of the alkali-cellulose is effected by blowing air through it, or by treating it with soluble peroxides, *e. g.*, 2 kilos of sodium peroxide are dissolved in 200 kilos of 17.5 per cent solution of caustic soda and 5 kilos wood pulp are immersed in the liquid at a temperature of 18° C. for about 4 hours. The product is then removed and pressed until it is about 15 kilos in weight, after which it is ground and at once converted into xanthate by the action of carbon bisulfide.—April 15, 1915.

**Cleaning and Polishing Compound. C. E. Challis, June 23, 1914. Brit. Pat. 14,963.** This consists of a mixture of kieselguhr, pumice, oxide of iron, rottenstone, emery, Neuberg chalk, oxalate of ammonia, and powdered soap. This mixture is made into a paste with oleic acid and a little Russian turpentine.—April 8, 1915.

# MARKET REPORT—JULY, 1915

AVERAGE WHOLESALE PRICES IN THE NEW YORK MARKET FOR LARGE QUANTITIES OF STANDARD CHEMICALS

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lime, gray | 100 Lbs. | 3.50 | @ | 3.55 |
| Alum, lump | 100 Lbs. | [illegible] | @ | 3.50 |
| Aluminum Sulfate, high grade | 100 Lbs. | 1.[illegible] | @ | 1.[illegible] |
| Ammonium Carbonate, domestic | Lb. | 9 | @ | [illegible] |
| Ammonium Chloride, gray | Lb. | 6[illegible] | @ | |
| Aqua Ammonium, 16°, drums | Lb. | 2[illegible] | @ | 2½ |
| Arsenic, white | Lb. | 4 | @ | |
| Barium Chloride | Ton | 100.00 | @ | 110.00 |
| Barium Nitrate | Lb. | | 15 | |
| Barytes, prime white, foreign | Ton | 20.00 | @ | 25.00 |
| Bleaching Powder, 35 per cent | 100 Lbs. | 1.62½ | @ | 1.75 |
| Blue Vitriol | Lb. | 7 | @ | [illegible] |
| Borax, crystals, in bags | Lb. | 5 | @ | 6 |
| Boric Acid, powdered crystals | Lb. | 9 | @ | 9[illegible] |
| Brimstone, crude, domestic | Long Ton | 22.00 | @ | 22.50 |
| Bromine, technical, bulk | Lb. | 85 | @ | 87 |
| Calcium Chloride, lump | Ton | — | @ | 11.78 |
| Calcium Chloride, granulated | Ton | | @ | 14.78 |
| Caustic Soda, 60 per cent domestic, in drums | 100 Lbs. | | 3.00 | |
| Caustic Soda, 70 @ 76 per cent | 100 Lbs. | 2.87½ | (basis) | |
| Caustic Soda, powdered or granulated, 76% | 100 Lbs. | 3.75 | @ | — |
| Chalk, light precipitated | Lb. | 4½ | @ | 5 |
| China Clay, imported | Ton | 30.00 | @ | 35.00 |
| Feldspar | Ton | 8.00 | @ | 12.00 |
| Fuller's Earth, foreign, powdered | 100 Lbs. | 80 | @ | 85 |
| Glauber's Salt, in bbls. | 100 Lbs. | 80 | @ | |
| Green Vitriol, bulk | 100 Lbs. | 90 | @ | 1.[illegible] |
| Hydrochloric Acid, commercial, 18° | 100 Lbs. | 1.50 | @ | 1.75 |
| Hydrochloric Acid, C. P., conc., 22° | 100 Lbs | 2.00 | @ | 2.25 |
| Iodine, resublimed | Lb. | 3.75 | @ | 3.80 |
| Lead Acetate, white crystals | Lb. | 11 | @ | 12⅛ |
| Lead Nitrate | Lb. | 11 | @ | 11½ |
| Litharge, American | Lb. | 7 | @ | 8 |
| Lithium Carbonate | Lb. | 1.00 | @ | 1.10 |
| Magnesium Carbonate | Lb. | 5½ | @ | 6 |
| Magnesite, "Calcined" | Ton | 25.00 | @ | 30.00 |
| Nitric Acid, 68 per cent, sp. gr. 1.42 | Lb. | 5¾ | @ | 6¼ |
| Nitric Acid, fuming | Lb. | 7⅞ | @ | 8¼ |
| Phosphoric Acid, sp. gr. 1.750 | Lb. | 28 | @ | 31 |
| Phosphorus | Lb. | 35 | @ | 90 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate, casks | Lb. | 21 | @ | 21½ |
| Potassium Bromide | Lb. | 1.10 | @ | 1.11 |
| Potassium Carbonate, calcined, 80 @ 85% | Lb. | 20 | @ | 21 |
| Potassium Chlorate, crystals, spot | Lb. | 42 | @ | |
| Potassium Cyanide, bulk, 98–99 per cent | Lb. | 25 | @ | 29 |
| Potassium Hydroxide | Lb. | 40 | @ | 42 |
| Potassium Iodide, bulk | Lb. | 3.15 | @ | 3.20 |
| Potassium Nitrate, crude | Lb. | 17¼ | @ | — |
| Potassium Permanganate, bulk | Lb. | 95 | @ | 1.00 |
| Quicksilver, flask, 75 lbs. | | 95.00 | @ | 100.00 |
| Red Lead, American | Lb. | 7¼ | @ | — |
| Salt Cake, glass makers' | 100 Lbs. | | 55 | |
| Saltpeter, crude | 100 Lbs. | | @ | — |
| Silver Nitrate | Oz. | 30½ | @ | 32½ |
| Soapstone in bags, $Na_2O$ | Ton | 10.00 | @ | 12.00 |
| Soda Ash, 48 per cent. $Na_2O$ | 100 Lbs. | 67½ | @ | 72½ |
| Sodium Acetate | Lb. | 5¾ | @ | 6½ |
| Sodium Bicarbonate, domestic | 100 Lbs. | 1.25 | @ | 1.50 |
| Sodium Bicarbonate, English | Lb. | 3½ | @ | 3¾ |
| Sodium Bichromate | Lb. | 10½ | @ | 11½ |
| Sodium Carbonate, dry | 100 Lbs. | 1.10 | @ | — |
| Sodium Chlorate | Lb. | 17½ | @ | 18 |
| Sodium Hydroxide, 60 per cent | 100 Lbs. | | 2.25 | |
| Sodium Hyposulfite | 100 Lbs. | 1.80 | @ | 2.00 |
| Sodium Nitrate, 95 per cent, spot | 100 Lbs. | — | @ | — |
| Sodium Silicate, liquid | 100 Lbs. | 85 | @ | 1.20 |
| Sodium Sulfide, 30%, crystals, in bbls. | Lb. | 1¾ | @ | 2¼ |
| Sodium Sulfite, crystals | Lb. | 2¾ | @ | 3¼ |
| Strontium Nitrate | Lb. | 17½ | @ | 18 |
| Sulfur, flowers, sublimed | 100 Lbs. | 2.20 | @ | 2.60 |
| Sulfur, roll | 100 Lbs. | 1.85 | @ | 2.15 |
| Sulfuric Acid, chamber, 60° | 100 Lbs. | | 85 | |
| Sulfuric Acid, conc., sp. gr. 1.842 | 100 Lbs. | 1.25 | @ | 2.00 |
| Sulfuric Acid, oleum (fuming) | 100 Lbs. | 1.50 | @ | 2.00 |
| Talc, American | Ton | 9.00 | @ | 13.00 |
| Terra Alba, American, No. 1 | 100 Lbs. | 75 | @ | 80 |
| Tin Bichloride, 50° | Lb. | 14¼ | @ | 15 |
| Tin Oxide | Lb. | 44 | @ | 45 |
| White Lead, American, dry | Lb. | 6¼ | @ | [illegible] |
| Zinc Carbonate | Lb. | 10 | @ | 12 |
| Zinc Chloride, granulated | Lb. | 12½ | @ | 14½ |
| Zinc Oxide, American process | Lb. | 16 | @ | 18 |
| Zinc Sulfate | 100 Lbs. | 6½ | @ | |

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid, C. P., in bbls. | Lb. | 65 | @ | 70 |
| Acetic Acid, 28 per cent, in bbls. | 100 Lbs. | 2.50 | @ | 2.65 |
| Acetic Acid, glacial, 99½%, in carboys | Lb. | 10½ | @ | 11 |
| Acetone, drums | Lb. | | 28 | |
| Alcohol, denatured, 180 proof | Gal. | 38 | @ | 39 |
| Alcohol, grain, 188 proof | Gal. | 2.64 | @ | 2.66 |
| Alcohol, wood, 95 per cent, refined | Gal. | 45 | @ | 47 |
| Amyl Acetate | Gal. | 2.60 | @ | 2.75 |
| Aniline Oil | Lb. | 1.25 | @ | 1.30 |
| Benzoic Acid, ex-toluol | Lb. | [illegible] | @ | |
| Benzol, 90 per cent ... spot | Gal. | 90 | @ | 1.00 |
| Camphor, refined in bulk, bbls. | Lb. | 43 | @ | 45 |
| Carbolic Acid, U. S. P., crystals, drums | Lb. | 1.50 | @ | |
| Carbon Bisulfide | Lb. | 7½ | @ | 8 |
| Carbon Tetrachloride, drums, 100 gals. | Lb. | 16 | @ | 17 |
| Chloroform | Lb. | 30 | @ | 35 |
| Citric Acid, domestic, crystals | Lb. | [illegible] | @ | 80 |
| Cresol, U. S. P. | Gal | 1.40 | @ | 1.50 |
| Dextrine, corn (carloads, bags) | 100 Lbs. | 3.10 | @ | 3.20 |
| Dextrine, imported potato | Lb. | — | @ | — |
| Ether, U. S. P., 1900 | Lb. | 15 | @ | 20 |
| Formaldehyde, 40 per cent | Lb. | 9 | @ | 10 |
| Glycerine, dynamite, drums included | Lb. | 21½ | @ | 22 |
| Oxalic Acid, in casks | Lb. | 34½ | @ | 35½ |
| Pyrogallic Acid, resublimed bulk | Lb. | 1.35 | @ | 1.55 |
| Salicylic Acid | Lb. | 2 | @ | 2½ |
| Starch, cassava | Lb. | 3¾ | @ | 4 |
| Starch, corn (carloads, bags) | 100 Lbs. | | 2.35 | |
| Starch, potato | Lb. | 5¾ | @ | |
| Starch, rice | Lb. | 7 | @ | 8 |
| Starch, sago | Lb. | 3⅜ | @ | 3[illegible] |
| Starch, wheat | Lb. | 7 | @ | 7½ |
| Tannic Acid, commercial | Lb. | 65 | @ | 66 |
| Tartaric Acid, crystals | Lb. | 50 | @ | |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax, pure, white | Lb. | 42 | @ | 45 |
| Black Mineral Oil, 29 gravity | Gal. | 12½ | @ | 13 |
| Castor Oil, No. 3 | Lb. | 9¾ | @ | 10¾ |
| Ceresin, yellow | Lb. | 10 | @ | 25 |
| Corn Oil | 100 Lbs. | 5.86 | @ | — |
| Cottonseed Oil, crude, f. o. b. mill | Gal. | 38 | @ | — |
| Cottonseed Oil, p. s. y. | Lb. | 6 | @ | 6[illegible] |
| Creosote, beechwood | Lb. | 90 | @ | 95 |
| Cylinder Oil, light, filtered | Gal. | 20 | @ | 25 |
| Fusel Oil, crude | Lb. | 2.40 | @ | 2.50 |
| Japan Wax | Lb. | 13 | @ | — |
| Lard Oil, prime winter | Gal. | 88 | @ | 90 |
| Linseed Oil, raw | Gal. | 53 | @ | 54 |
| Menhaden Oil, crude | Gal | 37 | @ | 38 |
| Naphtha, 68 @ 72° | Gal | — | @ | 12 |
| Neat's-foot Oil, 20° | Gal. | 93 | @ | 94 |
| Paraffine, crude, 120 & 122 m. p. | Lb. | 2½ | @ | 3 |
| Paraffine Oil, high viscosity | Gal. | 22 | @ | 23 |
| Rosin, "F" Grade, 280 lbs. | Bbl. | | 3.80 | |
| Rosin Oil, first run | Gal. | — | @ | 25 |
| Shellac, T. N. | Lb. | 13¾ | @ | 14¼ |
| Spermaceti, cake | Lb. | | 25 | |
| Sperm Oil, bleached winter, 38° | Gal. | 70 | @ | — |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid, double-pressed | Lb. | 12 | @ | 12½ |
| Tallow, acidless | Gal. | 62 | @ | 63 |
| Tar Oil, distilled | Gal. | 30 | @ | 31 |
| Turpentine, spirits of | Gal. | 42 | @ | 43 |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum, No. 1, ingots | Lb. | 31 | @ | 33 |
| Antimony, Hallets' | Lb. | | — | |
| Bismuth, New York | Lb. | 2.75 | @ | — |
| Bronze powder | Lb. | 65 | @ | 4.00 |
| Copper, electrolytic | Lb. | 19 | @ | 19¼ |
| Copper, lake | Lb. | 19½ | @ | 19¾ |
| Lead, N. Y. | 100 Lbs. | | 5.55 | |
| Nickel | Lb. | 42 | @ | 45 |
| Platinum, refined | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | | 47¾ | |
| Tin | 100 Lbs. | 36.37½ | @ | 36.50 |
| Zinc, N. Y. | Lb. | 20 | @ | 20¼ |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | 100 Lbs. | 3.46 | @ | 3.50 |
| Blood, dried | Unit | | 2.70 | |
| Bone, 4½ and 50, ground, raw | Ton | | 30.00 | |
| Calcium Cyanamid | Unit of Ammonia | | 2.30 | |
| Calcium Nitrate, Norwegian | 100 Lbs. | | — | |
| Castor Meal | Unit | | — | |
| Fish Scrap, domestic, dried, f. o. b. works | Unit | 2.5[illegible] | & | 10 |
| Kainit, minimum 12.4 per cent $K_2O$, bulk | Ton | | 35.00 | |
| Phosphate, acid, 16 per cent, bulk | Ton | 8.00 | @ | 9.00 |
| Phosphate rock; f. o. b. mine | | | | |
| Florida land pebble, 68 per cent | Ton | | 2.25 | |
| Tennessee, 70–80 per cent | Ton | 5.00 | @ | 5.50 |
| Potassium "muriate," basis 80 per cent | Ton | 230.00 | @ | 250.00 |
| Pyrites, furnace size, imported | Unit | | 14 | |
| Tankage, high grade | Unit | 2.65 | & | 10 |

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# THE CHEMICAL INDUSTRIES EXPOSITION

The National Exposition of Chemical Industries is now an assured success. Although it is the first undertaking of this kind in America, the enthusiastic endorsement of the suggestion by the technical press and the active support extended to the enterprise by the industries have already established the Exposition as an event of great importance to the present and future development of chemical industry.

The public have at last become interested in the important rôle of industrial chemistry and its relation to their comfort and safety. The essential relations of the chemist to the supply of wholesome food and drink, to the crop yields of our farms, to the metals recovered from the ores of our mines, to the gaiety of our garb and the wholesomeness of our civilization, to the business of war and the consequent necessity of defense, are all beginning to be realized by the people. This, then, is the psychological time for the chemical industries to make a public bow.

The Exposition has two important functions—one to stimulate the interest of and inform the public; and the other to benefit and broaden the profession through an exchange of technical knowledge and experience. The program, which is now assuming definite form, is carefully designed to accomplish each of the above ends and much more.

The President of the United States has been invited to attend the formal opening of the Exposition on Monday, September 20th. His acceptance will put a significant stamp of appreciation upon the value of chemical industry to America.

The government bureaus are giving most active coöperation. The Bureau of Commerce has provided an elaborate exhibit to illustrate the industrial resources of the United States. The Bureau of Mines will show, among other things, the results of some of their recent researches in the field of petroleum chemistry.

Many of the important technical societies have prepared special programs to be given in the Exposition halls. The organizations to be represented are: The American Institute of Chemical Engineers, the New York Section of the American Electrochemical Society, the American Institute of Mining Engineers, the Industrial Division of the American Chemical Society, the Technical Section of the American Paper and Pulp Association, the New York Section of the American Chemical Society, and the American Institute of Electrical Engineers. These meetings will be held in the evenings and will be open to the public.

Arrangements have been made for addresses on subjects of national importance. The following list of speakers is now almost complete and contains the names of many well-known specialists who are in a position to give first-hand information that will be undoubtedly of great value to professional workers as well as to the interested public.

JOHN BARRETT, Director Pan-American Union—*South American Opportunities*

W. D. COOLIDGE, General Electric Company—*The X-Ray*

LINN BRADLEY, The Research Corporation—*Results of Smoke, Dust and Fume Nuisance by Electrical Precipitation*

G. B. HECKEL, New Jersey Zinc Company—*Zinc*

F. W. KEOUGH, President National Association of Manufacturers—*Accident Prevention in the Chemical Industries*

J. L. LICHTNER, Hershey Chocolate Company—*The Manufacture of Chocolate*

GEO. FRANK LORD, duPont de Nemours Powder Company—*Farming with Dynamite*

H. A. HUSTON, German Kali Company—*Potash*

THOS. H. NORTON, Department of Commerce—*Foreign Markets for American Chemicals*

D. C. PIERCE, Barber Asphalt Company—*Where Street and Lake Material Comes From*

WELDING RING, President American Exporters' Association—*Transportation and Shipping Facilities with Foreign Countries*

S. P. SADTLER, S. P. Sadtler & Sons—*American Contributions to Industrial Chemistry*

I. F. STONE, President National Aniline & Chemical Company—*The Aniline Dye Situation*

J. L. TAYLOR, U. S. Bureau of Mines—*Explosives*

HARRINGTON EMERSON, The Emerson Company—*Efficiency in Chemical Industries*

R. S. FRINCK, President Frinck Pyrometer Company—*The Relation of Chemistry and Mechanical Manipulation to the Evolution of the Glass Industry.*

PERCY WILSON, Secretary Association of American Portland Cement Manufacturers—*The History of Cement*

HOWARD H. GROSS, President of Tariff Commission League—*Tariff Discussion*

Moving pictures of actual industrial operations are to be specially featured. The motion picture program has been arranged with the aid of the Bureau of Commercial Economics of Washington. The following partial list of subjects gives some idea of the educative value of this phase of the Exposition:

Hard Rubber Manufacturing
Manufacturing Uses of White Lead
The Tea Industry in Ceylon
From Ore to National Pipe
Boring and Piping Gas
Asphalt from Lake Trinidad to Street
Uses of Cement on the Farm
The Crime of Carelessness
The Man He Might Have Been
An American in the Making
Sewage Disposal and Filtration
Tanning Hides to Shoes
Electricity in a Home
Application of Cement
Sulfur Mining in Louisiana
Electricity in the Mine
Electricity on the Farm
Electric Power Transmission
Mine Explosion and Rescue
Safe Method of Bituminous Coal Mining
Zinc Mining, Milling and Smelting
Copper Mining, Milling and Smelting
The Manufacture of Paper
The Making of Saws
The Steel Industry
The Chocolate Industry
Tarvia
Fertilizer from Air
The Mining of Potash
Roofs from Rags
The Tin Industry
The Silk Industry
The Workman's Lesson
Wool to Clothing
Perfumery
From Cow to Consumer
Making Silver
Soap
Paint
Consuming Smoke
Hog Cholera
Nitro-Germ
The X-Ray
Electric Lighting
Manufacturing of Files
Motor Application

The exhibits of apparatus and machinery include laboratory and plant supplies for the manufacture of all classes of chemicals, drugs, foods, and metallurgical products. The list of exhibitors given below is complete to date (August 20th).

American Bitumastic Enamels Co.
American Chemical Society
Automatic Weighing Machine Co.
J. T. Baker Chemical Co.
William Beckers Aniline & Chemical Works
Bethlehem Foundry & Machine Co.
Buffalo Foundry & Machine Co.
Chadwick Boston Lead Co.
Condensite Co. of America
Detroit Range Boiler Co.
Dorr-Cyanide Machinery Co.
du Pont de Nemours Powder Co.
Elyria Enameled Products Co.
Fairview Fluorspar & Lead Co.
General Bakelite Company
Glens Falls Machine Works
Hanovia Chemical & Mfg. Co.
Huff Electrostatic Separator Co.
International Instrument Co.
Lead-lined Iron Pipe Co.
Macbeth-Evans Glass Co.
Metallurgical and Chemical Engineering
J. L. Mott Iron Works
Monsanto Chemical Works
National Aniline & Chemical Co.
Sweetland Filter Press Co.
Swenson Evaporator Company
Thwing Instrument Company
American Hard Rubber Co
Brown Instrument Co.
Boonton Rubber Mfg. Co.
Chemical Process Co.
Department of Commerce
Devine Co., J. P.
Driver-Harris Wire Co.
Durirron Castings Co.
Thos. A. Edison
Edward L. Rieha
Eimer & Amend
Emil Greiner Co.
Ernest Scott & Co.
Huyck & Sons, F. C.
Lenz & Naumann
Lungwitz, Emil E.
Koven & Bro., L. O.
Moore Filter Company
Norton Company
Pfaudler Company
Raritan Copper Works
Schaum & Uhlinger, Inc
Tolhurst Machine Works
Troegerlith Tile Co.
United Lead Co.
Valley Iron Works
Wilson-Maeulen Co.
Zaremba Co.

# ORIGINAL PAPERS

## THE IMPROVEMENT OF HIGH BOILING PETROLEUM OILS, AND THE MANUFACTURE OF GASOLINE AS A BY-PRODUCT THEREFROM, BY THE ACTION OF ALUMINUM CHLORIDE[1]

By A. M. McAfee

The conversion of high boiling petroleum oils into lower boiling oils of greater commercial value is an old problem, and many solutions of it have been proposed. Formerly, when kerosene was worth more than gasoline, naturally the effort was to increase the yield of kerosene from crude oil; nowadays, gasoline is worth more than kerosene, and naturally the effort is to increase the yield of gasoline. But in principle, gasoline making and kerosene making from high boiling petroleum oils are the same, and most of the proposed methods make both products. With very little variation, most of them will make gas equally well. A careful examination of these methods will show, in nearly all cases, the same principle, namely, what is called cracking—heating to a sufficient temperature to cause the high boiling oils to become unstable and break down into lower boiling oils. If the heat be intense enough and the time be long enough the product will be gas; less heat and a shorter time will make gasoline, and a still less heat and shorter time will make kerosene.

The inventors have rung the permutations on this simple idea; they heat under pressure and they heat under vacuum; they heat in the presence of gases; they heat in the presence of catalysts; they heat in tubes and they heat in boilers, etc., etc. It is safe to say that in 99 per cent of the methods which have been proposed for converting high boiling oils into lower boiling oils, "cracking" by heat is involved. Sometimes it is disguised in ornate language; sometimes it lurks behind intricate apparatus, but it is always there.

The difficulty, however, with all these cracking methods is a difficulty in principle. In breaking down the complex, high boiling hydrocarbons into several simpler ones, there is not enough hydrogen to saturate these newly formed bodies, and unsaturated hydrocarbons must necessarily result unless hydrogen be added or carbon subtracted. Hydrogen is too expensive and difficult to add and, though a part of the carbon is readily enough subtracted and deposited, this subtraction and deposition never goes far enough—although the still man might not be readily convinced of this. These cracked products are in large part unsaturated, and they are not desirable commercially. They are foul smelling; they are yellow in color and become rapidly more yellow on standing; they deposit large amounts of carbon on ignition in a gas engine; they burn with a smoky flame; they contain resinous bodies which cause gumming in use or on standing, etc., etc. They can, of course, be refined somewhat with sulfuric acid, but there must be too much of the acid used and too much of the oil is lost to permit in practice any thorough treatment with acid.

Aside from the poor quality of the liquid products obtained, the operation of the cracking process is attended with great difficulty where uniform results are desired. There are many variables on which the obtaining of such results depends—temperature, time, pressure and catalytic action of the walls of the containing vessel. A change in either of these variables makes a change in the products obtained. Using the same apparatus, the same pressure, and consuming the same time, a difference of a comparatively few degrees of temperature in cracking operations makes marked differences in the yield and quality of liquid products.

In most of the cracking processes, pressure is employed: 60 to 100 lbs. is usual and some have proposed much higher pressures. It is here that the greatest difficulty becomes manifest—the great danger to the operators and to the plant. There is always a deposition of hard (and flinty hard) coke on the inner walls of the heating element. Some who have had considerable experience in cracking oils have said that the coke is forced into combination with the iron, making it brittle and thus utterly unable to withstand the high temperature and pressure employed. At any rate, the deposition of the carbon occurs where the element is hottest, causing a local overheating at that point. Under such conditions the tensile strength of the steel becomes an unknown quantity; as likely as not it yields to the stress without any warning. Oil vapors of a temperature around 650° F. ignite spontaneously when they evolve from a still into the surrounding atmosphere. In cracking processes the temperature is 750 to 850° F. and even higher; hence, the manifest danger of cracking petroleum oils under such pressures.

When I took up the gasoline problem, some two and one-half years ago, I dismissed from consideration the idea of cracking oils. Up to this time, or since the Friedel and Crafts British patent, No. 4769, of 1877, there had been some degree of mild interest shown as regards the effect which aluminum chloride might have on petroleum oils, but no positive results had followed from this interest. It appeared to me that this reaction might have far more significance than was then apparent. I trust this paper may in a measure exemplify its significance.

I have found that with proper control of the vapors leaving the distilling system and entering the final condenser, and with sufficient time given the aluminum chloride, high boiling oils can be completely broken down into lower boiling oils, and no matter how unsaturated the high boiling hydrocarbons may be, the low boiling oils produced therefrom are sweet smelling, water white and saturated. The reaction gives little gas and only about the right amount of carbon to allow production of saturated products.

[1] Read before the Seventh Semi-Annual Meeting of the American Institute of Chemical Engineers, San Francisco August 28, 1915.

The carbon is deposited not in the form of a hard baked-on carbon, but as a granular, coky mass, easily removed from the still.

But there are other products than gasoline that can be made from petroleum which are commercially worth while, although in our efforts to increase the supply of gasoline we have apparently forgotten this fact. If the market value of the various products which can be obtained from crude petroleum be plotted, it will be found that there is a peak at the low boiling end and another at the high boiling end. Gasoline is worth more than kerosene and kerosene is worth more than gas oil, while the products following gas oil, paraffin and lubricating oils, are worth as much or more than the gasoline.

The problem before me, therefore, knowing the reactive power of aluminum chloride, was to apply it to crude petroleum so that good heavy oils could be obtained while at the same time converting the less valuable portions of the crude into gasoline. The solution of this problem is found in my patent.

In the practical operation of this process, crude petroleum of any kind is first distilled until the naturally occurring gasoline and kerosene, if there be any present, is distilled off. As you are probably aware, in many of our crude oils, and especially some of those from Texas, California and Mexico, there is substantially no gasoline present and very little kerosene. But in any event, the crude is first heated to free it of any moisture which it may contain, since the oil must be perfectly dry before adding the aluminum chloride.

The next step is to add anhydrous aluminum chloride to the remaining residual oil, and then bring the mixture to boiling in the still. Boiling is usually around 500° F. and generally remains between 500 and 550° F. during the entire distillation, extending over a period of 24 to 48 hours. There is no need of employing extra pressure or vacuum or special apparatus; any still with a stirrer in it suffices.

Granted sufficient time for the aluminum chloride to get in its work, the success or failure of this process depends upon the proper control of the temperature at which the oil vapors are allowed to leave the distilling system to enter the final condenser. Between the still and the final condenser are placed two air-cooled condensers connected in series, which separate the low boiling oils from the high boiling oils, returning the latter, together with any volatilized aluminum chloride, to the still. For a 1,000 barrel still the air condensers which we are now using are drums of oval cross-section, 3 ft. × 6 ft. × 6 ft. high. In addition to the air condensers, a 3 ft. dome is attached to the top of the still which serves to return most of the volatilized aluminum chloride and its compounds. The operation is so controlled that the vapor is kept at the desired temperature as indicated by a thermometer placed in the vapor line at the point of exit of vapor into the final or water-cooled condenser. The temperature at this point should not exceed 350° F., otherwise, not only will heavy oils distil over, but the aluminum chloride (or its compounds with hydrocarbons) will enter the condenser and clog it up. Under the first named condition, the distillate obtained will be a mixture of gasoline, solvent oil and kerosene which are afterwards separated by fractional distillation. These products are all water white, sweet smelling, saturated, and need no refining with sulfuric acid. In practice, no treatment is given them, except a washing with alkali, followed with water, to remove hydrogen sulfide. With proper back-trapping of high boiling oils into the still from the air-cooled condensers and a temperature of 300° F. in the vapor line, the distillate obtained will be gasoline alone, which is ready for the market when washed with an alkaline solution.

I have spoken of the time which should be given the aluminum chloride for the accomplishment of the desired results. It is a mistake to assume that with a given amount of aluminum chloride and boiling it up with oil, the desired results will be obtained. That is far from the truth. I do not wish to impose upon your patience by dismissing consideration of the mechanism of this reaction by simply saying it is catalytic. I am fairly well satisfied that it is one of association or combination in the liquid phase and dissociation in the vapor phase. It is well known that aluminum chloride exists in the solid and liquid states as $Al_2Cl_6$, and in the vapor state as $AlCl_3$. It is also well known with what avidity aluminum chloride in the solid or liquid state will combine with other salts to form double salts. The most common of these double salts is that of aluminum and sodium chloride which, at one time, as you know, was the source of metallic aluminum (Castner process). Aluminum chloride probably combines with these high boiling, complex hydrocarbons in much the same way as it combines with sodium chloride and when the boiling temperature is reached these double compounds become unstable and dissociate into lower boiling hydrocarbons, which, under the temperature control imposed in the vapor line, leave the distilling system as fast as produced; $Al_2Cl_6$ is again formed and is capable of combining further with other high boiling hydrocarbons remaining in the still, and free carbon is formed simultaneously. This view of the reaction here involved is confirmed, I believe, by the operating conditions mentioned heretofore as necessary for obtaining the desired results.

While the operation, using crude oil as the starting material, can be carried on to produce larger or smaller quantities of gasoline, in practice it is carried on so as to convert the gas oil fraction into low boiling hydrocarbons and leave most of the high boiling hydrocarbons, that is, the paraffins and lubricating oils. Accordingly, the operation is interrupted after a portion of the crude has been converted into low boiling products, and the high boiling oil remaining in the still is pumped off while hot; on cooling it is worked up into the usual paraffin and lubricating products. The aluminum chloride remains in the still enmeshed in a mass of coke, and the methods of its recovery are found in my patents, referred to below.

As illustrative of the action of aluminum chloride

on high boiling petroleum oils, results obtained on typical crudes are given in Tables I to III.

### TESTS ON THREE CRUDE OILS

For the sake of convenience, the distillate obtained by distilling the crude before the addition of aluminum chloride is termed "primary distillate," the oil remaining in the still being termed "primary residual oil;" the distillate obtained by distilling the primary residual oil with aluminum chloride is termed "secondary distillate" and the oil remaining in the still, "secondary residual oil." Fahrenheit temperature and Baumé gravity are used throughout. The distillation tests were made on 100-cc. samples contained in standard Engler flasks connected to a 22 in. Liebig condenser. All flash points noted are in open cup tester. Viscosities noted are on the Saybolt Universal Viscosimeter at 100° F. W. W. and S. W. are abbreviations for water white and standard white, respectively.

TABLE I—TESTS ON TEXAS CRUDE OIL (SP. GR. 20.8° BÉ.)

Distilled until Free from Moisture and until the Naturally Occurring Gasoline and Kerosene Had Been Distilled Over

YIELD FROM CRUDE OIL

| | Per cent crude oil |
|---|---|
| Primary distillate | 7.14 |
| Primary residual oil | 91.26 |
| Loss | 1.60 |
| Total | 100.00 |

TESTS ON PRIMARY DISTILLATE

Sp. gr. 36° Bé. Bromine No. 5.46

Distillation over 260° F.

| Per cent | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| Up to | 320° | 344° | 368° | 386° | 400° | 442° | 468° | 490° | 505° | 520° F. |

| FRACTIONAL DISTILLATION | Per cent crude | Sp. gr. °Bé. | Color | Per cent sulfur | Bromine No. |
|---|---|---|---|---|---|
| Gasoline | 0.303 | 58.0 | W. W. | 0.065 | 4.8 |
| Gas naphtha | 0.180 | 51.0 | S. W. | 0.103 | 3.1 |
| W. W. kerosene | 1.260 | 41.6 | W. W. | 0.071 | |
| S. W. kerosene | 1.530 | 40.9 | W. W. | 0.133 | |
| Gas oil | 3.791 | 31.2 | | 0.386 | |
| Loss | 0.076 | | | | |
| Total | 7.140 | | | | |

TESTS ON PRIMARY RESIDUAL OIL

Sp. gr. 19.8° Bé. Viscosity 302

Distillation over 480° F.

| Per cent | 10 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|
| Up to | 530° | 566° | 600° | 656° | 680° F. |

Mixture of Primary Residual Oil and 7.5 Per Cent by Weight of Anhydrous Aluminum Chloride Brought to Boiling

| Time | Temperature of distillate: Still °F. | Vapor line | Per cent charge | Sp. gr. °Bé. | Distillation test: Over °F. | Per cent below 350° F. | Per cent below 450° F. | Dry point |
|---|---|---|---|---|---|---|---|---|
| 1:00 P.M. | 454 | 268 | Showed up | | | | | |
| 1:30 P.M. | 479 | 290 | 2.86 | 55.9 | 110 | 68 | 80 | 490 |
| 1:45 P.M. | 488 | 300 | 2.86 | 55.2 | 110 | 69 | 84 | 490 |
| 2:15 P.M. | 495 | 302 | 2.86 | 54.4 | 110 | 66 | 80 | 490 |
| 2:45 P.M. | 504 | 290 | 2.86 | 54.1 | 110 | 66 | 81 | 490 |
| 3:15 P.M. | 508 | 290 | 2.86 | 53.5 | 110 | 65 | 80 | 490 |
| 4:15 P.M. | 518 | 340 | 2.86 | 53.7 | 110 | 65 | 80 | 490 |
| 4:45 P.M. | 523 | 340 | 2.86 | 53.7 | 110 | 65 | 83 | 490 |
| 6:00 P.M. | 525 | 340 | 2.86 | 53.5 | 105 | 60 | 82 | 490 |
| 7:00 P.M. | 530 | 344 | 2.86 | 53.3 | 100 | 58 | 81 | 490 |
| 8:30 P.M. | 530 | 340 | 2.86 | 53.5 | 100 | 58 | 81 | 490 |
| 10:30 P.M. | 542 | 340 | 2.86 | 53.2 | 100 | 60 | 83 | 490 |
| 1:00 A.M. | 547 | 320 | 2.86 | 52.6 | 100 | 60 | 83 | 490 |
| 4:00 A.M. | 547 | 300 | 2.86 | 52.4 | 100 | 60 | 83 | 490 |
| 6:30 A.M. | 552 | 290 | 2.86 | 52.8 | 100 | 58 | 83 | 495 |
| 10:00 A.M. | 551 | 305 | 2.86 | 50.6 | 100 | 58 | 83 | 500 |
| 1:00 P.M. | 557 | 302 | 8.57 | 49.7 | 100 | 55 | 85 | 510 |
| | From back trap. | | 1.39 | | | | | |

Operation stopped at end of 24 hrs.

YIELD FROM DISTILLATION PRIMARY RESIDUAL OIL WITH $AlCl_3$

| | Per cent charge | Per cent crude |
|---|---|---|
| Secondary distillate | 52.86 | 48.24 |
| Secondary residual oil | 31.14 | 28.42 |
| Loss (gas and coke) | 16.00 | 14.60 |
| Total | 100.00 | 91.26 |

TESTS ON SECONDARY DISTILLATE

Sp. gr. 51.1° Bé.

Distillation over 100° F

| Per cent | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| Up to | 174° | 228° | 265° | 294° | 324° | 357° | 388° | 428° | 475° | 500° F. |

| FRACTIONAL DISTILLATION: FRACTIONS | Per cent charge | Per cent crude |
|---|---|---|
| Gasoline | 36.18 | 17.45 |
| Gas naphtha | 26.62 | 12.85 |
| W.W. kerosene | 2.65 | 1.28 |
| S.W. kerosene | 9.53 | 4.59 |
| Gas oil | 21.80 | 10.52 |
| Loss | 3.22 | 1.55 |
| Total | 100.00 | 48.24 |

| PROPERTIES OF FRACTIONS | Gasoline | Gas naphtha |
|---|---|---|
| Color | W.W. | S.W. |
| Odor | Sweet | Sweet |
| Bromine No. | 4.2 | 3.2 |
| Dry test | O. K. | O. K. |
| Heat test | 4 | 3 |
| Sulfur | 0.056% | 0.054% |
| Gravity | 64.5 | 50.2 |

Distillation of Gasoline Fraction—Above 117° F.

| Per cent | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 98 (dry point) |
|---|---|---|---|---|---|---|---|---|---|---|
| Up to | 160° | 170° | 179° | 190° | 208° | 222° | 239° | 261° | 293° | 339° F. |
| Sp. gr. | 82.1 | 79.0 | 75.3 | 70.9 | 66.0 | 61.8 | 57.7 | 64.2 | 50.4 | .... |

Distillation of Gas Naphtha Fraction—Above 215° F.

| Per cent | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 98 (dry point) |
|---|---|---|---|---|---|---|---|---|---|---|
| Up to | 240° | 246° | 253° | 260° | 270° | 280° | 293° | 306° | 332° | 350° F. |
| Sp. gr. | 57.0 | 55.0 | 54.1 | 52.8 | 51.3 | 50.2 | 49.1 | 47.5 | 45.4 | .... |

TESTS ON SECONDARY RESIDUAL OIL (FREED OF $AlCl_3$)

| Color | Flash test | Fire test | Viscosity |
|---|---|---|---|
| Red-green bloom | 185° F. | 250° F. | 105 |

Secondary Residual Oil Reduced with Steam

| Yield | Per cent charge | Per cent crude |
|---|---|---|
| Gas oil | 10.00 | 2.84 |
| Lubricating oil | 90.00 | 25.58 |
| Total | 100.00 | 28.42 |

| TESTS ON LUBRICATING OIL | Red-green bloom |
|---|---|
| Color | |
| Sp. gr. | 21.9 |
| Flash test | 290° |
| Viscosity | 122 |

SUMMARY

Products from $AlCl_3$ Process (Per Cent Crude Oil)

| DISTILLATE | Gasoline | Gas naphtha | Kerosene | Gas oil | Lubricating oil | TOTAL |
|---|---|---|---|---|---|---|
| Primary | 0.30 | 0.18 | 2.79 | | | 82.17 |
| Secondary | 17.45 | 12.85 | 5.87 | 17.15 | 25.58 | |
| LOSS DUE TO: | | | | | | |
| Distilling primary distillate | | | | | 1.60 | 17.83 |
| Distilling with $AlCl_3$ | | | | | 14.60 | |
| Redistillation of primary distillate | | | | | 0.08 | |
| Redistillation of secondary distillate | | | | | 1.55 | |
| Total | | | | | | 100.00 |

COMPARISON OF $AlCl_3$ PROCESS WITH USUAL PROCESS

| Per cent of crude oil by | $AlCl_3$ process | Usual process |
|---|---|---|
| Gasoline | 17.75 | 0.00 |
| Gas naphtha | 13.03 | 0.10 |
| Kerosenes | 8.66 | 4.30 |
| Gas oil | 17.15 | 52.00 |
| Lubricating oils | 25.58 | 25.50 |
| Asphaltic residual oil | .... | 12.00 |
| SUM OF PRODUCTS | 82.17 | 93.90 |
| Loss | 17.83 | 6.10 |
| Total | 100.00 | 100.00 |

TEXAS CRUDE OIL—In ordinary practice no gasoline is obtained from this type of Texas crude (sp. gr. 20.8 Bé.). By the aluminum chloride process (see Table I) 17.75 per cent is obtained and those who are familiar with the tests on petroleum products will see that this gasoline is as good as the natural gasoline made from any crude petroleum. The gas naphtha, which might very well be mixed with the gasoline, has been increased from 0.1 to 13.03 per cent. It will be observed that these low boiling oils have been made at the expense of the gas oil fraction and the asphaltic residual oil, the latter being broken down completely. Gas oil is the least valuable constituent of the crude. The asphaltic residual oil is used for fuel or is made into asphalt. The yield of lubricating oil by the aluminum chloride process is about the same as that in the usual process, but the quality of the former is greatly improved by virtue of the saturating effect of the aluminum chloride and the elimination of asphaltic and resinous constituents from the oil.[1]

[1] Samples of the products were furnished for examination

It will not be necessary to go into so much detail with the remaining crudes of which I desire to speak, but I have wanted to give you these figures on Texas crude to show how regularly the reaction proceeds over a long period of time, what the physical characteristics of the products are, and the yield as compared with the usual process.

CADDO (LA.) CRUDE OIL—This crude (sp. gr. 41° Bé.) belongs to the same type as Pennsylvania crude, the type known as paraffin-base crudes. Their products are clean smelling and require but little acid in refining. But even this type of crude is considerably improved by the aluminum chloride process (see Table II), while at the same time the yield of gasoline is greatly increased. The paraffin residual oil from Caddo crude is black and tarry on account of the presence of asphaltic constituents, but these are not usually present in large enough amounts to prevent the manufacture of good paraffin and paraffin lubricating oil. The distillation with aluminum chloride destroys the asphaltic constituents, giving an amber colored residual oil which may be easily worked into a product known commercially as vaseline, or into paraffin and paraffin lubricating oils. At the same time the yield of gasoline from the crude is increased from 18 to 42.32 per cent.

OKLAHOMA CRUDE OIL—The residual oil from this crude (sp. gr. 34° Bé.) by the usual process is a black, tarry mass, containing a large amount of asphaltic constituents and also paraffin. The amount of asphaltic constituents is so great, as a rule, that it is difficult to make paraffin and paraffin lubricating oils of the same grade as that obtained from Pennsylvania or Caddo residuums. By the aluminum chloride process (see Table III) this residual oil is cleaned of its asphaltic constituents, and paraffin wax and paraffin lubricating oils of excellent quality are made therefrom. At the same time, the yield of gasoline from the crude is greatly increased, at the expense of the less valuable fractions of the crude.

Although the crude petroleums from the various oil-producing districts in this country differ greatly in quality and in chemical composition, yet they are generally divided into three types: asphaltic-base crude, paraffin-base crude, and paraffin-asphaltic-base crude. The oils I have spoken of in this paper are representative of each of these types: Texas, asphaltic-base crude; Caddo, paraffin-base crude; and Oklahoma, paraffin-asphaltic-base crude. To give figures on other crudes would be merely a repetition of the results obtained on one of these. I shall therefore not take the time to give further examples. I might add that among the samples here are products made by the aluminum chloride process from 14 gravity California crude and 20 gravity Mexican crude.

### RECOVERY OF ALUMINUM CHLORIDE

But all the good results of this process would be of no commercial value if the aluminum chloride could not be reclaimed. This chemical, when made on the ton scale, is not so expensive as it is when made on the pound scale, but nevertheless its cost

TABLE II—TESTS ON CADDO (LA.) CRUDE OIL, SP. GR. 41° BÉ.

Distilled to Free It from Moisture and Natural Gasoline

YIELD FROM CRUDE OIL

| Primary distillate | Primary residual oil | Loss | Total |
|---|---|---|---|
| 26.19 | 71.43 | 2.38 | 100.00 |

TESTS ON PRIMARY DISTILLATE

Sp. gr. 58.2° Bé.

Distillation over 160° F.

| Per cent | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 | dry point |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Up to.... | 215° | 232° | 247° | 260° | 276° | 296° | 315° | 343° | 402° | 450° | 500° F. |

| FRACTIONAL DISTILLATION | Per cent charge | Per cent crude |
|---|---|---|
| Gasoline | 82.00 | 21.48 |
| Kerosene | 15.00 | 3.93 |
| Loss | 3.00 | 0.78 |
| TOTAL | 100.00 | 26.19 |

Mixture of primary residual oil and 5 per cent by weight of aluminum chloride was brought to boiling and distilled during period of 48 hrs. Temperature of the vapor line at the point of exit into final condenser was held around 350° F.

YIELD FROM AlCl$_3$ DISTILLATION OF PRIMARY DISTILLATE

| | Per cent charge | Per cent crude |
|---|---|---|
| Secondary distillate | 58.33 | 41.67 |
| Secondary residual oil | 26.20 | 18.71 |
| Loss (Gas and coke) | 15.47 | 11.05 |
| TOTAL | 100.00 | 71.43 |

TESTS ON SECONDARY DISTILLATE

Sp. gr. 54.0° Bé.

Distillation over 102° F.

| Per cent.. | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 | 98 dry point |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Up to.... | 212° | 260° | 293° | 315° | 340° | 365° | 388° | 414° | 450° | 480° | 500° F. |

| FRACTIONS | Per cent charge | Per cent crude |
|---|---|---|
| Gasoline | 50.00 | 20.84 |
| Solvent oil | 40.00 | 16.67 |
| Gas oil | 6.00 | 2.50 |
| Loss | 4.00 | 1.66 |
| TOTAL | 100.00 | 41.67 |

| PROPERTIES OF FRACTIONS | Gasoline | Solvent oil |
|---|---|---|
| Color | W.W. | W.W. |
| Odor | Sweet | Sweet |
| Bromine No. | 2 | 5 |
| Dry test | O. K. | O. K. |
| Heat test | 2 | 2 |
| Sp. gr. | 58.0 | 48.1 |

Distillation of Gasoline Fraction—Above 120° F.

| Per cent. | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 | dry point) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Up to.... | 198° | 221° | 240° | 258° | 272° | 288° | 301° | 322° | 348° | | 362° F. |

Distillation of Solvent Oil Fraction—Above 340° F.

| Per cent. | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 dry point | 98 dry point |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Up to | 354° | 360° | 364° | 369° | 374° | 381° | 390° | 400° | 416° | 430° | 440° F. |

TESTS ON SECONDARY RESIDUAL OIL

| Color | Sp. gr. | Flash test | Fire test | Pour test |
|---|---|---|---|---|
| Red-green bloom | 36.5° Bé. | 260° F. | 300° F. | 90° F. |

Secondary Residual Oil Distilled

| Yield | Per cent charge | Per cent crude |
|---|---|---|
| Gas oil | 30.00 | 5.61 |
| Paraffin residual oil | 70.00 | 13.10 |
| TOTAL | 100.00 | 18.71 |

Tests on Paraffin Residual Oil

| COLOR | Flash test | Fire test | Pour test |
|---|---|---|---|
| Amber | 385° F. | 420° F. | 105° F. |

SUMMARY

Products from AlCl$_3$ Process (Per Cent Crude Oil)

| DISTILLATE | Gasoline | Solvent oil | Kerosene | Gas oil | Paraffin residual oil | TOTAL |
|---|---|---|---|---|---|---|
| Primary | 21.48 | | 3.93 | | | 25.41 |
| Secondary | 20.84 | 16.67 | | 8.11 | 13.10 | 58.72 |
| Loss Due to | | | | | | |
| Aluminum chloride distillation | | | | | 12.71 | 15.87 |
| Working distillates into standard products | | | | | 3.16 | |
| TOTAL | | | | | | 100.00 |

COMPARISON OF AlCl$_3$ PROCESS WITH USUAL PROCESS

| Per cent of crude oil | AlCl$_3$ process | Usual process |
|---|---|---|
| Gasoline | 42.32 | 18.00 |
| Solvent oil | 16.67 | 12.00 |
| Kerosene | 3.93 | 35.00 |
| Gas oil | 8.11 | 21.00 |
| Paraffin residual oil | 13.10 | 11.00 |
| SUM OF PRODUCTS | 84.13 | 97.00 |
| LOSS | 15.87 | 3.00 |
| TOTAL | 100.00 | 100.00 |

is high, and from a dollars and cents point of view, it is necessary to recover it. This is done by the processes set forth in my patents.

After a time, 48 hours or longer, aluminum chloride used in distilling oils, even the driest of oils, loses its catalytic activity and becomes converted into a coky mass. Analysis of the coky mass shows chlorine and aluminum present in the right proportions to form aluminum chloride, but the latter is, so to speak, masked. It does not display its ordinary reaction with petroleum hydrocarbons. The granular coky residue, after it comes from the oil-converting process, carries varying amounts of oils with it. If allowed to cool down in the presence of the body of oil, it may carry 40 to 50 per cent of its weight of oil. If the oil body has been separated while hot from the coky residue, the amount of oil will be reduced to 4 or 5 per cent.

After removing the oil, or the bulk of it, from the coky residue, the aluminum chloride can be extracted from the latter with water or steam to obtain a concentrated solution of hydrated aluminum chloride. Aluminum chloride in the hydrated state does not have the catalytic property of the anhydrous material, but the hydrated salt can be used as the raw material for making the anhydrous salt. To do this, advantage is taken of the property of hydrated aluminum chloride, breaking up when moderately heated to form aluminum oxide and hydrochloric acid gas. The alumina, when mixed with carbon and treated with hydrochloric acid vapors at a high temperature, reacts to form the anhydrous chloride, hydrogen and oxides of carbon. In utilizing this property, one portion of the hydrated chloride is heated to produce hydrochloric acid vapors and alumina, and these vapors on drying enter a further charge of alumina and carbon heated to redness. The hydrochloric acid vapors given off at a moderate temperature are thus utilized in further operations at high temperatures.

In another method of recovery, and the preferred one, the coky residue is heated to red heat in an atmosphere of chlorine which disengages the aluminum chloride from the carbon. Aluminum chloride volatilizes normally at a temperature around 365° F., but the coky residue may be heated to redness without much evolution of these vapors. If the heating is done in an atmosphere of chlorine, the aluminum chloride is unlocked; *i. e.*, it vaporizes away from the carbon and is condensed in suitable receivers.

Of course, the last and ultimate test of any process is whether it will work, and work successfully, without undue petting. That the aluminum chloride process is now an assured commercial success, is, of course, due to its own merits. But I cannot forego this opportunity to speak of the generous aid from the Gulf Refining Co., which has made success possible, and the valuable advice and help from its officers.

Although this account by no means covers the full scope of the aluminum chloride reaction with petroleum oils, yet to speak further would lead me outside of my subject. It is with deep satisfaction that I have been privileged to read this paper before the American Institute of Chemical Engineers, in the capacity of a recent initiate among you, and I trust I may have the pleasure of reading further papers before you in due course of time.

THE GULF REFINING COMPANY
BAYONNE, NEW JERSEY

TABLE III—TESTS ON OKLAHOMA CRUDE OIL (SP. GR. 34° BÉ.)

Distilled to Free It from Moisture and Natural Gasoline

YIELD FROM CRUDE OIL

| Primary distillate | Primary residual oil | Loss | Total Per cent |
|---|---|---|---|
| 20.83 | 78.31 | 0.86 | 100.00 |

TESTS ON PRIMARY DISTILLATE

Sp. gr. 54.1° Bé. Color W.W

Distillation over 152° F

| Per cent.. | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 | (dry point) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Up to.... | 210° | 226° | 242° | 252° | 271° | 290° | 313° | 348° | 408° | 488° | F. |

| FRACTIONAL DISTILLATION | Per cent charge | Per cent crude |
|---|---|---|
| Gasoline | 70.00 | 14.58 |
| Kerosene | 20.00 | 4.17 |
| Gas oil | 7.50 | 1.56 |
| Loss | 2.50 | 0.52 |
| TOTAL | 100.00 | 20.83 |

TESTS ON PRIMARY RESIDUAL OIL

| Color | Sp. gr. | Flash test | Fire test | Pour test |
|---|---|---|---|---|
| Black | 29.8° Bé. | 170° F. | 205° F. | 20 |

Distillation over 330° F.

| Per cent | 10 | 20 | 30 | 40 | 45 per cent |
|---|---|---|---|---|---|
| Up to | 436° | 484° | 543° | 590° | Below 600° F. |

MIXTURE OF PRIMARY RESIDUAL OIL AND 5 PER CENT BY WEIGHT OF ALUMINUM CHLORIDE WAS DISTILLED DURING PERIOD OF 48 HRS. TEMPERATURE OF THE VAPOR LINE AT THE POINT OF EXIT INTO FINAL CONDENSER WAS HELD AROUND 350° F.

YIELD FROM $AlCl_3$ DISTILLATION OF PRIMARY DISTILLATE

| | Per cent charge | Per cent crude |
|---|---|---|
| Secondary distillate | 64.61 | 50.60 |
| Secondary residual oil | 17.97 | 14.07 |
| Loss | 17.42 | 13.64 |
| TOTAL | 100.00 | 78.31 |

TESTS ON SECONDARY DISTILLATE

Sp. gr. 48.3° Bé.

Distillation over 140° F.

| Per cent. | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 | 98 (dry point) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Up to | 225° | 270° | 294° | 326° | 358° | 382° | 413° | 454° | 503° | 547° | 570° F |

| FRACTIONS | Per cent charge | Per cent crude |
|---|---|---|
| Gasoline | 40.60 | 20.24 |
| Kerosene | 50.00 | 25.30 |
| Gas oil | 7.50 | 3.80 |
| Loss | 2.50 | 1.26 |
| TOTAL | 100.00 | 50.60 |

TESTS ON GASOLINE

| | |
|---|---|
| Color | W.W. |
| Odor | Sweet |
| Bromine No | 1.8 |
| Dry test | 0 K |
| Heat test | 2 |
| Per cent S | 0.027 |
| Sp. gr | 64.5 |

Distillation of Gasoline Fraction Over 130° F

| Per cent | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | Residue |
|---|---|---|---|---|---|---|---|---|---|---|
| Up to.... | 160° | 186° | 200° | 213° | 222° | 238° | 252° | 270° | 299° | 8.3 per cent |
| Sp. gr. | 83.8 | 76.2 | 70.1 | 66.6 | 62.8 | 60.4 | 58.5 | 56.1 | 53.3 | 48.2 |

TESTS ON SECONDARY RESIDUAL OIL

| Color | Sp.gr | Pour test | Flash test |
|---|---|---|---|
| Red-green bloom | 28.2° Bé. | 90° F. | 230° F. |

Secondary Residual Oil Distilled

| Yield | Per cent charge | Per cent crude |
|---|---|---|
| Wax stock | 60.00 | 8.44 |
| Cylinder oil | 40.00 | 5.63 |
| TOTAL | 100.00 | 14.07 |

SUMMARY

Products from $AlCl_3$ Process (Per Cent Crude Oil)

| DISTILLATE | Gasoline | Kerosene | Gas oil | Residual oil | TOTAL |
|---|---|---|---|---|---|
| Primary | 14.58 | 4.17 | | | 83.72 |
| Secondary | 20.24 | 25.30 | 5.36 | 14.07 | |
| Loss Due to | | | | | |
| Aluminum chloride distillation | | | | 13.64 | 16.28 |
| Working distillate into standard products | | | | 2.64 | |
| TOTAL | | | | | 100.00 |

COMPARISON OF $AlCl_3$ PROCESS WITH USUAL PROCESS

| Per cent of crude oil | $AlCl_3$ process | Usual process |
|---|---|---|
| Gasoline | 34.82 | 12.50 |
| Kerosene | 29.47 | 41.00 |
| Gas oil | 5.36 | 35.00 |
| Residual oil | 14.07 | 9.00 |
| SUM OF PRODUCTS | 83.72 | 97.50 |
| Loss | 16.28 | 2.50 |
| TOTAL | 100.00 | 100.00 |

## THE FUSIBILITY OF COAL ASH IN MIXTURES OF HYDROGEN AND WATER VAPOR[1]

By A. C. Fieldner and Alex. L. Feild

In a previous paper by Fieldner and Hall,[2] experimental data were given on the influence of the following factors on the softening temperatures of a number of typical coal ashes:

1—Fineness of ash
2—Shape and inclination of test-piece
3—Rate of heating
4—Nature of surrounding atmosphere.

As a result of this work, which was undertaken with a view to standardizing a method of determining the "fusing" or softening temperature of coal ash, which would yield uniform results in different laboratories, the authors made the following recommendations regarding the first three factors: (1) The ash to be ground to a powder, all of which should pass through a 200 mesh sieve; (2) the ash to be molded, with the aid of dextrin solution, in the form of a Seger cone 1 in. high × $^3/_{16}$ in. wide at the base, erected with one side vertical on an infusible base made of equal parts of kaolin and alumina; (3) a rate of heating of 5° per minute from at least 200° below point of initial deformation until a deformation begins, and thence 2° per minute until the cone is down. No recommendation regarding the atmosphere surrounding the cone was made, although it was pointed out that an oxidizing atmosphere of air, free from all traces of reducing gases, was a satisfactory standard as regards mere duplication in different laboratories.

On the other hand, attention was called to the fact that much lower softening temperatures were obtained under certain reducing conditions not unlike those which may prevail in fuel beds where clinker formation takes place.

The present investigation was undertaken with the object of developing a method for determining the lowest possible softening temperature of a coal ash, and of showing whether the slag formed under the conditions imposed by such a method is comparable to that found in fuel-bed clinkers.

### GENERAL AND THEORETICAL

It was early apparent in the work of Fieldner and Hall[3] that the difference in the softening temperature of a given ash when operating in various atmospheres was due to the state of oxidation or reduction of the iron content of the ash in question. In an atmosphere of air the original ferric oxide of the ash entered slag formation as such, unless the temperature attained was sufficient for the thermal decomposition of this oxide to magnetite ($Fe_3O_4$); in an atmosphere of dry hydrogen or carbon monoxide free from carbon dioxide, a large proportion of the ferric oxide was reduced to metallic iron and thus became unavailable for slag formation; obviously both of these conditions must tend to give higher softening temperatures than a condition of intermediate reduction favorable to the formation of the easily fusible ferrous silicates. Since this latter condition is likely to occur in that part of the fuel bed where ash comes in contact with incandescent carbon, carbon monoxide, hydrogen and hydrocarbon gases, it is reasonable to suppose that this lowest softening temperature should have a closer relation to clinker formation than either of the higher results obtained in strongly reducing or oxidizing atmospheres.

The problem then resolves itself into an investigation of the effect of various mixtures of a reducing gas and its product of oxidation on the softening temperature with a view to finding that mixture which will give the lowest softening temperature.

For experimental reasons we have chosen hydrogen as the reducing gas, since any desired mixture of hydrogen and water vapor can be readily secured by bubbling the hydrogen through water at the proper temperature.

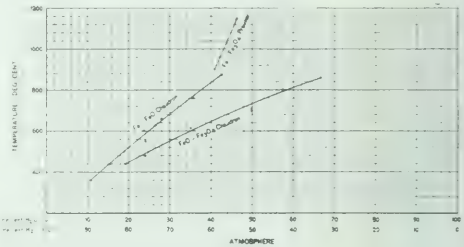


Fig. 1—Equilibrium Data of Preuner and of Chaudron

The equilibrium between hydrogen, water vapor, Fe

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2 \qquad (1)$$

and $Fe_3O_4$ was first studied by Deville[1] at various temperatures between 200° and 1000°, and later with greater precision by Preuner[2] at three temperatures. Preuner found the following mean values for the equilibrium constant:

| Temperature of solid phases | 900° C. | 1025–1050° C | 1150° C |
|---|---|---|---|
| $p_{H_2O}$ / $p_{H_2}$ | 0.69 | 0.78 | 0.86 |

Chaudron[3] has recently reported two series of equilibria of iron and its oxides in hydrogen and water vapor corresponding to the following reactions:

$$Fe + H_2O \rightleftarrows FeO + H_2 \qquad (2)$$

$$3FeO + H_2O \rightleftarrows Fe_3O_4 + H_2 \qquad (3)$$

His values for the equilibrium constants are as follows

| Reaction (2), Fe and FeO | | Reaction (3), FeO and $Fe_3O_4$ | |
|---|---|---|---|
| Temperature of solid phases ° C. | $p_{H_2O}$ / $p_{H_2}$ | Temperature of solid phases ° C. | $p_{H_2O}$ / $p_{H_2}$ |
| 360 | 0.12 | 440 | 0.24 |
| 440 | 0.18 | 480 | 0.32 |
| 500 | 0.23 | 500 | 0.33 |
| 550 | 0.32 | 615 | 0.54 |
| 600 | 0.31 | 700 | 1.00 |
| 630 | 0.36 | 710 | 1.00 |
| 660 | 0.39 | 800 | 1.35 |
| 760 | 0.55 | 860 | 2.00 |
| 875 | 0.74 | .. | .. |

[1] Presented at the Atlantic City Meeting of the American Society for Testing Materials, June 22, 1915; published by permission of the Director, U. S. Bureau of Mines.

[2] This Journal, **7** (1915), 309 and 474.

[3] Loc. cit.

[1] *Compt. rend.*, **70** (1870), 1105–1111 and 1201–1205.

[2] G. Preuner, *Z. physik. Chem.*, **47** (1904), 385–417.

[3] G. Chaudron, *Compt. rend.*, **159** (1914), 237–239.

No similar data are available on the behavior of ferric oxide ($Fe_2O_3$). Hence the above data for magnetite include the only information we have as to the probable or possible phases in which the iron oxide of coal ash may exist in various mixtures of hydrogen and water vapor at the sintering temperature of the ash.

In Fig. 1 are plotted the equilibrium data of Preuner, and of Chaudron. Assuming that $Fe_2O_3$ reacts as regards reduction in a similar manner as $Fe_3O_4$ it is evident that at temperatures up to 1150° no reduction to metallic iron can take place in a mixture of equal parts by volume of hydrogen and water vapor. At a temperature of 850°, according to Chaudron's figures, FeO would be the stable solid phase in mixtures containing not less than 43 nor more than 63 per cent of water vapor, it being assumed in both cases that a gas mixture of constant composition is passed over the heated oxide continuously, sweeping the gaseous products of the reaction out of the apparatus. It seems possible, therefore, that a minimum softening temperature of coal ash may be found in a mixture approximating equal parts by volume of hydrogen and water vapor, provided the heating is sufficiently slow to allow the reaction to approach equilibrium at the various temperatures.

## EXPERIMENTAL

FURNACE—The arrangement of furnace and saturator is shown in Figs. 2 and 3. A Heraeus platinum-foil resistance furnace which happened to be available was equipped with an extra heater of $^3/_{100}$-inch platinum wire, *h*, wound on the inside of the alundum tube *e* and connected in series with the platinum-foil[1] heating unit of the Heraeus furnace, as described in the previous paper.[2]

This alundum heater tube was supported on two alundum rings, leaving a $^1/_2$-in. air space between the heater tube and the Heraeus porcelain tube. Two additional alundum tubes, *c* and *u*, were placed similarly, one at each end of the platinum-wound tube.

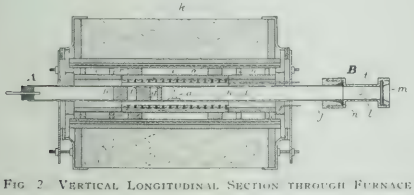

FIG. 2—VERTICAL LONGITUDINAL SECTION THROUGH FURNACE

Through the furnace, modified in this way, was passed a tube, *AB*, of fused silica, glazed on both sides, $^5/_8$ in. inside diameter and 17 in. long.

The gas mixture entered the silica tube through the brass end-piece *B*, which was specially designed to make a gas-tight connection by means of the brass bushing *j* and the asbestos packing *n*. A removable glass window, *m*, permitted removal and insertion of cones in the furnace, and observation of deformation, and of temperature with the optical pyrometer. The glass was held in place between asbestos washers by a threaded brass ring.

An air bath (*a*, Fig. 4) was placed around the end-piece *B*, to maintain its temperature above 100° C. and thus avoid any condensation of water vapor; the exit end *A* was made sufficiently short so that its temperature would be above 100° C. The gas mixture passed out through the glass capillary tube inserted in the rubber stopper at *A*.

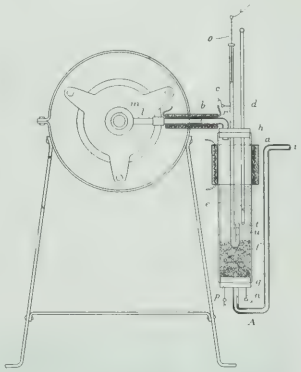

FIG. 3—FRONT ELEVATION OF FURNACE AND VERTICAL SECTION THROUGH SATURATOR

Alundum stops, *b*, *f* and g, were placed at intervals back of the middle of the inner heater to provide a suitable background for taking readings with the optical pyrometer. These stops were made of thin-walled alundum tubes closed at one end, fitting snugly in the silica tube. To avoid rapid devitrification of the fused silica tube, temperatures were not carried above 1400°.

"SATURATOR"—The apparatus by which various mixtures of hydrogen and water vapor were formed depends upon the saturation of pure hydrogen gas with water vapor at temperatures ranging from zero to within a degree or two of the boiling point. It is shown in Fig. 3 with furnace connections as used, except the hot-air bath surrounding the brass end-piece *m* and side tube *l*. The saturator consists of a glass tube, *e*, $1^3/_4$ in. in diameter and 9 in. long, closed at the ends with rubber stoppers. Through the upper stopper *h*, passes the thermometer *d*; the outlet tube *r*, communicating with the furnace through the brass tube *l*; and a compact, adjustable vapor-pressure thermo-regulator, with electrical connections controlling through a relay the current in the heating coil *f*. The thermo-regulator is essentially that described by Feild,[1] without the refinement of being independent of atmospheric pressure. It consists of a bent glass tube, in the short arm of which is a small quantity of liquid *u*—ether, alcohol, or water, depending on the temperature desired—resting on a mercury column, *c*. Above the liquid *u*, is a small quantity of its saturated vapor, *t*, the pressure of which depends only upon the temperature and determines the height of the mercury column *c*. This mercury column, *c*, makes and breaks contact with the platinum wire *O*. The temperature control, with a continuous stream of hydrogen bubbling around the glass beads *f* and through the water *e*, was within 0.1 to 0.2° C., which was sufficiently accurate for the purpose of the experiments. Hydrogen stored in a high-pressure cylinder was introduced at *i*,

[1] A nichrome heating element could as well be used for the outer heating unit.

[2] Fieldner and Hall, *Loc. cit.*

[1] Alex. L. Feild, an electrical contact vapor pressure thermo-regulator, *J. Am. Chem. Soc.*, **36** (1914), 72–76

and its flow so adjusted as to give the desired current of hydrogen and water vapor through the fused silica furnace tube. The water vapor present in the mixture of hydrogen and water vapor was prevented from condensing to liquid water on its passage to the furnace by two heating coils, *a* and *b*, constructed of nichrome wire wound on alundum cores and heated, similarly to the immersed coil *f*, by a current from a low-voltage transformer operating at about 11 volts. An air bath of asbestos paper (Fig. 4, *a*), heated by a small electric hot-plate, was placed around the brass end-piece *m*, and side tube *l*.

TESTING THE EFFICIENCY OF THE SATURATOR—Assuming complete saturation, the composition of the mixture of hydrogen and water vapor obtained from the saturator depends upon the temperature of the water in the saturator. The relative proportion of hydrogen and water vapor present is proportional to their respective partial pressures. The partial pressure of water vapor

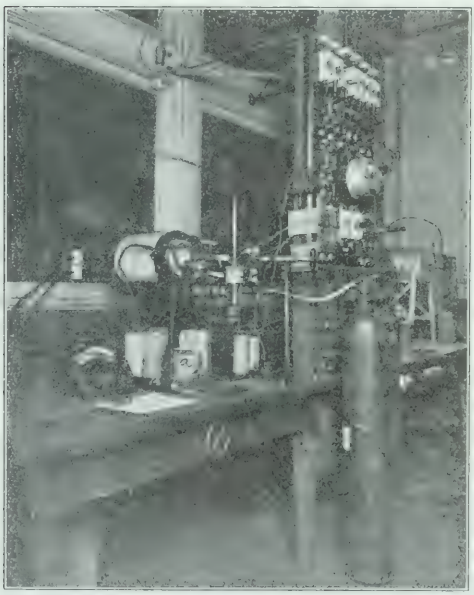

Fig. 4—Apparatus for Testing the Efficiency of the Saturator

at various temperatures is known. Hence, that of hydrogen can be calculated—the sum of the two being equal to atmospheric pressure plus a negligibly small pressure required to force the mixture through the furnace tube.

The apparatus[1] shown in Fig. 5 was designed for the analysis of the mixture of hydrogen and water vapor. These analyses were made to determine how closely the composition of the mixture corresponded to the theoretical, calculated from the temperature of the saturator water. The device was attached to the outlet end of the vitreosil furnace tube *d* (Fig. 5). It consists of the sampling bulb *a*, 50 mm. in diameter and 250 mm. long, communicating with a mercury manometer, *b*, closed at one end. The gas stream from the heated furnace was passed for 30 minutes through the sampling cylinder to remove all traces of air before a determination was to be made. In order to prevent condensation of water from the mixture, the entire apparatus was immersed in a jacket of boiling water, *h*, heated by the coil *e*. The outlet tube of the sampling cylinder passes through the rubber stopper in the bottom of the water jacket, and terminates in a capillary, *f*. The mixture is prevented from condensing in the inlet tube, by means of a heating coil, *c*. This tube also contains a portion drawn out to a capillary. When a sample was to be taken, both capillaries were sealed off with a blowpipe. The boiling water was then removed, replaced by water at room temperature, and the pressure indicated by the manometer observed, as well as the temperature of the water-jacket, after temperature equilibrium had been obtained. Since a portion of the water vapor condensed to liquid water at room temperature, the partial pressure of hydrogen at the same temperature was calculated by subtracting from the observed manometric pressure the vapor pressure of water for that temperature. The partial pressure of the hydrogen in the original mixture at 100° C. was calculated by multiplying the result by the ratio of the respective absolute temperatures. The partial pressure of the water vapor was then found by subtracting the partial pressure of the hydrogen at 100° C., from the barometric pressure observed at the time of taking the sample.

Fig. 5—Apparatus for Analyzing Hydrogen and Water Vapor Mixtures

ANALYSES OF HYDROGEN-WATER VAPOR MIXTURES

The analyses made by the method described above appear in Table I and the results are considered satisfactory.

Since these analyses, made upon samples containing large quantities of water vapor, differed from the theoretical by amounts probably within the limits of experimental error, it was not considered necessary to make further analyses upon samples containing small percentages of water vapor. Here without doubt the probability of securing a practically theoretical mixture is greater than where the hydrogen is passed through the water in the saturator at temperatures near the boiling point.

PREPARATION OF TEST-PIECE—The ash ground to 200 mesh was molded with the aid of dextrin solution into a slender triangular pyramid or Seger cone and mounted with one side vertical, in a refractory base according to the method described in a previous re-

[1] Described by G. A. Burrell

TABLE I—ANALYSES OF HYDROGEN-WATER VAPOR MIXTURES

| Exp. No. | Temperature of Water in Saturator | Correction for | | | Barometer reading Mm | Manometer reading Mm | Temp °C | Vapor pressure of water at (a)°C | Average Volume Percentages of Hydrogen and Water Vapor as Determined by Calculation from | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Experimental data | | Temperature of saturation | |
| | Uncorrected | Scale | Superheated steam | Corrected | | | | | Hydrogen | Water vapor | Hydrogen | Water vapor |
| $I_1$ | 81.0 | —0.16 | —0.19 | 80.65 | 736.9 | 323 | 22 | 19.61 | 52.1(a) | 47.9(a) | 50.6 | 49.4 |
| $I_2$ | ... | ... | ... | ... | ... | 338 | 28 | 28.01 | | | | |
| $II_1$ | 95.0 | ... | ... | 94.48 | 735.0 | 134 | 28 | 28.01 | 19.2 | 80.8 | 15.4 | 84.6 |
| $II_2$ | ... | ... | ... | ... | ... | 128 | 24 | 22.11 | | | | |
| $III_1$ | 97.0 | ... | ... | 96.48 | 751.2 | 84 | 29 | ... | 9.0 | 91.0 | 10.9 | 89.1 |
| $III_2$ | ... | ... | ... | ... | ... | 84 | 29 | ... | | | | |

(a) CALCULATION FOR $I_1$

323–19 ..... 22° C.

Then 304 × (373 ÷ 295) ..... 100° C.

384 ÷ 737 ..... Vapor

port.[1] On account of the small diameter of the fused silica tube, it was possible to use only the upper half of the standard $^3/_{16}$ inch by 1 inch cone which was adopted in the former experiments. The dextrin binder was burned off before placing the cone in the furnace by ignition at a red heat in a muffle.

MEASUREMENT OF TEMPERATURE—The temperatures were read with a Wanner optical pyrometer, which was sighted on the thin alundum disk just back of the cone. Correction for absorption of the glass window was made as described in the previous paper.[1]

The pyrometer was compared daily with the standard amyl acetate flame, and once each week a thin piece of Kahlbaum's pure copper foil was substituted for the ash cone and its melting point read in an atmosphere of hydrogen. The results were between 1075 and 1090° C. (M. P. = 1083°C.)

TABLE II—DESCRIPTION AND ORIGIN OF SAMPLES AND ANALYSES OF THEIR ASHES

| Lab. No. | Description | Location of Mine | | | | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | $Na_2O$ | $K_2O$ | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Bed | Nearest town | County | State | | | | | | | | | |
| 15848 | Bituminous | Thompson | Marvel | Bibb | Ala | 54.8 | 27.0 | 7.0 | 1.3 | 4.3 | 1.7 | 0.3 | 3.1 | 1.4 |
| 16586 | Semi-bituminous | Poca. No. 3 | Big Four | McDowell | W. Va. | 37.2 | 25.5 | 11.8 | 1.5 | 12.6 | 1.9 | 1.4 | 0.4 | 5.6 |
| 15844 | Bituminous | Mingo | Fork Ridge | Claiborne | Tenn | 42.2 | 30.6 | 19.0 | 1.2 | 1.3 | 1.0 | 1.3 | 2.0 | 0.5 |
| 16243 | Bituminous | No. 8 | Boonville | Warwick | Ind. | 37.1 | 17.6 | 35.9 | 0.7 | 3.2 | 0.9 | 0.4 | 1.8 | 2.5 |
| 15845 | Bituminous | Coal Creek | Oliver | Morgan | Tenn. | 12.3 | 12.2 | 69.7 | 0.4 | 3.9 | 0.7 | 0.3 | 0.6 | 0.2 |

EXPERIMENTAL RESULTS

Softening-temperature determinations were made upon five different samples of coal ash (see Table II) containing from 7 to 69 per cent of ferric oxide ($Fe_2O_3$), in various mixtures ranging from pure dry hydrogen to pure water vapor. The temperature was raised at the rate of 10 to 15° per minute to approximately 900°, then 5° per minute until deformation began, and 2° per minute thereafter until the cone was down. The dry hydrogen was obtained by bubbling the hydrogen through a wash bottle of concentrated sulfuric acid. The 100 per cent water-vapor atmosphere was obtained by cutting off the hydrogen from the saturator and heating the water to boiling.

All the results obtained are given in Table III, in which the softening temperature is given as a temperature interval, the lower figure before the hyphen being the temperature at which deformation (rounding of the apex or bending of the cone) began, and the higher figure following the hyphen being the temperature at which the cone had bent over so that the apex touched the base, or, failing to bend, had softened to a lump. This latter final deformation point is meant when reference is made to the "fusion," "softening" or "deformation" point of an ash.

The final deformation points are plotted in Fig. 6, in which the abscissae represent the percentages of water vapor in the mixture and the ordinates the temperatures of final deformation. The initial deformation points are plotted in a similar manner in Fig. 7.

It will be noted that both sets of curves have well-defined minima in the neighborhood of 40 to 70 per cent water vapor. The final deformation points, which were more accurately determined, show a fairly uniform minimum in mixtures ranging from 30 to 70 per cent water vapor. This is a fortunate circumstance, as it enables the formulation of a practical method of determining the lowest softening temperature of an ash in a mixture of approximately equal parts of hydrogen and water vapor. Apparently the gas mixture need be controlled only between limits of 30 and 70 per cent water vapor to insure the lowest softening temperature within the unavoidable experimental deviation in determinations of this character.

TABLE III—SOFTENING TEMPERATURES IN VARIOUS MIXTURES OF HYDROGEN AND WATER VAPOR

| Lab. No. | 15848 | 16586 | 15844 | 16243 | 15845 |
|---|---|---|---|---|---|
| % $Fe_2O_3$ | 7.0 | 11.8 | 19.0 | 35.9 | 69.7 |
| Atmos. % $H_2O$ | Softening Temperatures, °C. | | | | |
| 0.0 | 1322(a)–1360(b) | 1390–1402 | Above 1400 | 1304–1370 | Above 1400 |
| 0.7 | ... | ... | ... | 1331–1355 | ... |
| 5.7 | 1279–1290 | 1313–1360 | Above 1400 | ... | Above 1400 |
| 6.3 | ... | ... | ... | 1248–1263 | ... |
| 7.6 | ... | ... | ... | 1220–1270 | ... |
| 10.7 | ... | ... | 1340 | ... | ... |
| 12.4 | ... | 1279 1313 | 1155 1271 | ... | ... |
| 15.8 | ... | ... | ... | ... | 1304–1330 |
| 18.1 | ... | ... | ... | 1104–1198 | ... |
| 19.9 | ... | ... | 1173–1271 | ... | ... |
| 29.6 | ... | ... | ... | 1056–1064 | ... |
| 31.2 | 1179–1271 | 1227–1251 | 1173–1263 | ... | 1225 1322 |
| 41.7 | ... | ... | ... | 1048 1062 | ... |
| 51.2 | ... | ... | ... | 1072 1078 | ... |
| 57.5 | 1220–1292 | 1220–1258 | 1173–1255 | ... | 1104 1322 |
| 77.2 | ... | ... | ... | (c) 1095 | ... |
| 83.2 | ... | ... | ... | (c)–1095 | ... |
| 83.9 | 1173–1295 | 1241–1249 | 1227 1263 | ... | 1206 1350 |
| 90.3 | ... | 1227 1251 | 1206 1295 | (c) 1095 | ... |
| 94.8 | ... | ... | ... | 1048–1080 | ... |
| 100.0 | 1350–1370 | 1313–1322 | Above 1400 | 1304–1313 | Above 1402 |

(a) Beginning of deformation.
(b) End of deformation or "down" point of cone
(c) Starting point not observed

It will be noted that the gas mixture need be controlled only between limits of 30 and 70 per cent water vapor to insure the lowest softening temperature within the unavoidable experimental deviation in determinations of this character.

The pronounced effect of viscosity on the rate of deformation of the ash cones is shown in the relative positions of the curves of initial deformation in Fig. 7 and the curves of final deformation in Fig. 6. Sample 16586 has the highest initial-deformation temperature and next to the lowest final-deformation temperature in a 50 : 50 mixture of hydrogen and water vapor. This is due to the low viscosity of the melting eutectic formed from this ash, which contains 12.6 per cent of calcium oxide, a larger percentage of this basic oxide than occurred in any of the other samples.

The sharp rise of the softening-point curves at both the oxidizing and reducing end confirms the reasons

[1] Fieldner and Hall, *Loc. cit.*

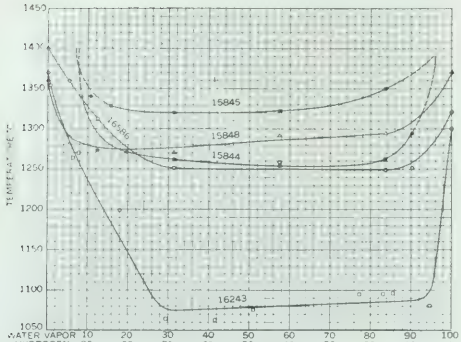


FIG. 6—EFFECT OF VARIOUS MIXTURES OF HYDROGEN AND WATER VAPOR ON THE SOFTENING POINT (FINAL DEFORMATION) OF COAL ASH

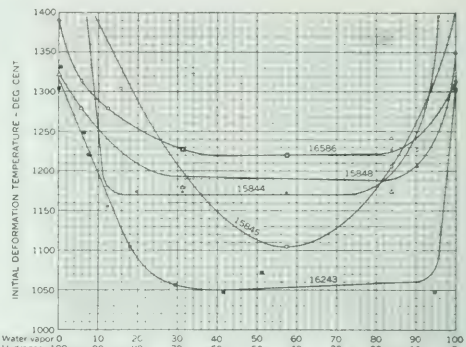


FIG. 7—EFFECT OF VARIOUS MIXTURES OF HYDROGEN AND WATER VAPOR ON THE TEMPERATURE OF INITIAL DEFORMATION OF COAL ASH

advanced in a previous paper[1] for the large variations in results obtained in different furnaces. It is evident that no concordant results can be obtained in oxidizing atmospheres containing small proportions of reducing gas or similarly in essentially reducing atmospheres with small admixtures of oxidizing gases, since in these regions the curves have a sharp inclination.

## RELATION OF SOFTENING TEMPERATURE IN ATMOSPHERES OF HYDROGEN AND WATER VAPOR TO CLINKER FORMATION UNDER FURNACE CONDITIONS

The general form of the softening-point curves in hydrogen and water vapor suggests a choice of three atmospheres under which uniform softening points may be determined, *viz.:* (1) 100 per cent hydrogen; (2) 50 per cent hydrogen and 50 per cent water vapor; (3) 100 per cent water vapor or 100 per cent air, which gives nearly the same result as is shown in Table IV.

TABLE IV—COMPARISON OF SOFTENING POINTS IN AIR AND WATER VAPOR

| LAB. NO. | Softening point in air 3/16 in. × 1 in. cones | Water vapor 3/32 in. × 1/2 in. cones |
|---|---|---|
| 15845 | 1458° C. | Above 1400° C. |
| 15844 | 1490 | Above 1400° C. |
| 15848 | 1425 | 1370 |
| 16243 | 1335 | 1313 |
| 16586 | 1322 | 1322 |

The atmosphere to be selected for a standard softening temperature test should be that one which produces a slag with the iron in the same state of oxidation as is usually found in fuel-bed clinkers. Determinations were therefore made of the relative percentages of ferrous, ferric and metallic iron in the glassy portions of furnace clinkers and in the ash cones fused in the three above-mentioned atmospheres.

## FERROUS, FERRIC AND METALLIC IRON IN FUSED ASH CONES AND CLINKER SLAGS

Twelve to fourteen ash cones, aggregating about 2 grams, were placed in a platinum boat, and heated in the silica tube of the furnace at the usual rate up to the softening temperature of the particular ash in the particular atmosphere in question. The boat and its contents were held at this temperature for 30 minutes to allow the softening reactions to approach equilibrium.

[1] Fieldner and Hall, *Loc. cit*

As in the case of softening-temperature determinations, the cones were heated to redness previous to the experiment to oxidize and remove the organic binder. At the end of the 30-minute heating period the electrical current was cut off and the furnace allowed to cool rapidly, without interrupting the gas stream. It would have been better to avoid any possibility of change during cooling to have quenched the fusion suddenly. However, the viscosity of these ash melts was so great that little change was probable at the rate of cooling used. The fused material appeared glassy.

Fusions were made of sample 16243 in 100 per cent hydrogen, 50 : 50 per cent mixture of hydrogen and water vapor, and 100 per cent water vapor; also of sample 15848 in 50 : 50 hydrogen-water vapor, and sample 13629 in air.

After cooling the furnace, the fusions were removed from the boat and were pulverized, first by impact in a diamond mortar of hardened steel, and then in an agate mortar, to 100 mesh, and analyzed for ferrous, ferric and metallic iron by the method of Mathesius.[1] The results given in Table V show well-defined differences in the state of oxidation of the iron content of the fusions in the various atmospheres. In hydrogen, 78 per cent of the iron was reduced to metal; in steam and air approximately 70 per cent remained as ferric iron; in the 50 : 50 per cent hydrogen-water vapor mixture, 80 per cent or more was present as ferrous iron.

Together with these analyses of fused ash cones are given similar analyses of the fused and glassy portions of several clinkers produced under working conditions in the fuel beds of different boiler furnaces operating with Pittsburgh coal. The coal, however, came from different mines. Clinker 20137 was obtained from the grate of a small hand-fired experimental furnace which was used for combustion investigations. Clinkers 20145 and 20452 were kindly furnished by Mr. A. A. Straub, steam engineer of the Duquesne Light Company of Pittsburgh. These clinkers were dumped from the fuel bed while hot and were quenched with water. Both of these clinkers were of the particularly trouble-

[1] Ludwig Mathesius, "Untersuchungen uber die Reduzierbarkeit von Eisenerzen in Stromenden Gasen"

TABLE V—ANALYSES OF FUSED CONES OF ASH, AND OF GLASSY PORTIONS OF FURNACE CLINKERS

| LAB. No. | DESCRIPTION | Maximum temp. of fusion ° C. | Total Fe Per cent | Percentage of total iron occurring as Metallic iron | Ferrous iron | Ferric iron | CHARACTER OF SLAG |
|---|---|---|---|---|---|---|---|
| 15848 | Ash fused in atmosphere of 50% hydrogen : 50% water vapor. | 1280 | 4.7 | 6 | 94 | Trace | Light-gray color. Not magnetic. |
| 16243 | | 1080 | 27.4 | Trace | 82 | 18 | Glassy black. Not magnetic. |
| 16243 | Ash fused in atmosphere of hydrogen. | 1370 | 28.6 | 78 | 21 | 1 | Black, metallic luster; contained magnetic particles of metallic iron. |
| 16243 | Ash fused in atmosphere of water vapor. | 1300 | 27.9 | Trace | 28 | 72 | Glassy black, surface had reddish tint; strongly magnetic. |
| 13629 | Ash fused in atmosphere of air. | 1400 | 15.5 | Trace | 30 | 70 | Dark red to almost black, glassy, highly magnetic. |
| 20137 | Clinker from a hand-fired furnace. | . | 14.5 | 12 | 79 | 9 | Dark gloss; some pieces slightly magnetic. |
| 20145 | Clinker from a boiler furnace equipped with Roney stoker, 20th Street station. | .. | 12.7 | 6 | 75 | 19 | Brown to black glass; some pieces slightly magnetic. |
| 20452 | Ditto, Brunot's Island station. | .. | 8.9 | 9 | 75 | 16 | Black glass, slightly magnetic. |

some taffy-like variety that flow over the grate bars and shut off the air supply for combustion. Fig. 8 is a photograph of clinker 20452. The straight-line edge is the side which adhered to the corrugated grate of the new model type D Roney stoker. The matrix of this clinker was a black glass which could be readily chipped out in quantity for analysis without including any piece of coke or unfused material. At the contact surface of coke and slag, particles of metallic iron could be identified. A microscopic examination of the powdered slag from this clinker as well as from the others, by Mr. A. A. Klein of the Bureau of Standards, showed the material to be essentially a glass with sillimanite

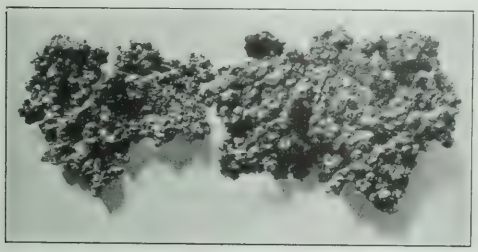

FIG 8—CLINKER NO. 20,452 FROM GRATE OF RONEY STOKER

($Al_2O_3$, $SiO_2$) as the only crystalline phase present, except sample 20137 which also contained an opaque iron mineral, probably magnetite.

A comparison of the analyses of the fused ash cones, and of the three fuel-bed clinkers given in Table V, shows that of the different atmospheres employed in the laboratory furnace, the 50 : 50 per cent hydrogen-water vapor mixture produced a slag which corresponded most closely in the state of oxidation of its iron content to the glassy portions of the furnace clinkers. In both cases approximately 80 per cent of the iron appeared as ferrous iron, the form in which it imparts the maximum fluxing action on the silicate mixture.

We may, therefore, conclude that the minimum softening temperature of a coal ash, as determined in a 50 : 50 per cent atmosphere of hydrogen and water vapor, is more representative of the temperature of clinker formation under furnace conditions than the more or less higher results obtained in strongly reducing atmospheres of hydrogen, or carbon monoxide, on the one hand, and oxidizing atmospheres of air, water vapor or carbon dioxide on the other.

SUMMARY

I—Softening temperatures of five different coal ashes have been determined in various mixtures of hydrogen and water vapor, ranging from 100 per cent hydrogen to 100 per cent water vapor.

II—These results plotted in the form of curves showed that for each of the ashes tested, there was a high softening temperature in pure hydrogen on one end, due to reduction of iron oxide to metallic iron; a similar high softening temperature in water vapor or air on the other end, due to the iron oxide remaining for the most part in the form of ferric iron or magnetite; and a more or less lower softening temperature in the middle portion ranging from 30 to 70 per cent water vapor, due to the reduction of iron to the ferrous state in which it combined to form the readily fusible ferrous silicates.

III—Analyses of actual clinker slags from two different boiler furnaces and one experimental furnace showed that fuel-bed conditions are such as to favor the formation of clinkers containing iron principally in the ferrous state.

IV—A new method of determining the minimum softening temperature of coal ash has been devised, in which the ash is heated in an atmosphere of approximately 50 per cent hydrogen and 50 per cent water vapor, whereby the iron oxide is caused to combine principally in the ferrous state, as actually found in fuel-bed clinkers.

ACKNOWLEDGMENTS

The authors take pleasure in acknowledging their indebtedness to Dr. G. A. Hulett, chief consulting chemist, for many helpful suggestions and criticisms; to A. E. Hall for assistance in building the furnace and in taking the preliminary observations; and to H. H. Hill for the careful analysis of the slags and clinkers.

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## PONTIANAK (JELLUTONG) RUBBER RESIN

BY CARLETON ELLIS AND A. A. WELLS

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Pontianak or Jellutong rubber resin has appeared on the market in relatively large quantities during the past few years and no little effort has been made to find profitable outlets for this material. At the present time, for various reasons, the available supply of the resin has been much reduced.

Jellutong is obtained largely from Sarawak, Dutch Borneo, Sumatra and the Malaysian Peninsula. The product from Sarawak was the first to be termed Pontianak and the name subsequently was applied to substantially similar products from the other localities mentioned.

For a time the rubber manufacturing industries did not look with favor upon this material but later it won for itself the place which it now holds.

In round numbers we may say that Jellutong contains 10 per cent rubber, 20 per cent resin and 70 per cent moisture, etc. The process of purification of the crude gum involves extraction with acetone or similar solvents to remove the resin. The resinous product thus obtained appears in commerce usually as white or yellowish, friable, lumpy masses carrying a variable amount of moisture. It was supposed at first that the resin would serve as a substitute for ordinary rosin and other resins. The properties of Pontianak rubber resin, however, proved to be such as to restrict its fields of application, and to such an extent that for a time the resin was regarded almost as a waste material. In this connection attention is called to a discussion of the subject by H. O. Chute.[1] Statistics on the Pontianak rubber industry are given by Schidrowitz.[2] Data on the composition and characteristics of the resin have been furnished by Hinrichsen and Marcusson[3] and Dubosc.[4] The last-named investigator notes the dissimilarity of this resin with the ordinary resins of commerce and hints for the acetone-soluble resin a constitution of a hydroxy nature, similar to cholesterol.

The resistance of Pontianak resin to the action of aqueous alkali solutions has led to its application as a coating material for cement and concrete.[5] It has also been proposed to use the resin in making paper sizing.[6] The volatile oils resulting from the destructive distillation of rubber resins have been suggested as a raw material for preparing isoprene.

In searching for new uses for the resin we have had occasion to carry out a large number of tests of various kinds to determine its properties. The results of some of these tests are given in the tabulations below.

## EXPERIMENTAL

DESCRIPTION OF SAMPLES—The samples of resin employed in this investigation were selected with reference to the heat treatment they had received, and to the characteristics they exhibited when placed in solution.

In Table I, we have tabulated certain of the changes taking place on heating Pontianak resin under various conditions. No. 2728 is the crude resin obtained from the extraction process free of moisture: 2977, 2991, 2974, 2847 and 3369*C* were heated in open vessels. In the case of 3369*D* a water-cooled reflux condenser was used, thus returning to the retort all the condensable products of distillation. Nos. 3369*E* and *F* were heated in a retort having a short air-cooled reflux condenser to permit the escape of acetic acid and similar relatively volatile bodies while retaining the oily bodies formed. A water-cooled condenser served to collect the former so that while the acetic acid and other relatively volatile bodies were removed as fast as formed, the oils were constantly returned to the retort. It will be noted from the table that after the resin is once heated well above the melting point the temperature at which it again fuses is lowered. This tendency seems to continue until, when the temperature is raised to about 343° C., destructive distillation proceeds rapidly and eventually the mass (using reflux condenser) becomes plastic and flowable at ordinary room temperature, and finally, on raising the temperature still higher, light and heavy oils come over. This oily material was freed from acetic acid and then redistilled and fractionated, affording a series of light colored oils of an unsaponifiable character.

A sample of the crude resin No. 2728 was examined for unsaponifiable matter by heating with alcoholic potash, diluting with water and extracting the unsaponifiable bodies with benzol. The results showed an average of about 95 per cent unsaponifiable matter.

TABLE I—EFFECT OF HEAT ON PONTIANAK RUBBER RESIN

| No. | Hours heated | Temp ° C. | Loss Per cent | Fusing point ° C. | Remarks |
|---|---|---|---|---|---|
| 2728 | None | | 0 | 126 | White powder |
| 2977 | 12 | 204 | 3.1 | 77 | Hard and clear |
| 2991 | 10 | 232 | 5.9 | 78 | Hard and clear |
| 2974 | 9 | 264 | 13.1 | 78 | Hard and clear |
| 2847 | 1 | 316 | | 77 | Hard and clear |
| 3369*C* | 3 | 343 | 50 | | Hard and clear |
| 3369*D* | 8 | 343 | 10 | 65 | Hard and clear |
| 3369*E* | 4 | 343 | 16 | | Plastic |
| 3369*F* | 6 | 343 | 18 | | Very plastic, flowable |
| 3360 | Destructive distillation | | | | Oil |

Apart from the formation of acetic and other volatile acids, heat treatment appears to increase the proportion of unsaponifiable bodies.

The iodine value generally shows an increase on heating the resin. A sample of the crude resin afforded an iodine number of 36, while No. 3369*F* gave a value of 62 and the oil obtained by destructive distillation (freed of water-soluble acids) exhibited an iodine number of 93. By the addition of small amounts of oil-soluble manganese compounds to these oils or soft plastics rather marked siccative properties were manifested.

As some attention has been directed towards Pontianak rubber resin as a promising material in the preparation of varnishes and paint oils and as considerable disappointment has arisen because of lack of knowledge of the solubility phenomena of this resin, Table II details at some length the behavior of the resin in a number of the solvents commonly used in the varnish and paint industry. As a practical consideration, high-grade commercial solvents were used in preference to chemically pure ones. The numerical data involve the use of customary U. S. weights and measures in order to be more readily available to the varnish maker.

Commercial 90 per cent benzol, "commercially" pure spirits of turpentine, light benzine or "varnish makers' naphtha," heavy benzine and solvent naphtha were selected particularly because of their general use in varnish making. The heavy benzine employed was a commercial petroleum hydrocarbon solvent, having

[1] *India Rubber World*, July, **1909.**

[2] *Ibid.*, Dec., **1911.**

[3] [illegible], 24, [illegible].

[4] *Caout. et Gutta-percha*, **8**, 5756.

[5] *India Rubber World*, Nov., **1911**; also U. S. Patent [illegible] and 999,708 of Aug. 1, **1911**, 1,005,818 of Oct. 17, **1911**; and 1,006,737 of Oct. 24, **1911.**

[6] *The Paper Mill and Wood Pulp News*, Dec. 2, **1911**; also U. S. Patent 1,007,681 of Nov. 7, **1911.**

a flash point of about 110° F., commonly used as a substitute for spirits of turpentine.

Most of the samples detailed in Table II had been made up from one to two years. By ageing in this manner, very exact results could be obtained as to the permanent character of the solution. Solutions which were not permanent when first made up, gradually threw down a portion of the resin until a stable solution was obtained. Thus we note that in more than half the samples, some resin, varying from a few flocculated particles to a percentage large enough equal, in a rough way, indicated the relative amount of resin in true solution. In determining the percentage of resin in the supernatant liquid, weighed amounts of the solution were dried to constant weight.

One of the interesting features of Table II is that relating to the condition of thin films of the solutions when allowed to dry on glass plates. In a great many cases frosted slow-drying films were obtained. It will be noted that these were usually formed wherever the percentage of solid material in the containers was greatest, although there are exceptions. Sample No.

TABLE II BEHAVIOR OF PONTIANAK RUBBER RESIN IN HIGH GRADE COMMERCIAL SOLVENTS

No. 2728—Crude Pontianak resin melted and thinned with solvents
No. 2826—Fused Pontianak resin melted and thinned with solvents.
No. 2775—Crude resin melted and thinned with solvents.
No. 3028—A and B—dry fused Pontianak resin melted and thinned.
C—Crude resin pulverized to pass 40 mesh, benzol added and shaken in the cold until dissolved.
No. 2813—Crude resin melted and thinned with solvents.
No. 2977—Fused resin heated to 204° C. for 12 hrs. and thinned with solvents.
No 2991—Fused Pontianak resin heated to 232° C. for 10 hrs. and thinned with solvents.
No. 2974—Fused Pontianak resin heated to 264° C. for 9 hrs and thinned with solvents.
No. 2832—Pontianak resin heated to 264° C. for 1 hr. and thinned with solvents.
No. 2847—Pontianak resin (light yellow color) heated to 316° C. for 1/2 hr. and thinned with solvents.
No. 2822—Pontianak resin heated to 320° C. and thinned with solvents.
No. 3369—D—Pontianak resin heated 5 hrs. at about 343° C. with a water-cooled reflux condenser.
E—Resin heated 4 hrs. same as above except air-cooled reflux.
F—Same as E except heated 6 hrs.

| No. | Resin used Oz. | NAME (COMMERCIAL) AND AMOUNT OF SOLVENT USED Turpentine | Heavy benzine | Solvent naphtha | Benzol | Light benzine | CONDITION OF SOLUTION | Per cent resin in clear solution | RESIDUE AFTER EVAPORATION | FILM ON GLASS |
|---|---|---|---|---|---|---|---|---|---|---|
| 2728 | 15½ | | | | 24 fl. oz. | 24 fl. oz. | 70% solid | 52(a) | Granular | Frosted |
| 2826*A* | 2 | 2 fl. oz. | | | | | Solid | | | Frosted |
| *B* | 2 | 3 fl. oz. | | | | | Almost solid | | | Clear |
| *C* | 2 | 4 fl. oz. | | | | | 40% solid | 38 | Clear | Clear |
| *D* | 2 | 1 fl. oz. | 1 fl. oz. | | | | Solid | | | Almost clear |
| *E* | 2 | 1 fl. oz. | 2 fl. oz. | | | | 80% solid | 40 | Clear | Frosted |
| *F* | 2 | 1 fl. oz. | 3 fl. oz. | | | | 65% solid | 35 | Light; clear | Frosted |
| 2775*A* | 4 | | | 4 fl. oz | | | 90% solid | 46 | Almost clear | Frosted |
| *B* | 4 | | | 8 fl. oz. | | | 5% solid | 29 | Clear; granular specks | Clear |
| 3028*A* | 1 | | | | 1 fl. oz. | | All liquid | 38 | Clear | Clear |
| *B* | 1 | | | | 1 fl. oz | | All liquid | 39 | Clear | Clear |
| *C* | 1 | | | | 1 fl. oz | | All liquid | 37 | Clear | Clear |
| 2813*A* | 4 | | | | 4 fl. oz. | 2 fl. oz | Almost clear | 46 | Frosted | Frosted |
| *B* | 4 | | | | 4 fl. oz. | 1 fl. oz. | 15% solid | 52(a) | Granular | Frosted |
| 2977*A* | 2 | | | | 2 fl. oz | | 90% solid | 59 | Dark; clear | Frosted |
| *B* | 2 | | | | 3 fl. oz | | All liquid | 50 | Mottled; dark | Frosted |
| *C* | 2 | | | | | 3 fl. oz | 50% solid | 43 | Dark; clear | Frosted |
| *D* | 2 | | | | | 4 fl. oz. | 5% solid | 41 | Dark; clear | Frosted |
| *E* | 2 | | 3 oz | | | | 5% solid | 42 | Dark; clear | Clear |
| *F* | 2 | | 4 oz. | | | | 2% solid | 37 | Dark; clear | Almost clear |
| 2991*A* | 2 | | | | 3 fl. oz. | | All liquid | 49 | Dark; almost clear | Clear |
| *B* | 2 | | | | | 3 fl. oz | 2% solid | 44 | Dark; clear | Clear |
| *C* | 2 | | | | | 4 fl. oz. | 2% solid | 40 | Mottled | Clear |
| *D* | 2 | | 3 fl oz | | | | 5% solid | 42 | Dark; clear | Clear |
| *E* | 2 | | 4 fl oz | | | | 2% solid | 39 | Dark; almost clear | Clear |
| 2974*A* | 2 | | | | 3 fl oz | | All liquid | 48 | Dark; clear | Clear |
| *B* | 2 | | | | 4 fl oz | | All liquid | 41 | Dark; clear | Clear |
| *C* | 2 | | | | 5 fl oz | | All liquid | 36 | Dark; clear | Clear |
| *D* | 2 | | | | | 4 fl. oz | 2% solid | 40 | Dark; clear | Clear |
| *E* | 2 | | | | | 5 fl. oz | All liquid | 37 | Dark; clear | Clear |
| *F* | 2 | | 4 oz | | | | 20% solid | 38 | Dark; clear | Clear |
| 2832*A* | 1 | | | 1 fl oz | | | 95% solid | | | Frosted |
| *B* | 1 | | | 1½ fl oz | | | 40% solid | 42 | Mottled | Frosted |
| *C* | 1 | | 2 oz | | | | 60% solid | 33 | Clear | Frosted |
| *D* | 1 | | | | | 2 oz. | 50% solid | 36 | Clear | Frosted |
| *E* | 1 | | | 1 oz | | 1 oz. | 55% solid | 36 | Dark; clear | Frosted |
| 2847*A* | 1 | | | | | 2 fl. oz | 10% solid | 39 | Clear | Clear |
| *B* | 1 | | | | 1 fl oz | | Clear | 56 | Dark; clear | Clear |
| *C* | 1 | | 2 fl oz | | | | 5% solid | 37 | Clear | Clear |
| *D* | 1 | | 1 fl oz | | | 1 fl oz | 20 % solid | 38 | Dark; clear | Clear |
| 2822*A* | 1 | | | 1 fl oz | | | All liquid | 54 | Dark, clear | Clear |
| *B* | 1 | | 1 oz | | | | All liquid | 45 | Dark; clear | Clear |
| *C* | 1 | | | 1½ fl oz | | | Solid | | | Clear |
| *D* | 1 | | 2 fl oz | | | | All liquid | 45 | Dark; clear | Clear |
| *E* | 1 | | | | | 2 oz. | All liquid | 40 | Dark; clear | Clear |
| *F* | 1 | ½ oz | 1 oz | ½ oz | | | All liquid | 38 | Dark; clear | Clear |
| 3369*D* | 5 | | 5½ oz | | | | All liquid | 53 | Dark; clear | Light; clear |
| *E* | 10 | | Equal vol. | | | | All liquid | 58 | Dark; opaque | Dark; clear |
| *F* | 10 | | Equal vol. | | | | All liquid | 56 | Dark; opaque | Dark; clear |

(a) As the residue after evaporation was somewhat plastic, and had the odor of benzine, evidently some of the solvent had been retained thus making 52 per cent too high.

to make the entire contents of the container solid, was not in true solution.

From Table II it will be observed that there are at least two factors on which depend the amount of resin held in permanent solution: (1), the nature of solvent used and (2), the heat treatment of the resin. In general we may say that benzol is the most active solvent, while benzine is the weakest. A good idea of the values of different solvents was obtained by examining the condition of the liquids in the containers. The percentage of solid matter, other things being 3369*D*, although the percentage of resin is 58 as a maximum, does not show the maximum amount which can, with this treatment, be placed in solution. As a matter of fact, the *plastic* resin can be added to a solvent in any quantities and still not form a precipitate on standing.

In Table III, we have tried to classify the solubilities with reference both to the heat treatment and the solvents employed, thus making the whole scheme more comprehensive. The effect on the solubility of the length of time of heat treatment as well as the

temperatures employed are here concisely shown. For example, No. 2977 is more soluble in benzol than No. 2847, although heated at a temperature lower by over 100° C., but on the other hand being heated 11 hours longer. The same is true of Nos. 3369 and 2822, using heavy benzine as solvent, in the proportion of one part solvent to one part resin. With two parts solvent to one part resin, we see that 204° for 12 hours,

TABLE III—SOLUBILITIES OF PONTIANAK RUBBER RESIN WITH REFERENCE TO TREATMENT AND SOLVENT USED

| Solvents and parts used in each case to 1 part of resin | | | | | | Per cent of resin in clear solution | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | No. 2728 | No. 2977 | No. 2991 | No. 2974 | No. 2832 | No. 2847 | No. 2822 | No. 3369 |
| Benzol (benzene) | Light benzine | Heavy benzine | Solvent naphtha | Turpentine | | Crude resin melted and thinned | Fused resin heated to 204° C. for 12 hrs and thinned | Fused resin heated to 232° C. for 10 hrs and thinned | Fused resin heated to 264° C. for 9 hrs and thinned | Resin heated to 264° C. for 1 hr. and thinned | Resin heated to 316° C. for ½ hr and thinned | Resin heated to 316° C. and thinned | Resin heated to 343° C. for ½ hr. and thinned |
| 1 | | | | | | 38 | 59 | | | | 56 | | |
| 1½ | | | | | | | 50 | 49 | 48 | | | | |
| 2 | | | | | | | | | 41 | | | | |
| 2½ | | | | | | | | | 36 | | | | |
| | 1½ | | | | | | 43 | 44 | | | | | |
| | 2 | | | | | | 41 | 40 | 40 | 36 | 39 | 40 | |
| | 2½ | | | | | | | | 37 | | | | |
| | | 1 | | | | | | | | | | 45 | 58 |
| | | 1½ | | | | | 42 | 42 | | | | | |
| | | 2 | | | | | 37 | 39 | 38 | 32 | 37 | 45 | |
| | | | | | 2 | 38 | | | | | | | |
| | | | 1 | | | 46 | | | | | | 54 | |
| | | | 1½ | | | | | | | 42 | | | |
| | | | 2 | | | 29 | | | | | | | |
| 1 | ¼ | | | | | 52(a) | | | | | | | |
| 1 | ½ | | | | | 46 | | | | | | | |
| 1½ | 1½ | | | | | 52(a) | | | | | | | |
| | 1 | 1 | | | | | | | | | 38 | | |
| | 1 | | | 1 | | | | | | 36 | | | |
| | | 1 | | | 2 | 40 | | | | | | | |
| | | 1½ | | | 2 | 35 | | | | | | | |
| | | 1 | | 2 | 2 | | | | | | | 38 | |

(a) Upon evaporation, the residue was very granular and had the odor of benzine, hence it is very probable that some solvent was still in the resin, thus making these results too high.

232° for 10 hours, 264° for 9 hours, and 316° for ½ hour give practically the same results, while heating to 264° for 1 hour affords a degree of solubility less than any of these. On heating to 321°, however, the greatest amount of resin was in solution.

The mixtures of various solvents did not in many cases seem to be more active than each one taken separately. The influence of alkali on the plastic resin in thin layers is shown by the following:

Samples, made up of equal parts of plastic resin and heavy benzine and in some cases with additions of 10 to 20 per cent of various saponifiable siccative oil, were flowed in thin layers on glass plates and allowed to dry for several days. The plates were then immersed in an aqueous 5 per cent caustic soda solution for 5 days. Upon removing the plates and rinsing, the samples containing 20 per cent of drying oil were found quite badly decomposed, those containing 10 per cent were only slightly affected, while those containing only the dried plastic resin were scarcely softened, the resin when again dried, being in apparently as good condition as before the test.

## CONCLUSIONS

I—Of the solvents or thinners commonly used in varnish and paint oil making, benzol is the most energetic on Pontianak rubber resin.

II—Heating the resin for an extended period makes it more soluble and increases the proportion of unsaturated bodies. Temperatures above 650° F. exert a marked influence both as to solubility and chemical and physical properties.

III—Pontianak rubber resin is very inert to alkalies and, practically speaking, may be regarded as substantially unsaponifiable.

MONTCLAIR, NEW JERSEY

# THE QUANTITY OF GASOLINE NECESSARY TO PRODUCE EXPLOSIVE MIXTURES IN SEWERS[1]

BY G. A. BURRELL AND H. T BOYD

Received June 4, 1915

The Bureau of Mines and the City of Pittsburgh are coöperating in an endeavor to determine the causes of explosions in sewers and means for their prevention. The results of the investigation are being published in reports of the Bureau of Mines. In this report are shown the quantities of gasoline which must be introduced into sewers in order to produce explosive mixtures of gasoline vapor and air under certain conditions. Many different conditions affect this quantity, such as size of the sewer, velocity of the sewage, temperature of the sewer air, volatility of the gasoline, rate of inflow of the gasoline, etc., so that only under identical conditions of tests are duplicate results obtained.

## EXPERIMENTAL

The particular sewer wherein the tests here recorded were conducted is one of the largest of the Pittsburgh sewers. It is 8 ft. 3 in. wide and 8 ft. 6 in. high. In Fig. 1 is shown a plan of the sewer, with conditions such as existed when the first test was conducted on September 30, 1914. At the points 1, 2, 3, 4, 5 and 6 are shown the manholes where samples of gas were collected. The distance from No. 1 manhole, where the gasoline was dumped into the sewer, to the sewer outlet, the Allegheny River, is 2706 feet. The distance between the different manholes is marked on the diagram.

The velocity of the sewer was established as follows: Pine floats 6 in. square were dropped into the upper manhole No. 1 at a given signal. Stop-watches were set at the same instant, and as the floats passed each succeeding manhole (which fact was determined by a man standing at the foot of a ladder in each manhole) the time was caught on a stop-watch.

As a result of these tests it was established that the average velocity of the sewer was 6.45 linear feet per second. The depth of the flow was about 8 in. The amount of flow was 19.6 cu. ft. per second and the grade of the sewer 0.90 per cent. The temperature of the water in the sewer was 21° C. (69.8° F.). The temperature of the air just above the water was 20.3° C. (68.54° F.), and of the air above ground 20° C. (68° F.).

### TEST NO. 1

At 2.10 P.M., 55 gallons of refinery gasoline, sp. gr. 67.5° Baumé, were rapidly dumped from an open barrel into the sewer at manhole No. 1, by turning the barrel on end, allowing the gasoline to run in all at once.

[1] Published with the permission of the Director of the Bureau of Mines

The fractionation analysis of this gasoline appears in Table I.

TABLE I—FRACTIONATION ANALYSIS(a) OF GASOLINE USED IN TEST NO. 1

| | | | |
|---|---|---|---|
| First drop..... | 31° C. | Up to 120° C ... | 65 5 per cent |
| Up to 40° C..... | 1.46 per cent | Up to 130°..... | 76.5 |
| Up to 50°..... | 3.4 | Up to 140°..... | 84.0 |
| Up to 60°..... | 7.0 | Up to 150°..... | 91.0 |
| Up to 70°..... | 13.0 | Up to 160°..... | 97.5 |
| Up to 80°..... | 20.5 | Over 160°..... | 1.9 |
| Up to 90°..... | 29.5 | | |
| Up to 100°..... | 41.7 | Total..... | 99.4 per cent |
| Up to 110°..... | 54.5 | Loss..... | 0.6 per cent |

(a) Made by M. S. Evans, Chief, Bureau of Tests, City of Pittsburgh.

Samples of gas were collected by lowering exhausted, glass sample tubes on the end of long poles and breaking off their tips by striking them against the sewer walls. The sewer air immediately rushed into the glass containers through the very small opening thus afforded. The arrangement of this device is shown in Fig. 2. M. S. Evans, chief of the Bureau of Tests, City of Pittsburgh, worked out the details and made the device for holding the vacuum bottles. This was the arrangement adopted for the first test.

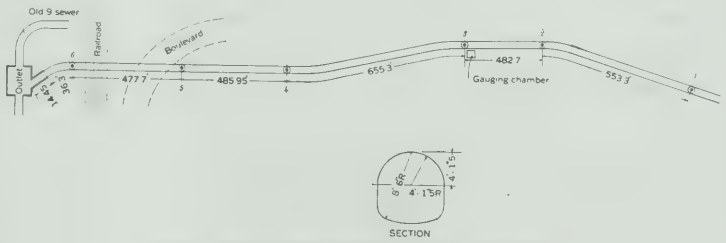


FIG. 1—PLAN OF SEWER WHERE TESTS WERE CONDUCTED

On the subsequent tests samples of the sewer air were drawn from the sewer into bottles by means of a small pump with a long hose attachment. This arrangement is shown in Fig. 3.

Before the gasoline was dumped, a sample of sewer air was taken at Station No. 2. This was done to determine whether any gasoline was already in the sewer. The sample analyzed as follows:

$CO_2$, 0.06 per cent. Combustible gas, trace (too small for identification)

hence, no allowance was made in other analyses.

Samples of sewer air were collected on schedule time, from 2.12 P.M. to 4.45 P.M. as shown in Table II.

TABLE II -TIMES AT WHICH SAMPLES OF SEWER AIR WERE COLLECTED

| Sample No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Manhole No. 2..... | 2.12 | 2.22 | 2.32 | 2.42 | 2.52 | 3.25 | 4.25 | .... | .... |
| Manhole No. 3..... | 2.13 | 2.23 | 2.33 | 2.43 | 2.53 | 3.30 | 4.25 | .... | .... |
| Manhole No. 4..... | 2.16 | 2.21 | 2.26 | 2.31 | 2.41 | 2.51 | 3.01 | 3.45 | 4.30 |
| Manhole No. 6..... | 2.20 | 2.30 | 2.40 | 2.50 | 3.00 | 3.50 | 4.35 | .... | .... |

The analysis[1] of these samples gave the results shown in Table III.

One gallon of gasoline, if entirely vaporized, produces about 32 cu. ft. of vapor at ordinary temperature and pressure. Adopting 1.5 per cent[2] as the low

TABLE III—ANALYSES OF SAMPLES TAKEN DURING TEST NO. 1

| Manhole No. 2 % by vol. | | | Manhole No. 3 % by vol | | | Manhole No. 4 % by vol. | | | Manhole No. 6 % by vol. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time P.M. | $CO_2$ | Gasoline | Time P.M. | $CO_2$ | Gasoline | Time P.M. | $CO_2$ | Gasoline | Time P.M. | $CO_2$ | Gasoline |
| 2.12 | 0.05 | 0.89 | 2.13 | 0.05 | 2.19 | 2.16 | 0.08 | 0.67 | 2.20 | 0.04 | 0.20 |
| 2.22 | 0.05 | 0.27 | 2.23 | 0.10 | 0.23 | 2.21 | 0.10 | 0.28 | 2.30 | 0.05 | Trace |
| 2.32 | 0.12 | 0.25 | 2.33 | 0.06 | 0.10 | 2.26 | 0.07 | 0.12 | 2.40 | 0.09 | None |
| 2.42 | 0.10 | 0.18 | 2.43 | 0.06 | 0.04 | 2.31 | 0.05 | 0.11 | 2.50 | .... | None |
| 2.52 | 0.08 | 0.136 | 2.53 | 0.06 | Trace | 2.41 | 0.05 | Trace | 3.00 | .... | None |
| 3.25 | 0.06 | Trace | 3.30 | 0.05 | Trace | 2.51 | 0.05 | Trace | 3.45 | .... | None |
| 4.25 | 0.01 | None | 4.25 | 0.05 | Trace | 3.01 | 0.10 | None | 4.35 | .... | None |
| | | | | | | 3.45 | 0.05 | None | | | |
| | | | | | | 4.30 | 0.05 | None | | | |

explosive limit of gasoline-vapor-air mixtures, 55 gallons of gasoline would produce enough vapor to render explosive the air in 1900 ft. of a 9-ft. sewer, assuming perfect mixing of the sewer air and gasoline vapor. It will be noted how far theoretical conditions differ from the conditions of the test: (1) The gasoline flowing with the sewer water was rapidly carried past any particular point; (2) only the lighter portions had a chance to evaporate at any point; (3) gasoline vapor is about three times as heavy as air, so that mixing of vapor with air at an appreciable distance above the sewer water would be slow. Sample No. 1 (manhole No. 2), taken 2 minutes after the introduction of the gasoline, shows 0.89 per cent of gasoline. Sample No. 1 (manhole No. 3) shows 2.19 per cent, and was taken 3 minutes after the gasoline was poured in. In other words, the relation between the movement of the gasoline down the sewer and the distance between the manholes and time of collecting samples was such that at manhole No. 3 there was more gasoline vapor 3 minutes after the introduction of the gasoline than at No. 2 manhole, 2 minutes after the gasoline was poured in. The significant fact is that 2.19 per cent was the largest quantity of gasoline vapor found in any sample. Only very small proportions were found at any manhole 10 minutes after the introduction of the gasoline. It is evident that 1 barrel of gasoline (55 gallons) poured all at once in a manhole of a fast-flowing sewer renders the air explosive for only a few minutes at any particular point.

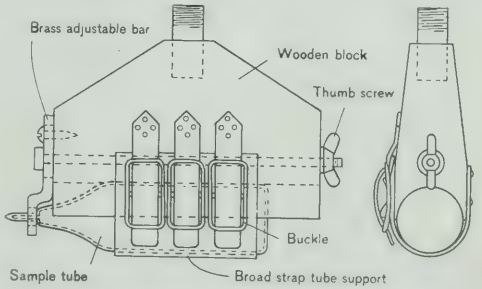


FIG. 2 DEVICE FOR HOLDING EVACUATED SAMPLE TUBES

TEST NO. 2

There follows a description of the second test made to determine the quantity of gasoline necessary to render sewer air explosive under certain conditions.

In this test the covers of the manholes were not removed (as was the case in the previous tests). The hose connection to the pump was let down in some

[1] Methods of analysis are shown in a previous report, THIS JOURNAL, 5 (1913), 112.

[2] See THIS JOURNAL, 7 (1915), 414.

cases to within 2 in. of the sewer water and in other cases to within 2 ft. The most important difference over the first test was in the fact that the gasoline, instead of being dumped into the sewer all at once, was allowed to dribble down manhole No. 1 at the rate of 5 gallons per minute, requiring 11 minutes for the barrel of 55 gallons to empty itself. The temperature of the sewer air at 11.40 A.M. was 20° C. (68° F.). The temperature of the outside air was 24° C. (75° F.). A sewer-air sample, collected at station No. 2 before the gasoline was dumped, contained 0.20 per cent of carbon dioxide and no traces of combustible gas. The results of the analyses of samples of sewer air collected at the four manholes appear in Table IV.

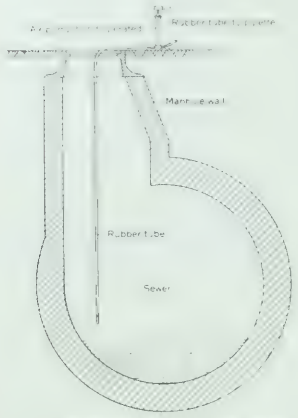


FIG. 3.—METHOD OF COLLECTING SEWER AIR SAMPLES

Some interesting results were obtained by alternately raising the hose from 2 inches above the water to 2 feet above. As will be noticed, the highest percentage of gasoline obtained from the samples taken 2 feet above was only 0.70 per cent. It will also be noted that the sewer rapidly cleared itself of gasoline vapor at any one point in a very short time. There were required 11 minutes to dump in the gasoline; 13 minutes after the inflow of gasoline had ceased there was found (No. 2 Station) 1.14 per cent of the vapor, 2 in. above the water; 18 minutes after the inflow of gasoline, only a trace of vapor was left in the sewer air. At No. 4 manhole, the gasoline vapor was not swept out so quickly. In 16 minutes the amount was 1.10 per cent (2 in. above), and in 31 minutes 0.12 per cent. During certain periods, at 2 inches above the water, very dangerous atmospheres existed, but in all cases, at 2 feet above the water, the quantities discovered could not propagate flame. Upon ignition of the gasoline at any time extending over a period of, say, 15 minutes after the gasoline was dumped in, a rapid sheet of flame would have swept along the sewer. The test shows, therefore, that 5 gallons of gasoline per minute introduced into the sewer under the above conditions would produce a dangerous condition as long as the flow lasted.

TABLE IV.—ANALYSES OF SAMPLES COLLECTED DURING TEST NO. 2

DATE—Oct. 8, 1914. Velocity of Sewer Water, 5.38 ft. per sec. Amount of Flow, 10.95 ft. per sec. Surface of Area of Flow, per second, 31.53 sq. ft.

| MANHOLE NO. 2 | | | MANHOLE NO. 3 | | | MANHOLE NO. 4 | | | MANHOLE NO. 6 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time after entrance of gasoline Minutes | Height of hose above water Inches | Per cent of gasoline | Time after entrance of gasoline Minutes | Height of hose above water Inches | Per cent of gasoline | Time after entrance of gasoline Minutes | Height of hose above water Inches | Per cent of gasoline | Time after entrance of gasoline Minutes | Height of hose above water Inches | Per cent of gasoline |
| 1.5 | 2 | 0.26 | 3.0 | 2 | 1.28 | 4.5 | 2 | 0.65 | 6.5 | 2 | 0.02 |
| 3 | 2 | 1.01 | 4.5 | 2 | 1.63 | 6 | 24 | 0.55 | 8 | 2 | 0.06 |
| 5 | 2 | 1.51 | 6.5 | 2 | 1.67 | 8 | 2 | 1.02 | 10 | 2 | 0.13 |
| 7 | 24 | 0.27 | 8.5 | 24 | 0.46 | 10 | 24 | 0.59 | 12 | 2 | 0.05 |
| 9 | 2 | 1.07 | 10.5 | 2 | 1.17 | 12 | 2 | 1.13 | 14 | 24 | 0.25 |
| 11 | 24 | 0.12 | 12.5 | 24 | 0.40 | 14 | 24 | 0.70 | 16 | 2 | 0.45 |
| 13 | 2 | 1.14 | 14.5 | 2 | 0.83 | 16 | 2 | 1.10 | 18 | 24 | 0.08 |
| 18 | 24 | 0.10 | 19.5 | 24 | 0.16 | 21 | 24 | 0.23 | 26 | 2 | 0.12 |
| 28 | 2 | Traces | 29.5 | 2 | Traces | 31 | 2 | 0.12 | 36 | 24 | Traces |
| 38 | 2 | None | 39.5 | 24 | None | 41 | 24 | None | 46 | 2 | Traces |
| 48 | 24 | None | 49.5 | 2 | None | 51 | 2 | None | 51 | 24 | None |

TEST NO. 3

In order to better understand what effect on the vaporization of gasoline a sewer outlet entirely submerged (by high water of the Allegheny River, for instance) would have, Test No. 3 was conducted on October 26, 1914. A bulkhead was built in the sewer at manhole No. 3 on the map. Part of the flow was diverted into the old sewer adjacent by means of sandbags placed farther up, and then the water in the sewer was allowed to back up gradually. The gasoline was dumped into the 5th manhole above at the rate of 5 gallons per minute. The effect of having the sewer outlet submerged by high water in Allegheny River would be a slowing-up of the velocity of the sewer, and consequently with the same inflow of gasoline there would result greater evaporation of gasoline in the sewer over a given length of time than if the gasoline were rapidly swept away by a fast current. In other words, there should be required a smaller quantity of gasoline to produce a dangerous condition, or the same quantity of gasoline would stay longer at a given spot. Samples were taken at the four other stations on regular schedule, alternately 2 inches and 2 feet above, from 11.10 A.M. until 3.30 P.M. The results given in Table V were obtained.

The results of this test prove that with a sewer submerged by high water extremely dangerous conditions can result from a small amount of gasoline. As will be noted from these analyses, there existed, between Stations No. 3 and No. 4, a distance of about 500 feet, a dangerous condition 5 hours after the gasoline was run in. It will also be observed that the percentages of gasoline were gradually but noticeably increasing at Stations No. 1 and No. 2 above them. It can be readily seen that if, as might happen, a sewer were submerged for several days or a week at a time, a very dangerous condition would result if 5 gallons of gasoline were to escape (through the carelessness of employees) into it from garages and drycleaning establishments or other places located on its drainage basin.

TEST NO. 4

The last of the four tests was carried out November 6th. Conditions were kept the same as on October 26th with the exception that one-half the quantity of gasoline was used ($27\frac{1}{2}$ gallons) and samples were not taken till the gasoline had been entirely dumped. One-half barrel of gasoline was dumped into the sewer

TABLE V.—ANALYSES OF SAMPLES COLLECTED DURING TEST NO. 3

| MANHOLE NO. 1 | | | MANHOLE NO. 2 | | | MANHOLE NO. 3 | | | MANHOLE NO. 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | Height of hose above water Inches | Per cent of gasoline | Time | Height of hose above water Inches | Per cent of gasoline | Time | Height of hose above water Inches | Per cent of gasoline | Time | Height of hose above water Inches | Per cent of gasoline |
| 11.10 | 2 | 1.47 | | | | | | | 11.10 | 2 | 0.96 |
| 11.20 | 24 | 0.08 | | | | | | | 11.20 | 24 | 0.76 |
| 11.30 | 2 | 0.08 | 11.30 | 2 | 0.09 | 11.30 | 2 | 0.86 | 11.30 | 2 | 1.15 |
| 12.00 | 24 | 0.05 | 12.00 | 24 | 0.12 | 12.00 | 24 | 0.84 | 12.00 | 24 | 0.95 |
| 12.30 | 2 | 0.10 | 12.30 | 2 | 0.07 | 12.30 | 2 | 0.86 | 12.30 | 2 | 1.15 |
| | | | | | | | | | 12.40 | 24 | 0.90 |
| 1.00 | 24 | 0.10 | 1.00 | 24 | 0.11 | 1.00 | 24 | 0.82 | 1.00 | 2 | 1.05 |
| 1.30 | 2 | 0.10 | 1.30 | 2 | 0.04 | 1.30 | 2 | 0.63 | 1.30 | 24 | 0.89 |
| 2.00 | 24 | 0.13 | 2.00 | 24 | 0.09 | 2.00 | 24 | 0.53 | 2.00 | 2 | 1.02 |
| 2.30 | 2 | 0.12 | 2.30 | 2 | 0.13 | 2.30 | 2 | 0.55 | 2.30 | 24 | 0.36 |
| 3.00 | 24 | 0.14 | 3.00 | 24 | 0.14 | 3.00 | 24 | 0.80 | 3.00 | 2 | 1.24 |
| 3.30 | 2 | 0.20 | 3.30 | 2 | 0.20 | 3.30 | 2 | 0.68 | 3.30 | 24 | 1.06 |

at 11.45 A.M. and samples were collected every half hour, starting at 12 M., until 4.30 P.M., at four manholes intervening between this point and the bulkhead. The analyses are shown in Table VI.

TABLE VI—ANALYSES OF SAMPLES COLLECTED DURING TEST NO. 4

| Time | Height of hose above water Inches | PERCENTAGES OF GASOLINE VAPOR Manhole No. 1 | Manhole No. 2 | Manhole No. 3 | Manhole No. 4 |
|---|---|---|---|---|---|
| 12.00 | 2 | 0.81 | 0.30 | 0.58 | 0.50 |
| 12.30 | 24 | 0.07 | 0.06 | 0.35 | 0.14 |
| 1.00 | 2 | 0.08 | 0.06 | 0.36 | 0.51 |
| 1.30 | 24 | 0.08 | 0.05 | 0.33 | 0.33 |
| 2.00 | 2 | 0.07 | 0.06 | 0.27 | 0.42 |
| 2.30 | 24 | 0.07 | 0.02 | 0.23 | 0.39 |
| 3.00 | 2 | 0.08 | 0.07 | 0.22 | 0.54 |
| 3.30 | 24 | 0.08 | 0.08 | 0.18 | 0.38 |
| 4.00 | 2 | 0.09 | 0.11 | 0.21 | 0.52 |
| 4.30 | 24 | 0.08 | 0.07 | 0.14 | 0.14 |

Several samples were taken at a manhole above the point where the gasoline was emptied. The samples analyzed as follows:

| Percentages in | Sample No. 1 | Sample No. 2 |
|---|---|---|
| Carbon dioxide ($CO_2$) | 0.07 | 0.10 |
| Gasoline | None | None |

These two samples were taken to ascertain whether or not the gasoline vapor has a tendency to travel up the sewer when the outlet is submerged. It seems probable from the results of these two samples that the vapor moved but very few feet up the sewer above the point where the gasoline entered.

It will be noticed, on comparing Test No. 4 with Test No. 3, especially manhole No. 4 of October 26th, that the results of the analyses are almost in the same ratio as the quantities of gasoline used, *i. e.*, the samples collected on November 6th, when one-half barrel of gasoline was used, show only approximately one-half the percentage of gasoline vapor as compared with the samples collected October 26th, when one barrel of gasoline was utilized. The gasoline used for both tests was of the same grade. Consequently, since one barrel contained twice the volume of lighter hydrocarbons in one-half barrel, it should furnish in the sewer about twice the percentage of vapor.

### VAPOR PRESSURES OF DIFFERENT GRADES OF GASOLINE

Of much importance on the question of explosions in sewers caused by gasoline is the volatility of the gasoline, or the rate of evaporation. Gasoline of high volatility, when dumped into a sewer, evaporates much more rapidly, and other things being equal will make explosive a greater volume of sewer air in a given time than gasoline that is not so volatile. To obtain information regarding this matter, vapor pressure determinations were made of five different grades of gasoline. The results are shown in Fig. 4. The determinations were made by introducing the gasoline into a 15 cc. glass bulb connected with a mercury vacuum pump and a mercury manometer. First the glass bulb containing the gasoline was cooled at a temperature of —78° C. (the temperature of solid carbon dioxide and acetone) and the air removed from the system by means of the pump. At a temperature of —78° C. none of the gasoline samples had an appreciable vapor pressure. Next the bulb with its

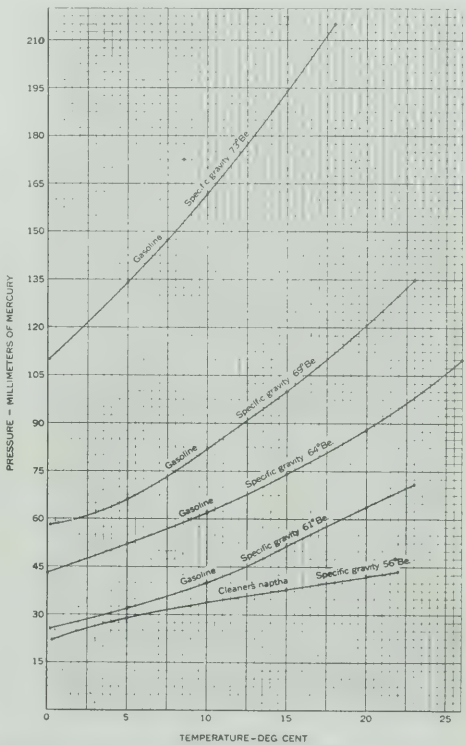


FIG 4—VAPOR PRESSURE CURVES OF DIFFERENT GRADES OF GASOLINE

gasoline was surrounded by a stirred constant temperature bath and the pressure in millimeters of mercury noted at different temperatures. Sufficient time was allowed before taking readings for equilibrium to take place. Pressure readings could be made with an accuracy of ±1 millimeter of mercury and temperature readings with an accuracy of ±0.2° C

Great differences will be noted in the results. For instance, at ordinary temperature, 17.5° C., the vapor pressure of cleaners' naphtha is 40 mm. of mercury; of 61° Bé. gasoline, 82 mm.; of 69° Bé. gasoline, 110 mm.; and of 73° Bé., 212 mm. When these vapor pressures are expressed in terms of the percentage by volume of gasoline vapor that will mix with air at the temperatures given, the results become:

| | |
|---|---|
| Cleaners' naphtha, | 40/760 × 100 = 5.0 per cent |
| 61° Bé. gasoline, | 82/760 × 100 = 11.0 per cent |
| 69° Bé. gasoline, | 110/760 × 100 = 15.0 per cent |
| 73° Bé. gasoline, | 212/760 × 100 = 28.0 per cent |

In other words, air will uniformly mix with almost 6 times as much vapor from 73° Bé. gasoline as from cleaners' naphtha at a temperature of 17.5° C.

Gasoline is not a definite compound and the specific gravity test is a poor criterion of the nature of a particular distillate; hence, the above figures are only approximate to what the vapor pressure of different distillates from gasoline of the specific gravities given must be, but they indicate the relative danger of explosions due to dumping into a sewer gasoline of different grades.

## SUMMARY

One barrel (55 gallons) of gasoline dumped into the sewer, all at once, resulted in the formation of an explosive mixture for a few minutes only at any one particular point. This condition existed close to the surface of the sewer water and did not extend very far into the upper sewer air.

When one barrel (55 gallons) of gasoline was dumped into the sewer at the rate of 5 gallons per minute, the highest percentage of gasoline vapor 2 feet above the sewer water was 0.70 per cent. The gasoline vapor was practically all swept past the manholes in from 18 to 30 minutes. Under these same conditions of test, except with the velocity of the sewer water much less, dangerous atmospheres existed in the sewer 5 hours after the gasoline was poured in.

## ACKNOWLEDGMENTS

The authors wish to acknowledge the valuable assistance rendered them in conducting these tests, by Mr. W. H. Coster, Superintendent of the Board of Fire Prevention, Dept. of Public Safety, Mr. M. S. Evans, Chief of the Bureau of Tests, and Mr. J. Chas. Palmer, Division Engineer, Bureau of Highways and Sewers, all of the staff of the Department of Public Works, City of Pittsburgh. They were present at all tests, made numerous suggestions and helped in many ways. Mr. N. S. Sprague, Superintendent of the Bureau of Engineering, City of Pittsburgh, also rendered valuable assistance.

U. S. BUREAU OF MINES, PITTSBURGH

# THE ANALYTICAL DISTILLATION OF PETROLEUM -II[1]

By W. F. Rittman and E. W. Dean

Received June 26, 1915

In a previous paper[2] attention was called to the need in the scientific and in the commercial petroleum world of an accurate and satisfactory method for the quantitative distillation of crude oil and its products. The results of a series of redistillation experiments showed that a method of efficient separation, involving the use of a Hempel column of moderate dimensions, attained a degree of separation of 56 per cent, on the arbitrary and empirical scale fixed by experimental conditions. The Ubbelohde-Engler method, representing moderate separation, was rated at 26 per cent on the same scale. The Allen-Jacobs method of minimum separation obtained a degree of separation of 14 per cent. It was shown also that a single Hempel distillation was more efficient than two successive open flask distillations.

[1] Published with the permission of the Director of the Bureau of Mines.

[2] Rittman and Dean, THIS JOURNAL, 7 (1915), 185.

## SCOPE OF THE PRESENT PAPER

The experiments described in the present paper deal chiefly with a comparison of results attained by the use of various types of fractionating apparatus. Crude oil distillations have been made with representatives of nearly all types of still-heads now in use and figures are given which should be readily intelligible to the petroleum technologist. Attention has been given in the experiments both to degree of efficiency attained and to mechanical details.

In the earlier paper no attempt was made to determine the relative advantages of various specific methods. It was, however, clearly indicated that the class involving efficient fractionation seemed most promising, as they attained most nearly the desired end, which is the separation of the oil into its constituents. The method of minimum separation seems to have advantages for the examination of emulsified or difficultly distillable oils but it involves rather tedious manipulation, and for that reason as well as on account of its inherently inefficient fractionation, it is not to be recommended for general use. The whole problem, except for the matter of "cracking," seems to resolve itself into applying the principle of efficient fractionation in some way which will be satisfactory to the laboratory worker.

A further series of experiments has been outlined which should furnish definite and conclusive evidence with regard to the matter of cracking. It seems improbable, however, that the results obtained will alter in any way the conclusions drawn from the present investigation. With Pennsylvania crude oil there is strong evidence that no cracking occurs at temperatures up to at least 300° C. and in addition it has been shown that the possibility of cracking is but slightly greater with efficient than with moderate separation.

## GENERAL OUTLINE OF PROCEDURE

It was decided to make first a comparison of stills from as comprehensive a list as would in any possibility be available to the petroleum chemist. Stills were not, however, purchased indiscriminately but consideration was given in most cases to the possibility of too efficient condensation. At temperatures ranging between 250° and 300° C. any moderately long tube will act as an air condenser and, on this account, few still-heads of excessive length were secured.

Still-heads of all types listed in the catalogues of chemical supply houses were purchased and, in

addition, several not in common use, but of theoretical importance, were made to order.[1]

A 10-gallon sample of Pennsylvania crude petroleum was obtained and portions were used for all distillations of the series. Efficiency of separation was not measured by the rather tedious method outlined in the previous paper, as results sufficiently explicit for present purposes could be more easily obtained. The magnitude of the first cut was taken as an indication of relative degree of efficiency and it was found possible to differentiate the various stills with entire clearness on this basis.

Experimental work was divided into three general sections:

I—Comparisons were made of the various types of still-heads. From the results of these experiments one type was selected which was clearly indicated as most desirable.

II—A careful study was made of the results obtained by various modifications of the selected type.

III—Some experiments were performed to study possible cracking effects in the particular still which the earlier experiments had indicated as most advantageous.

[1] Special glass apparatus was constructed by Mr F E Donath, glass blower in the Pittsburgh laboratory of the Bureau of Mines.

Metal apparatus was made by Mr. W. F. Hausstein, chief instrument maker in the Pittsburgh laboratory of the Bureau of Mines, and by Mr. W. Farnham of the Industrial Department, Havemeyer Chemical Laboratories of Columbia University.

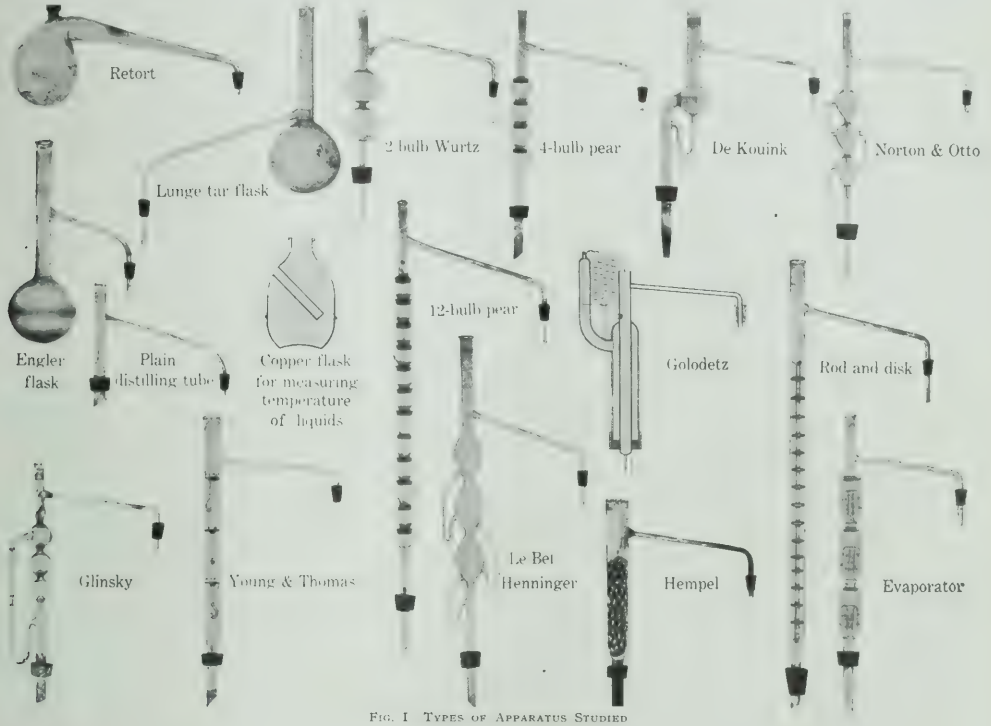


FIG. I TYPES OF APPARATUS STUDIED

EXPERIMENTAL DETAILS

No modifications were made in the procedure outlined for the earlier series[1] of experiments except in the matter of rate of distillation. This was increased somewhat and kept approximately the same as the standard among petroleum technologists, which is 2 to 2.5 cc. per minute.

All results are recorded in terms of percentage by weight. Unless otherwise specified, initial charges of 200 grams were employed.

Several of the distilling vessels were made with bulb and fractionating column in one piece. Most of the still-heads were, however, detachable and were employed in connection with a 250 cc. copper Kjeldahl flask which had been modified (see Fig. I) so as to permit the easy measurement of temperatures of the liquid oil. The cork joints between distilling bulb and fractionating column proved troublesome but it was found that by the exercise of sufficient care they could be made tight with a paste of litharge and glycerine.

The results obtained by the individual stills are shown in Table I. These are of little interest in detail unless it is desired to learn the characteristic behavior of any special type. Specific gravity figures have been obtained in all cases but do not seem to be particularly instructive. Of more importance are

[1] Rittman and Dean, *Loc. cit.*

TABLE I—RESULTS OF DISTILLATIONS MADE WITH VARIOUS COLUMNS SHOWN IN FIG. I

1—Bubble Tower

| Temp. | Percentages | | | | Specific gravities | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| 125 | [illegible] | | | | | | | |
| 150 | 4.9 | 5.2 | 4.9 | 5.0 | 0.708 | 0.709 | 0.707 | 0.708 |
| 175 | 7.7 | 7.5 | 7.8 | 7.6 | 0.732 | 0.734 | 0.733 | 0.733 |
| 200 | 7.7 | 7.9 | 7.8 | 7.8 | 0.753 | 0.754 | 0.752 | 0.753 |
| 225 | 7.6 | 7.4 | 7.5 | 7.5 | 0.766 | 0.767 | 0.768 | 0.767 |
| 250 | 7.1 | 7.1 | 6.8 | 7.0 | 0.778 | 0.779 | 0.780 | 0.779 |
| 275 | 6.5 | 6.7 | 7.0 | 6.7 | 0.789 | 0.790 | 0.789 | 0.789 |
| 300 | 6.5 | 6.3 | 5.9 | 6.2 | 0.799 | 0.800 | 0.800 | 0.800 |
| 325 | 6.2 | 6.6 | 6.9 | 6.6 | 0.809 | 0.811 | 0.811 | 0.810 |

Average variation, 2.1 per cent

2—Packed Tower

| Temp. | Immersed in liquid | | Just below surface | | At middle of outlet | |
|---|---|---|---|---|---|---|
| °C. | Per cent | Sp. gr. | Per cent | Sp. gr. | Per cent | Sp. gr. |
| 100 | 0.0 | | 2.1 | 0.689 | | |
| 125 | 0.8 | | 2.5 | 0.691 | 4.5 | 0.729 |
| 150 | 4.1 | | 8.7 | 0.724 | 7.6 | 0.733 |
| 175 | 7.0 | 0.729 | 8.3 | 0.747 | 10.0 | 0.756 |
| 200 | 7.3 | 0.747 | 8.3 | 0.764 | 11.0 | 0.773 |
| [illegible] | | 0.762 | 8.3 | 0.780 | 6.7 | 0.789 |
| 250 | 6.5 | 0.723 | 6.8 | 0.792 | 8.0 | 0.798 |
| 275 | 6.0 | 0.784 | 6.5 | 0.804 | 9.1 | 0.816 |
| 300 | 8.1 | 0.797 | 7.4 | 0.815 | 7.3 | 0.827 |

3—Lunge Tube Filled

| Temp. | Percentages | | | | Specific gravities | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| 100 | 0.8 | [illegible] | | | | | | |
| 125 | 3.8 | 3.9 | 4.2 | 4.0 | 0.699 | 0.696 | 0.706 | 0.700 |
| 150 | 7.7 | 7.7 | 7.1 | 7.4 | 0.727 | 0.727 | 0.730 | 0.728 |
| 175 | 7.8 | 9.1 | 8.4 | 8.4 | 0.748 | 0.747 | 0.751 | 0.749 |
| 200 | 8.4 | 6.8 | 7.8 | 7.6 | 0.765 | 0.763 | 0.767 | 0.765 |
| 225 | 5.8 | 7.8 | 7.4 | 7.0 | 0.777 | 0.777 | 0.780 | 0.778 |
| 250 | 7.3 | 6.2 | 6.1 | 6.5 | 0.787 | 0.789 | 0.793 | 0.790 |
| 275 | 6.1 | 6.8 | 6.5 | 6.3 | 0.797 | 0.799 | 0.802 | 0.799 |
| 300 | 7.4 | 7.3 | 7.5 | 7.4 | 0.810 | 0.811 | 0.814 | 0.812 |

Average variation, 5.9 per cent

4—Lidholm Bubble Method

| Temp. | Percentages | | | | | Specific gravities | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | D | Av. | A | B | C | D | Av. |
| 100 | 2.6 | 2.7 | 3.0 | 3.0 | 2.8 | 0.678 | 0.683 | 0.683 | 0.686 | 0.682 |
| 125 | 5.1 | 5.7 | 5.3 | 5.5 | 5.4 | 0.712 | 0.713 | 0.715 | 0.714 | 0.713 |
| 150 | 7.9 | 7.7 | 7.6 | 7.8 | 7.7 | 0.737 | 0.738 | 0.738 | 0.739 | 0.738 |
| 175 | 7.2 | 7.9 | 7.6 | 7.0 | 7.4 | 0.755 | 0.757 | 0.756 | 0.757 | [illegible] |
| 200 | 6.8 | 6.9 | 7.4 | 7.5 | 7.1 | 0.769 | 0.770 | 0.771 | 0.772 | 0.771 |
| 225 | 7.1 | 6.9 | 6.7 | 7.1 | 7.0 | 0.782 | 0.783 | 0.782 | 0.783 | 0.782 |
| 250 | 6.8 | 7.3 | 6.7 | 6.8 | 6.9 | 0.794 | 0.795 | 0.794 | 0.794 | 0.794 |
| 275 | 6.7 | 7.1 | 6.5 | 7.1 | 6.8 | 0.804 | 0.806 | 0.805 | 0.805 | 0.805 |

Average variation, 3.3 per cent

5—Plate Distilling Tower

| Temp. | Percentages | | | | Specific gravities | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| 100 | 3.2 | 2.8 | 3.2 | 3.1 | 0.683 | 0.688 | 0.685 | 0.685 |
| 125 | [illegible] | | | 4.8 | 0.714 | 0.715 | 0.715 | 0.715 |
| 150 | 7.5 | 7.3 | 7.3 | 7.4 | 0.738 | 0.737 | 0.737 | 0.737 |
| 175 | 8.0 | 8.0 | 8.4 | 8.1 | 0.757 | 0.755 | 0.756 | 0.756 |
| 200 | 7.9 | 7.5 | 7.2 | 7.5 | 0.771 | 0.769 | 0.770 | 0.770 |
| 225 | 6.6 | 6.9 | 7.3 | 6.9 | 0.782 | 0.781 | 0.782 | 0.782 |
| [illegible] | 7.0 | 7.5 | 6.6 | 7.0 | 0.795 | 0.793 | 0.794 | 0.794 |
| 275 | 7.2 | 7.3 | 7.1 | 7.2 | 0.806 | 0.804 | 0.806 | 0.805 |

Average variation, 2.5 per cent

6—Tower with Wetted Surface

| Temp. | Percentages | | | | Specific gravities | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| [illegible] | [illegible] | | | | | | | |
| [illegible] | 4.4 | | | | | | | |
| 125 | 5.3 | | | | 0.718 | | | |
| 150 | 7.0 | | | | 0.741 | | | |

Column flooded, due to small bore of tube from flask to first bulb.

7—Empty Tube

| Temp. | Percentages | | | | Specific gravities | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| 100 | 4.3 | 4.3 | 4.5 | 4.4 | 0.681 | 0.681 | 0.680 | 0.681 |
| 125 | 5.7 | 5.1 | 5.8 | 5.5 | 0.732 | 0.722 | 0.722 | 0.722 |
| 150 | 8.5 | 9.2 | 8.0 | 8.5 | 0.745 | 0.744 | 0.743 | 0.744 |
| 175 | 7.0 | 7.3 | 7.1 | 7.1 | 0.761 | 0.764 | 0.760 | 0.762 |
| 200 | 6.1 | 6.7 | 6.6 | 6.5 | 0.773 | 0.775 | 0.773 | 0.774 |
| 225 | 6.2 | 6.2 | 5.8 | 6.1 | 0.784 | 0.786 | 0.783 | 0.784 |
| 250 | 7.2 | 6.2 | 6.7 | 6.7 | 0.794 | 0.795 | 0.793 | 0.794 |
| 275 | 7.2 | 6.6 | 7.3 | 7.0 | 0.807 | 0.806 | 0.805 | 0.806 |

Average variation, 3.8 per cent

8—Bubble Tower Modified

| Temp. | Percentages | | | | Specific gravities | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| 100 | [illegible] | | | 4.8 | 0.682 | 0.682 | 0.682 | 0.682 |
| 125 | 5.6 | 5.5 | 5.7 | 5.6 | 0.722 | 0.727 | 0.721 | 0.723 |
| 150 | 7.1 | 6.7 | 7.0 | 6.9 | 0.744 | 0.745 | 0.744 | 0.744 |
| 175 | [illegible] | | 0.6 | 8.6.7 | 0.759 | 0.759 | 0.758 | 0.759 |
| 200 | 6.9 | 7.5 | 6.7 | 7.0 | 0.770 | 0.771 | 0.772 | 0.771 |
| 225 | 6.9 | 6.3 | 6.5 | 6.6 | 0.782 | 0.782 | 0.782 | 0.782 |
| 250 | 6.5 | 6.5 | 7.0 | 6.6 | 0.792 | 0.793 | 0.793 | 0.793 |
| 275 | 7.0 | 7.1 | 6.8 | 7.0 | 0.805 | 0.806 | 0.805 | 0.805 |

Average variation, 2.0 per cent

9—Norton and Otto Tower

| Temp. | Percentages | | | | Specific gravities | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| 100 | [illegible] | | | | | | | |
| 125 | 4.4 | | | | 0.683 | | | |
| 150 | 5.7 | | | | 0.726 | | | |
| 175 | 6.7 | | | | 0.744 | | | |
| 200 | 6.8 | | | | 0.760 | | | |
| [illegible] | 7.2 | | | | 0.773 | | | |

Column flooded, due to narrowness of tubes.

10—Glinsky, with Glass Valves(a)

| Temp. | Percentages | | | | Specific gravities | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| 100 | 5.6 | 5.9 | 5.2 | 5.6 | 0.686 | 0.688 | 0.681 | 0.685 |
| 125 | 5.9 | 6.1 | 5.4 | 5.8 | 0.725 | 0.726 | 0.723 | 0.725 |
| 150 | 6.8 | 7.7 | 8.2 | 7.6 | 0.746 | 0.748 | 0.746 | 0.747 |
| 175 | 6.9 | 7.1 | 7.3 | 7.1 | 0.759 | 0.762 | 0.761 | 0.761 |
| 200 | 5.8 | 6.3 | 6.6 | 6.2 | 0.772 | 0.775 | 0.774 | 0.774 |
| 225 | 6.8 | 6.7 | 6.8 | 6.8 | 0.783 | 0.785 | 0.785 | 0.784 |
| 250 | 6.2 | 7.4 | 6.2 | 6.6 | 0.793 | 0.797 | 0.795 | 0.795 |
| 275 | 6.6 | 6.7 | 7.2 | 6.8 | 0.805 | 0.810 | 0.808 | 0.808 |

Average variation, 4.1 per cent

11—Vigreux and Thomas Dephlegmator

| Temp. | Percentages | | | | Specific gravity | | | |
|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | Av. | A | B | C | Av. |
| 100 | 5.9 | 5.6 | 5.6 | 5.7 | 0.684 | 0.682 | 0.682 | 0.683 |
| 125 | 5.8 | 5.6 | 6.1 | 5.8 | 0.731 | 0.730 | 0.730 | 0.730 |
| 150 | 6.3 | 6.3 | 5.9 | 6.2 | 0.747 | 0.747 | 0.747 | 0.747 |
| 175 | 6.7 | 6.7 | 6.7 | 6.7 | 0.763 | 0.763 | 0.763 | 0.763 |
| 200 | 6.8 | 6.8 | 6.4 | 6.7 | 0.773 | 0.772 | 0.772 | 0.772 |
| 225 | 6.3 | 6.3 | 6.7 | 6.4 | 0.784 | 0.782 | 0.783 | 0.783 |
| 250 | 6.1 | 6.3 | 6.2 | 6.2 | 0.794 | 0.794 | 0.794 | 0.794 |
| 275 | [illegible] | [6.0] | 6.9 | 0.806 | 0.805 | 0.805 | 0.805 | |

Average variation, 1.9 per cent

12—Twelve-Bulb Pear(a)

| Temp. | Per cent | Specific gravity |
|---|---|---|
| °C. | | |
| 100 | 5.7 | 0.682 |
| 125 | 6.7 | [illegible] |
| 150 | 6.1 | [illegible] |
| 175 | 7.1 | 0.764 |
| 200 | 7.0 | 0.776 |
| 225 | 6.1 | 0.785 |

The column flooded and stopped distillation.

13—Le Bel-Henninger(a)

12 inches

| Per cent | Specific gravity |
|---|---|
| 5.9 | 0.684 |
| [illegible] | [illegible] |
| [illegible] | [illegible] |
| [illegible] | [illegible] |
| 6.7 | 0.775 |
| [illegible] | [illegible] |

Column flooded and stopped distillation.

14—Golodetz (copper)

8 inches

| Per cent | Specific gravity |
|---|---|
| 6.2 | 0.682 |
| [illegible] | [illegible] |
| 6.4 | 0.748 |
| 6.9 | 0.765 |
| [illegible] | 0.777 |
| [illegible] | 0.792 |
| 8.0 | 0.804 |

Results abnormal. Strong indications of cracking (see p. 757).

15—Hempel Drop Tube Beads Seal

| Temp. | Percentages | | | | | | | Specific gravities | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | D | E | F | Av. | A | B | C | D | E | F | Av. |
| 100 | 6.2 | 6.5 | 5.9 | 6.1 | 6.5 | 6.3 | 6.3 | 0.698 | 0.695 | 0.696 | 0.694 | 0.689 | 0.684 | 0.693 |
| 125 | 6.4 | 6.0 | 6.5 | 6.4 | 6.2 | 6.1 | 6.3 | 0.733 | 0.732 | 0.732 | 0.732 | 0.731 | 0.730 | 0.732 |
| 150 | 5.6 | 6.2 | 5.9 | 5.9 | 6.2 | 6.3 | 6.0 | 0.751 | 0.748 | 0.747 | 0.747 | 0.747 | 0.746 | 0.747 |
| 175 | 7.0 | 6.9 | 6.7 | 7.0 | 6.7 | 6.8 | 6.8 | 0.764 | 0.762 | 0.762 | 0.762 | 0.761 | 0.762 | 0.763 |
| 200 | 6.2 | 6.2 | 6.3 | 6.4 | 6.4 | 6.5 | 6.3 | 0.775 | 0.773 | 0.773 | 0.772 | 0.772 | 0.774 | 0.773 |
| 225 | 6.5 | 6.4 | 6.4 | 6.0 | 6.5 | 6.4 | 6.4 | 0.785 | 0.783 | 0.783 | 0.782 | 0.783 | 0.783 | 0.783 |
| 250 | 6.9 | 6.1 | 6.5 | 6.4 | 6.5 | 6.5 | 6.5 | 0.796 | 0.793 | 0.794 | 0.794 | 0.794 | 0.793 | 0.794 |
| 275 | [5.5] | 7.0 | 6.9 | 7.1 | 7.2 | 6.8 | 7.0 | 0.806 | 0.804 | 0.806 | 0.806 | 0.805 | 0.805 | 0.805 |

Average variation, 2.2 per cent.

16—Rod and Disk(a)

| Temp. | Percentages | Specific gravity |
|---|---|---|
| °C. | | |
| 100 | 6.5 | 0.685 |
| 125 | 5.4 | 0.732 |
| 150 | 6.4 | 0.749 |
| 175 | 7.0 | 0.764 |
| 200 | 6.8 | 0.775 |
| 225 | 6.5 | 0.785 |
| 250 | [illegible] | 0.797 |

Distillation stopped by excessive reflux condensation.

17—Three Section Evaporator

| Temp. | Percentages | | | | | | | Specific gravities | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| °C. | A | B | C | D | E | F | Av. | A | B | C | D | E | F | Av. |
| 100 | 6.2 | 6.9 | 6.5 | 6.7 | 6.6 | 6.6 | 6.6 | 0.684 | 0.687 | 0.687 | 0.687 | 0.686 | 0.686 | 0.686 |
| 125 | 5.4 | 6.8 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 0.729 | 0.732 | 0.731 | 0.732 | 0.731 | 0.731 | 0.731 |
| 150 | 6.7 | 6.3 | 7.4 | 6.5 | 6.7 | 6.7 | 6.7 | 0.749 | 0.752 | 0.751 | 0.750 | 0.751 | 0.751 | 0.751 |
| 175 | 7.2 | 7.0 | 7.1 | 7.1 | 7.1 | 7.1 | 7.1 | 0.761 | 0.766 | 0.765 | 0.763 | 0.764 | 0.764 | 0.764 |
| 200 | 6.4 | 5.6 | 6.9 | 6.9 | 6.5 | 6.3 | 6.3 | 0.774 | 0.775 | 0.776 | 0.775 | 0.775 | 0.775 | 0.775 |
| 225 | 6.4 | 6.4 | 5.1 | 6.6 | 6.1 | 6.3 | 6.4 | 0.783 | 0.784 | 0.783 | 0.785 | 0.784 | 0.784 | 0.784 |
| 250 | 6.7 | 6.6 | 6.9 | 6.4 | 6.7 | 6.7 | 6.7 | 0.795 | 0.792 | 0.792 | 0.792 | 0.793 | 0.793 | 0.793 |
| 275 | 7.1 | 6.9 | 6.5 | 7.1 | 6.9 | 6.8 | 7.0 | 0.807 | 0.808 | 0.808 | 0.806 | 0.807 | 0.808 | 0.807 |

Average variation, 4.3 per cent

(a) Purchased from Chemical Supply House. (b) Rittman and Dean, [illegible]. (c) Made to special order.

the figures for variations among the cuts of duplicate distillations, which are indicative, in a general way, of the readiness with which checks may be obtained by the laboratory worker. These figures have, of course, too limited a basis to be regarded as any sort of an exact measure but they are of some weight as the distillations were all conducted by one operator and with an equal degree of care in manipulation.

A study of Table II and of Fig. II shows that when comparisons are made on the basis of the magnitude of the first cut, a number of the still-heads are shown to be practically equal in efficiency. Still-heads represented by Sections 10 to 17 of Table II are sufficiently alike so that choice may be made among them by considering other factors than the degree of efficiency attained. The 12-bulb pear, the rod and disk, and the Le Bel-Henninger are immediately eliminated for petroleum because they fail to permit

TABLE II—SUMMARY OF TABLE I

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. °C | Allen-Jacobs | Retort (B) | Lunge | Ubbelohde | Plain distilling tube | 2-Bulb Wurtz | 4-Bulb Pear | De Konink | Norton and Otto | Glinsky | Young and Thomas | 12-Bulb Pear | Le Bel-Henninger | Golodetz | 6-Inch Hempel | Rod disk | Evaporator |
| 100 | 0.0 | 0.5 | 1.0 | 2.8 | 3.1 | 4.4 | 4.4 | 4.8 | 4.9 | 5.6 | 5.7 | 5.7 | 5.9 | 6.2 | 6.3 | 6.5 | 6.6 |
| 125 | 1.0 | 2.5 | 4.0 | 5.4 | 4.8 | 5.3 | 5.5 | 5.6 | 5.7 | 5.8 | 5.8 | 6.7 | 5.8 | 5.7 | 6.3 | 5.9 | 6.0 |
| 150 | 5.0 | 8.7 | 7.4 | 7.7 | 7.4 | 7.0 | 8.5 | 6.9 | 6.7 | 7.6 | 6.2 | 6.1 | 7.0 | 6.4 | 6.8 | 6.4 | 6.7 |
| 175 | 7.6 | 8.3 | 8.4 | 7.4 | 8.1 | | 7.1 | 6.7 | 6.8 | 7.1 | 6.7 | 7.1 | 6.7 | 8.0 | 6.8 | 7.0 | 7.1 |
| 200 | 7.8 | 8.3 | 7.6 | 7.1 | 7.5 | | 6.5 | 7.0 | 7.2 | 6.2 | 6.7 | 7.0 | 6.7 | 7.9 | 6.3 | 6.3 | 6.3 |
| 225 | 7.5 | 8.3 | 7.0 | 7.0 | 6.9 | | 6.1 | 6.6 | | 6.8 | 6.4 | 6.1 | | 8.5 | 6.4 | 6.5 | 6.1 |
| 250 | 7.0 | 6.8 | 6.5 | 6.9 | 7.0 | | 6.7 | 6.6 | | 6.6 | 6.2 | | | 8.0 | 6.5 | 7.1 | 6.7 |
| [illegible] | 6.7 | 6.5 | 6.3 | 6.8 | 7.2 | | 7.0 | 7.0 | | 6.8 | 6.9 | | | | 7.0 | | 6.9 |
| [illegible] | 6.2 | 7.4 | 7.4 | | | | | | | | | | | | | | |
| 325 | 6.6 | | | | | | | | | | | | | | | | |
| Up to 150 | 6.0 | 11.7 | 12.4 | 15.9 | 15.3 | 16.7 | 18.4 | 17.3 | 17.3 | 19.0 | 17.7 | 18.5 | 18.7 | 18.3 | 18.6 | 18.8 | 19.3 |

the passage of vapor when higher temperatures are reached. The Golodetz, which on theoretical grounds seems the most desirable still-head of all, behaves in

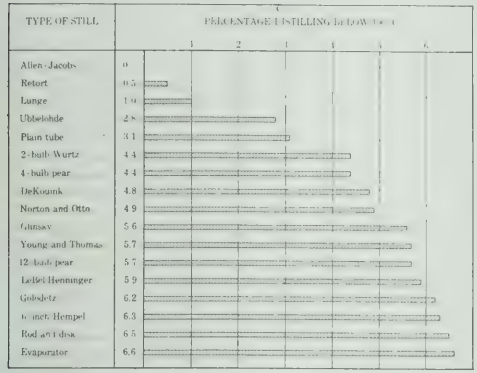


FIG. II— RELATIVE MAGNITUDES OF CUTS TO 100° OBTAINED BY USE OF VARIOUS TYPES OF STILLS

**Both the Allen-Jacobs and Ubbelohde Methods Involve the Use of an Engler Flask**

an abnormal manner[1] with regard to the size of cuts above 175°. Much work was done with this still, using another sample of oil, and reliable results seemed to be unobtainable.

The four still-heads whose merits remain to be discussed are the Glinsky, Young and Thomas, Hempel, and evaporator. The Young and Thomas, and evaporator are, perhaps, best in many ways but they are not available on the market and in addition are rather fragile and complicated. The Glinsky is a little less efficient and while it can be easily purchased is subject to objection on the grounds of fragility and costliness. All indications seem to point to the Hempel as most promising and from the results of the present experiments it seems to be in a class by itself. Its one inherent disadvantage is the amount of phlegm or condensed vapor held up by the fractionating column. This has not, however, been found to interfere seriously in distillations involving an initial charge of 100 grams or more.

Some of the numerous advantages of the Hempel still-head may be mentioned. The apparatus is efficient, cheap, readily available or improvisable, easy to manipulate and clean, and in addition it permits the elimination of the troublesome cork joint between distilling bulb and fractionating column. None of the other types possess this advantage except the pear and the rod and disk: both of these, however, fail to attain the necessary degree of efficiency unless they are of excessive length, in which case too much condensation occurs and the stills fail to work through the necessary range of temperature.

### STUDY OF THE HEMPEL COLUMNS

The possibilities of the Hempel column were studied in considerable detail and with regard to the following factors (see Fig. III):

1—Influence of height of column.
2—Influence of diameter of column.
3—Influence of mechanical details.

INFLUENCE OF HEIGHT—Three Hempel columns were obtained, respectively 4, 6 and 10 inches in height from constriction to outlet tube. They were 1 inch in diameter and held columns of aluminum beads respectively 3, 5 and 9 inches in height. The still-heads were used in connection with the copper flask described in an earlier connection. Results of distillations with these columns appear in Table III.

The last column in Table III brings out the fact that when vapors from crude petroleum pass through a fractionating column of the Hempel type at the moderate rate at which laboratory distillations are conducted they come very nearly to equilibrium with the condensed liquid after passing through a comparatively short length of the filling material. Increasing the length of the column as much as 200 per cent does not materially affect the results obtained. This is made evident when it is noted that the 10-in.

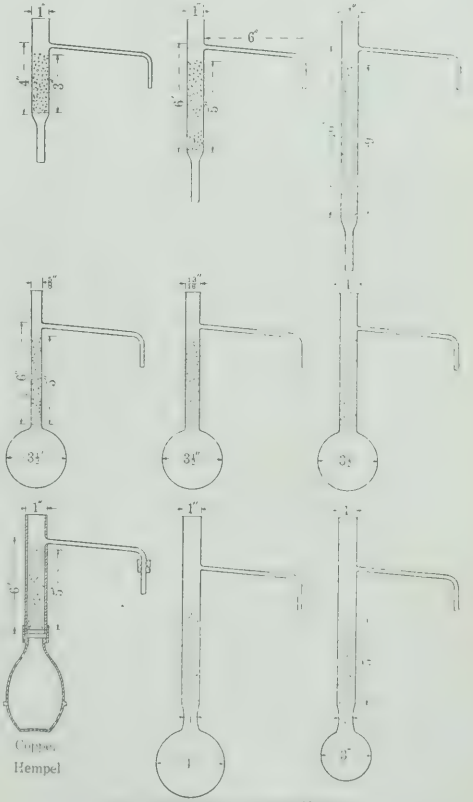


FIG. III HEMPEL COLUMNS TESTED

column was merely of the same order of efficiency as the 4-in. For mechanical reasons the 6-in. height seemed to be an optimum. The 10-in. was unwieldy

[1] The only logical explanation of this action which has occurred to the writers is that, on account of some details of construction, pressure is developed in the still and cracking caused.

and produced too much condensation at higher temperatures; the 4-in. tended to be unreliable in producing checks unless the rate of distillation was regulated with much care.

TABLE III—RESULTS WITH HEMPEL COLUMNS OF VARIOUS HEIGHTS (DIAMETER, 1 INCH)

| Temp. | Percentages | | | | | | Specific gravities | | | | | | Av. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | A | B | C | D | E | F | A | B | C | D | E | F | Av. |
| **FOUR-INCH COLUMN** | | | | | | | | | | | | | |
| 100 | 5.7 | 5.9 | 5.9 | [7.0] | 5.6 | ... | 0.690 | 0.692 | 0.691 | 0.687 | 0.687 | ..... | 0.689 | 5.8 |
| 125 | 6.1 | 6.2 | 6.4 | 6.3 | 5.8 | ... | 0.730 | 0.730 | 0.730 | 0.733 | 0.731 | ..... | 0.731 | 6.2 |
| 150 | 6.2 | 6.5 | 7.0 | 6.4 | 6.1 | ... | 0.748 | 0.747 | 0.746 | 0.748 | 0.747 | ..... | 0.747 | 6.4 |
| 175 | 7.0 | 6.6 | 6.6 | 6.7 | 6.9 | ... | 0.761 | 0.762 | 0.762 | 0.762 | 0.761 | ..... | 0.762 | 6.8 |
| 200 | 6.2 | 6.4 | 6.3 | 6.4 | 6.2 | ... | 0.773 | 0.772 | 0.772 | 0.773 | 0.772 | ..... | 0.772 | 6.3 |
| 225 | 6.3 | 6.7 | 6.2 | 6.2 | 6.7 | ... | 0.783 | 0.782 | 0.783 | 0.783 | 0.782 | ..... | 0.783 | 6.4 |
| 250 | 6.5 | 6.3 | 6.4 | 6.5 | 6.2 | ... | 0.792 | 0.794 | 0.794 | 0.793 | 0.793 | ..... | 0.793 | 6.4 |
| 275 | 7.3 | 7.3 | 7.2 | 6.7 | 7.1 | ... | 0.806 | 0.805 | 0.805 | 0.806 | 0.805 | ..... | 0.805 | 7.1 |
| | Average variation, 2.4 per cent | | | | | | | | | | | | | |
| **SIX-INCH COLUMN** | | | | | | | | | | | | | |
| 100 | 6.2 | 6.5 | 5.9 | 6.1 | 6.5 | 6.3 | 0.698 | 0.695 | 0.696 | 0.694 | 0.689 | 0.684 | 0.693 | 6.3 |
| 125 | 6.4 | 6.0 | 6.5 | 6.4 | 6.2 | 6.1 | 0.733 | 0.732 | 0.732 | 0.732 | 0.731 | 0.730 | 0.732 | 6.3 |
| 150 | 5.6 | 6.2 | 5.9 | 5.9 | 6.2 | 6.3 | 0.751 | 0.748 | 0.747 | 0.747 | 0.747 | 0.746 | 0.747 | 6.0 |
| 175 | 7.0 | 6.9 | 6.7 | 7.0 | 6.7 | 6.7 | 0.764 | 0.762 | 0.762 | 0.762 | 0.762 | 0.761 | 0.762 | 6.8 |
| 200 | 6.2 | 6.2 | 6.3 | 6.4 | 6.4 | 6.5 | 0.775 | 0.773 | 0.773 | 0.772 | 0.772 | 0.774 | 0.773 | 6.3 |
| 225 | 6.5 | 6.4 | 6.4 | 6.0 | 6.5 | 6.4 | 0.785 | 0.783 | 0.783 | 0.782 | 0.783 | 0.783 | 0.783 | 6.4 |
| 250 | 6.9 | 6.1 | 6.5 | 6.4 | 6.5 | 6.5 | 0.796 | 0.793 | 0.794 | 0.794 | 0.793 | 0.794 | 0.794 | 6.5 |
| 275 | [5.5] | 7.0 | 6.9 | 7.1 | 7.2 | 6.8 | 0.806 | 0.804 | 0.806 | 0.806 | 0.805 | 0.805 | 0.805 | 7.0 |
| | Average variation, 2.2 per cent | | | | | | | | | | | | | |
| **TEN-INCH COLUMN** | | | | | | | | | | | | | |
| 100 | 6.3 | 6.3 | 7.0 | 6.9 | 7.3 | 6.7 | 0.688 | 0.692 | 0.687 | 0.685 | ..... | 0.684 | 0.687 | 6.7 |
| 125 | 5.9 | 6.3 | 6.3 | 6.3 | 6.3 | 5.8 | 0.732 | 0.733 | 0.732 | 0.731 | ..... | 0.728 | 0.731 | 6.2 |
| 150 | 6.1 | 5.8 | 6.3 | 6.8 | 6.2 | 6.0 | 0.746 | 0.749 | 0.748 | 0.748 | ..... | 0.745 | 0.747 | 6.2 |
| 175 | 6.7 | 6.5 | 6.8 | 6.9 | 6.5 | 6.9 | 0.762 | 0.762 | 0.763 | 0.762 | ..... | 0.759 | 0.762 | 6.8 |
| 200 | 6.1 | 6.2 | 6.1 | 6.2 | 6.5 | 6.3 | 0.772 | 0.772 | 0.772 | 0.773 | ..... | 0.772 | 0.772 | 6.2 |
| 225 | 6.4 | 6.5 | 6.5 | 6.5 | ... | ... | 0.782 | 0.782 | 0.783 | 0.783 | ..... | ..... | 0.783 | 6.5 |
| 250 | 6.8 | 6.6 | 6.8 | 6.4 | ... | ... | 0.793 | 0.794 | 0.794 | 0.793 | ..... | ..... | 0.793 | 6.6 |
| 275 | 7.1 | 7.3 | 7.1 | 7.4 | ... | ... | 0.804 | 0.806 | 0.806 | 0.807 | ..... | ..... | 0.806 | 7.2 |
| | Average variation, 2.4 per cent | | | | | | | | | | | | | |

INFLUENCE OF DIAMETER—Having demonstrated that a 6-in. column with 5 in. of beads seemed to be an optimum as far as the factor of height was concerned, the next experiments were concerned with the matter of diameter. Distillations were run with three 6-in. columns, respectively, $^5/_8$ in., $^{13}/_{16}$ in. and 1 in. in diameter. These columns were sealed directly on glass bulbs and were made without any constriction at the base of the column. Reasons for this will be set forth in the subsequent section on mechanical advantages and possibilities. Results, shown in Table IV, indicate that the influence of diameter on the efficiency of a Hempel column used in petroleum distillation, is slight. Differences are of about the same order as those among figures for columns of different heights.

INFLUENCE OF MECHANICAL DETAILS—After having demonstrated that for petroleum distillation the effects attained by Hempel columns of widely varying dimensions differ but slightly it was deemed advisable to study the influence of various mechanical details. The following were given consideration:

*a*—Shape, size and material of distilling bulb.

*b*—Material of column.

*c*—Filling material in column.

*d*—Size of charge.

To determine the degree of importance of the distilling bulb, series of experiments were performed in which similar Hempel columns were used in connection with different types of vessels. Comparisons were made between effects produced by glass bulbs of capacities respectively 500 cc. and 300 cc. Distillations were made in 300 cc. bulbs with and without a constriction at the base of the fractionating column. In addition a copper distilling flask was used in connection with one of the standard 6-in. columns. The results are given in the first four columns of Table V.

TABLE IV—RESULTS WITH HEMPEL COLUMNS OF VARIOUS DIAMETERS (HEIGHT, 6 INCHES, WITH 5 INCHES OF BEADS)

| Temp. | Percentages | | | | | Specific gravities | | | | | Av. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C. | A | B | C | D | E | A | B | C | D | E | Av. |
| **DIAMETER, $^5/_8$ INCH** | | | | | | | | | | | |
| 100 | 5.9 | 6.0 | 5.9 | ... | ... | 0.681 | 0.685 | 0.685 | ... | ... | 0.684 | 5.9 |
| 125 | 6.4 | 6.1 | 5.7 | ... | ... | 0.729 | 0.730 | 0.731 | ... | ... | 0.730 | 6.1 |
| 150 | 6.9 | 6.7 | 6.4 | ... | ... | 0.744 | 0.747 | 0.748 | ... | ... | 0.747 | 6.6 |
| 175 | 6.9 | 7.2 | 7.3 | ... | ... | 0.758 | 0.761 | 0.762 | ... | ... | 0.760 | 7.1 |
| 200 | 6.6 | 6.7 | 6.6 | ... | ... | 0.771 | 0.775 | 0.772 | ... | ... | 0.773 | 6.6 |
| 225 | 6.0 | 6.2 | 6.2 | ... | ... | 0.781 | 0.785 | 0.784 | ... | ... | 0.783 | 6.2 |
| 250 | 7.0 | 6.9 | 6.7 | ... | ... | 0.792 | 0.795 | 0.794 | ... | ... | 0.794 | 6.9 |
| 275 | ... | ... | 7.0 | ... | ... | ... | ... | 0.809 | ... | ... | 0.809 | 7.0 |
| | Average cut, 6.3 per cent | | | | | Average variation, 1.9 per cent | | | | | | |
| **DIAMETER, $^{13}/_{16}$ INCH** | | | | | | | | | | | | |
| 100 | 5.9 | 5.5 | 6.0 | 5.9 | ... | 0.684 | 0.682 | 0.683 | 0.684 | ..... | 0.683 | 5.8 |
| 125 | 6.5 | 6.1 | 6.3 | 6.0 | ... | 0.730 | 0.730 | 0.728 | 0.730 | ..... | 0.730 | 6.2 |
| 150 | 6.2 | 6.1 | 5.8 | 6.1 | ... | 0.749 | 0.748 | 0.745 | 0.746 | ..... | 0.747 | 6.1 |
| 175 | 6.8 | 7.0 | 6.7 | 6.6 | ... | 0.762 | 0.762 | 0.762 | 0.761 | ..... | 0.762 | 6.8 |
| 200 | 6.1 | 6.3 | 6.7 | 7.0 | ... | 0.774 | 0.773 | 0.772 | 0.772 | ..... | 0.773 | 6.5 |
| 225 | 6.5 | 6.2 | 6.2 | 6.0 | ... | 0.784 | 0.783 | 0.782 | 0.783 | ..... | 0.783 | 6.2 |
| 250 | 6.6 | 6.7 | 6.5 | 6.5 | ... | 0.795 | 0.795 | 0.793 | 0.794 | ..... | 0.794 | 6.6 |
| 275 | 6.4 | 5.9 | 6.1 | 6.0 | ... | 0.806 | 0.805 | 0.804 | 0.804 | ..... | 0.805 | 6.1 |
| 300 | 6.5 | 6.5 | 6.6 | 6.6 | ... | 0.815 | 0.816 | ... | 0.815 | ..... | 0.815 | 6.5 |
| | Average cut, 6.3 per cent | | | | | Average variation, 2.1 per cent | | | | | | |
| **DIAMETER, 1 INCH** | | | | | | | | | | | | |
| 100 | 6.2 | 5.9 | 6.1 | 5.7 | 5.8 | 0.687 | 0.683 | 0.685 | 0.683 | 0.683 | 0.684 | 5.9 |
| 125 | 5.9 | 6.3 | 6.1 | 6.0 | 6.5 | 0.733 | 0.731 | 0.734 | 0.730 | 0.731 | 0.732 | 6.2 |
| 150 | 6.2 | 6.4 | 6.3 | 6.1 | 6.1 | 0.749 | 0.747 | 0.747 | 0.747 | 0.747 | 0.747 | 6.2 |
| 175 | 6.4 | 6.3 | 6.4 | 6.9 | 6.7 | 0.763 | 0.763 | 0.763 | 0.762 | 0.763 | 0.763 | 6.5 |
| 200 | 6.7 | 6.6 | 6.8 | 6.7 | 6.1 | 0.773 | 0.773 | 0.774 | 0.772 | 0.772 | 0.773 | 6.6 |
| 225 | 6.0 | 6.4 | 6.2 | 6.1 | 6.5 | 0.783 | 0.784 | 0.784 | 0.782 | 0.784 | 0.783 | 6.2 |
| 250 | 6.4 | 6.3 | 6.4 | 6.6 | 6.5 | 0.795 | 0.794 | 0.795 | 0.793 | 0.795 | 0.794 | 6.4 |
| 275 | 6.2 | 6.4 | 6.0 | 6.2 | 6.2 | 0.805 | 0.806 | 0.806 | 0.804 | 0.805 | 0.805 | 6.2 |
| 300 | 6.6 | 6.3 | 6.7 | 6.8 | 6.7 | 0.816 | 0.816 | 0.817 | 0.816 | 0.816 | 0.816 | 6.6 |
| | Average cut, 6.3 per cent | | | | | Average variation, 2.2 per cent | | | | | | |

It appears that by using Hempel columns of approximately equal dimensions like results are obtained, whether the distilling bulb is smaller or larger, constricted or unconstricted, glass or copper.

Distillations made in an apparatus with both column and bulb of copper (Table V, No. 8) proved to be but slightly different from the ones employing a glass column.

Distillations were made, using glass instead of aluminum beads as filling material, and it was learned that this factor is of little influence as far as the numerical results of an analysis are concerned.

Finally distillations were run with an initial charge of 100 grams of oil and here there was a tendency for the cuts at higher temperatures to be consistently a little low. This effect was undoubtedly due to the influence of the lag of the distilled oil in the condenser tube.

Table V summarizes the effects of all the types of

TABLE V—SHOWING CLOSE AGREEMENT AMONG RESULTS (PERCENTAGES) OF DIFFERENT HEMPEL DISTILLATIONS

| Hempel column | 6 × 1 in. Col. with 5 in. of Beads | | | Flask in Fig. III | | Slender column (See Table IV) | Medium column (See Table IV) | Copper Hempel Diam.: 1 in Beads: 5 in | Same as 4 but with 100 g charge of oil | Average 1–5 | Average 1–9 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Flask Temperature ° C. | Copper 1 | Bur. of For. Creosote Regular 2 | Small bulb 3 | Al beads 4 | Glass beads 5 | 6 | 7 | 8 | 9 | | |
| 100 | 6.3 | 6.2 | 6.2 | 5.9 | 6.2 | 5.9 | 5.8 | 6.2 | 6.5 | 6.2 | 6.1 |
| 125 | 6.3 | 6.1 | 6.5 | 6.2 | 6.1 | 6.1 | 6.2 | 5.8 | 5.8 | 6.2 | 6.1 |
| 150 | 6.0 | 6.4 | 6.4 | 6.2 | 6.2 | 6.6 | 6.1 | 6.7 | 6.1 | 6.2 | 6.3 |
| 175 | 6.8 | 6.7 | 6.6 | 6.5 | 6.6 | 7.1 | 6.8 | 7.0 | 6.8 | 6.6 | 6.8 |
| 200 | 6.3 | 6.6 | 6.5 | 6.6 | 6.7 | 6.6 | 6.5 | 6.6 | 6.1 | 6.5 | 6.5 |
| 225 | 6.4 | 6.5 | 6.4 | 6.2 | 6.3 | 6.2 | 6.2 | 6.2 | 6.2 | 6.4 | 6.3 |
| 250 | 6.5 | 6.6 | 6.5 | 6.4 | 6.4 | 6.9 | 6.6 | 6.6 | 6.2 | 6.5 | 6.5 |
| 275 | [7.0] | 6.1 | 5.9 | 6.2 | [6.8] | [7.0] | 6.1 | 6.2 | 6.1 | 6.0 | 6.1 |
| Average cut | ... | ... | ... | ... | ... | ... | ... | ... | ... | 6.3 | 6.34 |
| Average variation | ... | ... | ... | ... | ... | ... | ... | ... | ... | 1.6 | 2.3 |

[] Bracketed results omitted from average. They include drainage of condenser at end of distillation.

6-in. Hempel columns which have been employed and shows that the average variation among cuts (2.3 per cent) is practically the same among the different methods as among duplicate distillations by any one method. The agreement is even more impressive when comparisons are limited to glass columns 6 in. long and 1 in. in diameter. Here the average variation is only 1.6 per cent.

The figures in Table V clearly demonstrate the fact that by using efficient fractionating columns of approximately equal dimensions the majority of the other factors which control results of distillation are rendered of negligible influence.

### MECHANICAL ADVANTAGES OF DIFFERENT TYPES OF APPARATUS

In the absence of trials in the hands of a considerable number of operators it is difficult to arrive at final conclusions regarding the mechanical advantages of different types of apparatus. On the basis of present experience, however, it has appeared that the simple

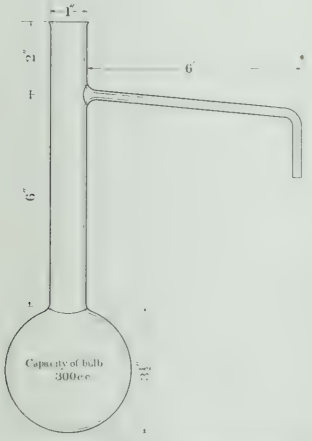


FIG. IV—HEMPEL FLASK OF OPTIMUM DIMENSIONS FOR PETROLEUM DISTILLATION

flask with an unconstricted column 1 in. in diameter and holding 5 in. of aluminum beads is most satisfactory (see Fig. IV). There seems to be little question as to the desirability of employing a fractionating column of approximately the size indicated. The details of material and method of construction are a little less definitely established but it is believed that the flask selected approaches an optimum with regard to simplicity and convenience of operation. It was at one time thought that an apparatus entirely of copper might be best but objections developed after some use. An inherent disadvantage is the impossibility of watching the behavior of the boiling oil during the course of a distillation.

A column of large bore is better than one of small as it minimizes the possibility of flooding and also reduces the danger of variations caused by air currents and atmospheric temperature changes. Dispensing with a constriction at the base of the fractionating column has seemed desirable for the following reasons: it permits the use of a shorter and less unwieldy flask, tends to lessen the possibility of flooding and in addition makes easier the cleaning of the distilling vessel. There are numerous simple mechanical devices by which the column of beads may be easily and conveniently supported. One which has been used is a copper wire, shaped into a spiral at one end and with a hook at the other, which can be pushed into the outlet tube of the flask.

Aluminum beads seem better than glass though there is no marked difference in the degree of efficiency attained (see Table V, No. 4). Glass beads fit together more closely and on that account are more liable to flood.

### CRACKING

The minimization or elimination of cracking is desirable in the analytical distillation of petroleum and on that account consideration has been given to it in the present connection. The importance of this factor of cracking seems to have been considerably overestimated, and an idea is prevalent that it is caused by the superheating incident to the running back of condensed vapors into the hot liquid in the bulb of a distilling flask. The following statements, which would be accepted as axiomatic by any modern chemist, serve to indicate the erroneousness of the above explanation of the mechanism of cracking.

"The cracking of heavy hydrocarbons by heat is to be regarded as simply an instance of the general rule that organic compounds are decomposed by heat. It is well known that the simpler petroleum hydrocarbons are stable at much higher temperatures than those of higher molecular weight."[1]

With this point of view it is obvious that cracking is due to the superheating of the heavy hydrocarbons of the boiling liquid in the distilling vessel and not to the superheating of the products of reflux condensation in the fractionating column. There are two temperature factors of importance, one that of the boiling liquid and the other that at which heat is transmitted to it. It does not seem that with a system of external heating the latter factor can be of much influence in distilling systems of the size employed in the laboratory. The problem seems to resolve itself into one of determining the temperature of the liquid in the bulb.

Approximate measurements of liquid temperatures were made in a number of the distillations and it was found that with the 6 in. Hempel apparatus the liquid was about 75° hotter than the vapor at the beginning of a distillation and 40° hotter at the end when the temperature of the vapor was about 300°. The final difference in the open flask method was about 10° so that a distillation of this sort could be carried up the temperature scale only about 30° farther than one involving efficient fractionation, with the possibility of cracking the same in both cases.

In addition to the above comparative evidence some of a more direct nature was secured by distillation experiments which, however, dealt only with Pennsylvania crude oil. Cracking is a time reaction and the amount of decomposition should be proportional to the

[1] Brooks, Bacon, Padgett and Humphrey, THIS JOURNAL, 7 (1915), 180.

time during which the oil is kept at a given temperature capable of producing the "cracking" effect. It is, therefore, obvious that if there is any cracking in the course of a distillation there should be twice as much in the course of two, and that successive distillations of the same sample of petroleum should cause a progressive increase in the percentage of constituents distilling below some given temperature. On this basis the following procedure was adopted:

A sample of oil was distilled in the usual manner up to a given temperature, all the distillate being collected in a single tared receiver. After stopping the distillation and letting the condenser drain, the amount distilled was determined by weighing. It was then poured back into the cooled distilling flask and another distillation conducted up to the same temperature. If cracking occurred in the first distillation it should also

TABLE VI—EXPERIMENTS TO TEST FOR "CRACKING"

| Apparatus (Hempel) | | Copper | Glass Medium bore Constricted neck | Glass Large bore Unconstricted neck |
|---|---|---|---|---|
| Temp. of vapor at end of distillation | | 280° C | 314° C | 315° C |
| Per cent by weight of repeated distillations | *a* | 57.0 | 63.0 | 64.8 | 70.1 |
| | *b* | 56.7 | 64.5 | 64.8 | 69.6 |
| | *c* | 56.7 | 66.1 | 65.3 | 70.0 |
| | *d* | .... | 66.7 | 66.2 | .... |
| | *e* | | | 66.3 | |
| Residue (per cent) | | 42.0 | 33.0 | 32.5 | 28.6 |
| Sum of residue and last distillate | | 98.7 | 99.7 | 98.8 | 98.6 |
| Per cent loss | | 1.3 | 0.3 | 1.2 | 1.4 |

have occurred in the second and the cut up to the given temperature would be greater in the second instance. The results of several of these experiments are given in Table VI. It is obvious that even up to 325° C. (uncorrected) there is no appreciable amount of cracking with the sample of Pennsylvania crude oil employed.

It is proposed in a later connection to experiment further in this direction and learn the behavior of other typical crude oils. For the present, however, it seems sufficiently clear that the reflux condensation involved in the various methods of efficient fractionation is not a source of danger in the production of cracking.

## CONCLUSIONS

A former paper showed the fundamental advantages of a method of efficient fractionation for the analytical distillation of petroleum. The present series of experiments has brought out the following facts:

I—Comparisons of a large number of types of distilling apparatus showed that several (Glinsky, Young and Thomas, long pear, Le Bel-Henninger, Golodetz, Hempel, long rod and disk and evaporator) produce approximately equal results.

II—Of the several, the Hempel is easily first on the basis of mechanical advantage, the Glinsky, Young and Thomas and evaporator being the only ones comparable to it.

III—With the moderate rate of distillation employed for the fractionation of petroleum the dimensions of Hempel columns may vary widely, both in length and bore, with but slight effect on the results produced.

IV—With columns of equal dimensions other mechanical factors are of minor importance. The size, shape and material of the distilling bulb have no appreciable influence. Glass beads are not as good mechanically as aluminum but they attain the same degree of fractionation. The size of the initial charge of oil is of some slight importance on account of the introduction of variation through the lag of the liquid in the condenser tube.

V—Mechanical advantages seem to be greatest for the one-piece glass apparatus with unconstricted neck of 1-in. bore and 6-in. length from bulb to outlet.

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## A COMPARISON OF METHODS FOR DETERMINING PUTRESCIBILITY OR OXYGEN DEMAND

By FRANK E. HALE AND THOMAS W. MELIA

Received April 7, 1915

The experiments described in this paper were carried out a year ago in connection with the work of the committee, headed by Dr. Arthur Lederer, appointed to establish standard methods for Putrescibility or Oxygen Demand of Sewage,[1] etc. Pressure of routine work has prevented further experiments which we hoped to make to sustain the conclusions here presented.

No results are reliable as representative of parts per million of oxygen required to prevent putrescibility unless such results can be consistently obtained and are supported by the results of different methods.

This laboratory has for several years used the Dilution Method as described by Jackson and Horton.[2] The essential features are dilution with aerated distilled water of known oxygen content, employment of methylene green, zinc double salt (the quantity originally specified corresponds to the amount of methylene blue recently recommended by Lederer[3] as yielding best results and least antiseptic power), dilutions differing by two volumes sufficient to obtain one bottle remaining colored, use of medicine droppers inserted through one-hole rubber stoppers, incubation for four to five days, and noting the days at which different dilutions become colorless. The original oxygen of the distilled water multiplied by (one plus the highest dilution becoming colorless) equals the p. p. m. oxygen required to prevent putrescibility. Our dilutions have been made in cylinders without preventing aeration of the sewage.

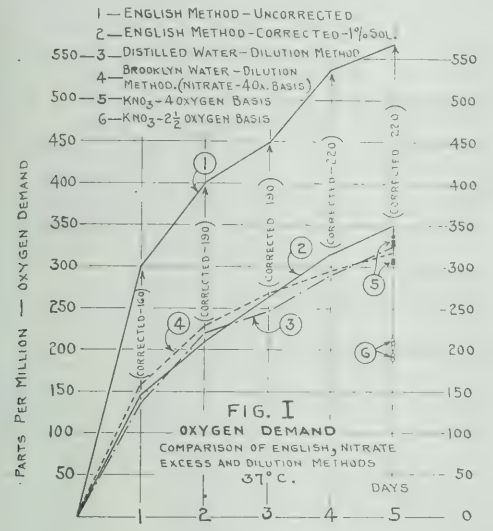
In the present work comparison was made between the above method, using both distilled water and Brooklyn tap water, the English Excess Oxygen Dilution Method with some modifications, and the Lederer Nitrate Method, using excess nitrate. The bottles used in each case were of 300 cc. capacity.

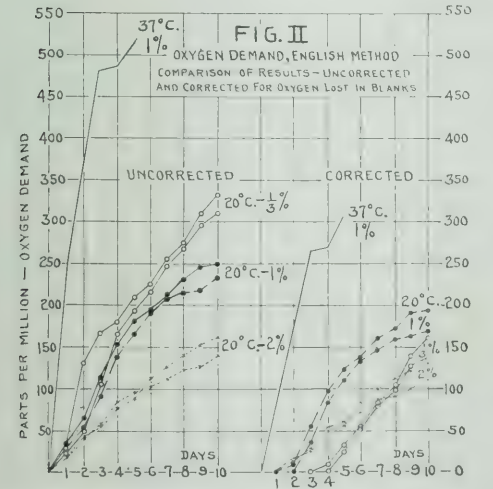
For the English method the bottles were filled with aerated distilled water through a funnel, keeping the funnel full, and overflowed to half their volume to displace air and the first water coming in contact with air. Then 3 cc. of sewage were introduced underneath by pipette forcing out some distilled water. Medicine droppers inserted through rubber stoppers were filled with the distilled water and inserted collapsed

[1] THIS JOURNAL, **6** (1914), 887.
[2] *Ibid.*, **1** (1909), 328.
[3] *Am. J. Pub. Health*, **4** (1914), 741.

for 37° C. incubation, glass stoppers for 20° C. There was no aeration of the diluted sewage. Bottles were filled with the liquids at room temperature. Several bottles were filled, oxygen determined at once on one, and then on one every day.

For the Lederer method a solution of sodium nitrate was made and dilutions of this made in test tubes such

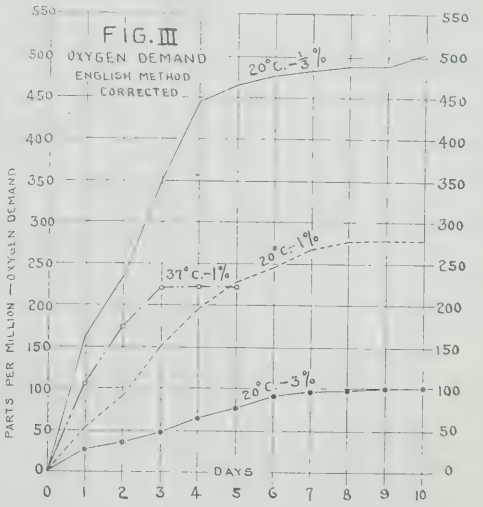


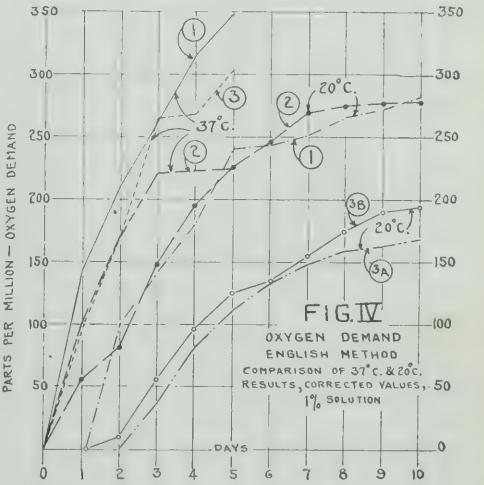




that 1 cc. added below the surface to a bottle filled with sewage gave varying excess amounts of nitrate. The bottles were filled by siphoning the sewage from a large bottle and overflowing to force out air and sewage in contact with air. At the end of 5 days' incubation at 37° C. the nitrate and nitrite were determined, the former by the Phenolsulfonic Acid Method upon 10 cc. of the incubated sewage mixture. Medicine droppers inserted through rubber stoppers were used.

The results of this comparison of methods are given in Table I. Fig. I represents graphically the results obtained at 37° C. incubation.

Lederer[1] states as a result of his experiments and also upon authority of many pre-workers that the




nitrate yields 2.5 oxygen atoms for 1 nitrogen atom. Several years ago we noted that less high dilutions were obtained with Brooklyn tap water than with distilled water by the Dilution Method and the required amount of oxygen could be obtained only by assuming that

[1] *Jour. Infect. Dis.*, **11**, May, 1914

nitrate yielded 4 oxygen atoms for 1 nitrogen atom in accordance with the following equation:

$$HNO_3 + H_2O = NH_3 + 2O_2$$

It may be assumed that carbonic acid combines during the reduction with the alkali of the alkaline nitrates to form nitric acid so that complete reaction would be expressed by the following:

$$2KNO_3 + H_2CO_3 + 2H_2O = K_2CO_3 + 2NH_3 + 4O_2$$

Analyses for ammonia proved sufficient amount present to confirm the reaction. The same reaction has been noted by one of us[1] in the utilization of the rubber stopper, with glass stopper, with open tubes as experimented with by Phelps in Ohio River investigations, and with open bottles, at both 37° C. and 20° C. The results shown in Table II were astonishing to say the least. One would naturally assume that an open bottle would absorb oxygen from the air. In every case oxygen was lost. Saturation at the temperature apparently had no direct relationship although losses were usually greater at 37° C. than at 20° C. The presence of rubber did not apparently explain the loss since the open bottle and glass stoppers also suffered serious losses. There are doubtless some

TABLE I PUTRESCIBILITY EXPERIMENTS. COMPARISON OF DIFFERENT METHODS (EXPRESSED AS OXYGEN DEMAND, P. P. M.)

| Time Days | Dilution method: Distilled water (Oxygen 8.53 p. p. m.) 37° C. Dil. | P. p. m. oxygen | Brooklyn water (Oxygen 10.8 p. p. m.) (Nitrate used 0.45 g.) 37° C. Dil. | Oxygen p. p. m. Basis 2 : 1 | Basis 4 : 1 |
|---|---|---|---|---|---|
| 1 | 15 | 136 | 12 | 155 | 165 |
| 2.... | 25 | 222 | 18 | 215 | 229 |
| 3 | 29 | 247 | 20 | 252 | 268 |
| 4.... | 33 | 290 | 22 | 275 | 293 |
| 5.... | 37 | 324 | 24 | 300 | 319 |
| 6 | | | | | |
| 7 | | | | | |
| 8 | | | | | |
| 9 | | | | | |
| 10 | | | | | |

| Excess nitrate method (Lederer) 37° C. 1 cc. nitrate solutions to 300 cc. sewage. Original oxygen introduced p. p. m. | | | | | | | English Excess Dilution Method (1–99 dilution of unsaturated sewage Oxygen used 50–60%) Oxygen at start 9.01 p. p. m. 37° C. | | 8.85 p. p. m. 20° C. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Uncorrected | Corrected | Uncorrected | Corrected |
| Basis 2 : 1 | 612 | 506 | 275 | 245 | 214 | | 300 | 140 | 20 | 0 |
| Basis 4 : 1 | 979 | 490 | 441 | 392 | 343 | | 399 | 209 | 142 | 100 |
| | | | | | | | 451 | 261 | 195 | 138 |
| | | | | | | Average | 536 | 316 | 236 | 179 |
| Basis 2 : 1 | 212 | 192 | 207 | 205 | 191 | 201 | 569 | 349 | 298 | 241 |
| Basis 4 : 1 | 339 | 307 | 341 | 328 | 306 | 324 | | | | |
| Probable error(a) | ±30 | ±15 | ±5 | ±3 | | | | | 301 | 244 |
| | | | | | | | | | 309 | 252 |
| | | | | | | | | | 322 | 265 |
| | | | | | | | | | 330 | 273 |
| | | | | | | | | | 338 | 281 |

(a) As based on nitrate determination at start and after 5 days' incubation.

oxygen of nitrate in corrosion of iron pipe by water. Here the exact equivalent of ammonia was recovered by analysis to meet the equation with corresponding reduction of nitrate to zero. As Lederer has worked mainly at 20° C. the reaction may be different at that temperature.

It will be noted in Fig. I that a ratio of 2.5 oxygen to 1 nitrogen gives results which are altogether too low, whereas a ratio of 4 oxygen to 1 nitrogen gives results exactly corresponding with the dilution results of ±320 p. p. m. The curve with Brooklyn tap water agrees very well upon the 4 to 1 assumption although the amount of nitrate used is so small that the effect is not very different from that caused by the 2.5 to 1 ratio which gives 300 p. p. m. in 5 days.

The English method apparently gave results almost twice as great as the Dilution Method. Investigation was made as to the cause of this discrepancy and when

TABLE II ANALYSIS OF SEWAGE USED IN THE EXPERIMENTS OF TABLE I

Source: Manhattan Sewage from Manhole at 35th Street & 7th Ave., New York City—Hotel District

| Parts Per Million | | Parts Per Million | |
|---|---|---|---|
| Nitrogen as free ammonia | 72.7 | | |
| Nitrogen as albuminoid ammonia | 21.3 | Fixed solids | 1224 |
| Nitrite | 0.016 | Hardness | 84 |
| Nitrogen as nitrate | 0.25 | Alkalinity | 295 |
| Total solids | 1489 | Chlorine | 302 |
| Loss on ignition | 265 | Iron | 1.20 |
| | | Oxygen consumed | 72 |

corrections are made for blanks run with distilled water these results also agree with the Dilution Method as shown in the corrected curve.

When aerated distilled water is bottled in the usual way without the addition of sewage, incubated at 20° C. or 37° C. and oxygen determined, there is a loss of oxygen dependent upon the time of incubation, temperature of incubation, type of stopper, and probably also amount of oxygen content. Comparisons were made with the medicine dropper, with solid physical phenomena accountable. Gas always collects under the stoppers and we believe that a certain amount of oxygen is carried with it and not reabsorbed until the oxygen content is nearly exhausted. Upon removing the stopper to introduce reagents for oxygen determination in the English method this oxygen gas

TABLE III PARTS PER MILLION LOSS OF OXYGEN IN DISTILLED WATER

| Days | Jackson's bulb pipette Initial oxygen | Loss | Rubber stopper Init. O | Loss | Glass stopper Init. O | Loss | Phelps open tube Init. O | Loss | Open bottle Init. O | Loss |
|---|---|---|---|---|---|---|---|---|---|---|
| Incubated at 37° C. | | | | | | | | | | |
| 1..... | 8.12 | 1.55 | | | | | 6.49 | 0.40 | 6.49 | 0.49 |
| 2..... | 8.12 | 1.87 | | | | | 6.49 | 0.40 | 6.49 | 0.49 |
| 3..... | 8.12 | 1.87 | | | | | 6.49 | 0.49 | 6.49 | 0.56 |
| 4..... | 8.12 | 1.87 | | | | | 6.49 | 0.56 | 6.49 | 0.56 |
| 5..... | 8.12 | 1.92 | | | | | 6.49 | 0.56 | 6.49 | 0.57 |
| 2..... | 8.16 | 2.26 | 7.79 | 1.38 | 8.16 | 0.92 | 7.79 | 1.38 | | |
| 2..... | 8.16 | 2.24 | 7.79 | 1.38 | 8.16 | 0.92 | 7.79 | 1.40 | | |
| 2..... | 8.16 | 2.24 | 7.79 | 1.38 | 8.16 | 0.94 | | | | |
| 2..... | 8.16 | 2.14 | 7.79 | 1.38 | 8.16 | 0.96 | 8.12 | 1.93 | | |
| 2..... | 8.16 | 2.08 | 7.79 | 1.38 | 8.16 | 0.96 | 8.12 | 1.95 | | |
| 5 | | | | | | | 8.12 | 4.31 | 8.12 | 3.87 |
| Incubated at 20° C. | | | | | | | | | | |
| 1..... | 8.12 | 0.33 | | | 8.12 | 0.41 | 6.49 | 0.17 | 6.49 | 0.17 |
| 2..... | 8.12 | 1.22 | | | 8.12 | 0.41 | 6.49 | 0.17 | 6.49 | 0.17 |
| 3..... | 8.12 | 1.32 | | | 8.12 | 0.57 | 6.49 | 0.24 | 6.49 | 0.32 |
| 4..... | 8.12 | 1.32 | | | 8.12 | 0.57 | 6.49 | 0.24 | 6.49 | 0.32 |
| 5..... | 8.12 | 1.32 | | | 8.12 | 0.57 | 6.49 | 0.24 | 6.49 | 0.32 |
| 3..... | 8.16 | 1.42 | 7.79 | 0.59 | 8.14 | 0.57 | 7.79 | 1.14 | | |
| 3..... | 8.16 | 1.42 | 7.79 | 0.59 | 8.14 | 0.57 | 7.79 | 1.16 | | |
| 3..... | 8.16 | 1.42 | 7.79 | 0.59 | 8.14 | 0.57 | | | | |
| 3 | 8.16 | 1.14 | 7.79 | 0.59 | 8.14 | 0.57 | 8.12 | 1.18 | | |
| 3..... | 8.16 | 1.16 | 7.79 | 0.61 | 8.14 | 0.59 | 8.12 | 1.89 | | |

under the stopper is lost. The Phelps open tube lost oxygen like an open bottle since reagents for oxygen determination were introduced through the tube and any trapped oxygen was determined.

In the Dilution Method oxygen is completely removed and any oxygen under the stopper reabsorbed. At least if any oxygen were there the methylene green would show it. Consequently no correction applies to the Dilution Method. This is also true of the nitrate method since nitrate is not reduced until oxygen is gone.

Together with the other collaborators of Dr. Lederer we endeavored to carry through determinations by the

[1] *Am. Jour. Pub. Health*, **3** (1913), 1338.

English method at different dilutions of sewage in an endeavor to find the best dilution, also if possible a percentage value at 5 days that could be calculated to a complete absolute value. It was common experience among the collaborators that different dilutions did not agree with each other. Fig. II shows two such series upon the same sewage with values uncorrected and with values corrected. There is no sane reason why the results of different dilutions should not agree aside from errors of multiplication, that is, any error with 1 per cent dilution would be three times as great in effect as the same error with 3 per cent dilution. We believe loss of oxygen errors account in great measure for these discrepancies with the English method. The corrected values on Fig. II show closer agreement at 10 days than the uncorrected value. Agreement is not close at 5 days or other intermediate points. The reason for this may be that oxygen loss may not take place in the same degree or with the same rapidity with the different dilutions as with distilled water alone. The 2 per cent values at 5 days on Fig. II agree quite closely with

TABLE IV OXYGEN DEMAND ENGLISH METHOD

| Days of incubation | O absorbed in diluted sewage P. p. m. A | B | Per cent A | B | Ratio of oxygen absorbed in 5 10 days Per cent A | B | P. p. m. oxygen absorbed expressed as to sewage Uncorrected A | B | Corrected A | B |
|---|---|---|---|---|---|---|---|---|---|---|
| 1½% sewage in mixture, 20° C. incubation, 8.13 p. p. m. O at start | | | | | | | | | | |
| 1 | 0 08 | 0.09 | | | | | 24 | 27 | 0 | 0 |
| 2 | 0 44 | 0.17 | | | | | 132 | 51 | 0 | 0 |
| 3 | 0 56 | 0.35 | | | | | 168 | 105 | 0 | 0 |
| 4 | 0.60 | 0.55 | | | | | 180 | 165 | 9 | 0 |
| 5 | 0.70 | 0.65 | 9 | 8 | 63 | 63 | 210 | 195 | 39 | 24 |
| 6 | 0.75 | 0.74 | | | | | 225 | 222 | 54 | 51 |
| 7 | 0.84 | 0.83 | | | | | 252 | 249 | 81 | 78 |
| 8 | 0.92 | 0.90 | | | | | 276 | 270 | 105 | 99 |
| 9 | 1.03 | 0.99 | | | | | 309 | 297 | 138 | 126 |
| 10 | 1.11 | 1.03 | 14 | 12 | | | 333 | 309 | 162 | 138 |
| 1% sewage in mixture, 20° C. incubation, 8.05 p. p. m. O at start. | | | | | | | | | | |
| 1 | 0.30 | 0.25 | | | | | 30 | 25 | 0 | 0 |
| 2 | 0.52 | 0.65 | | | | | 52 | 65 | 0 | 8 |
| 3 | 0.93 | 1.12 | | | | | 93 | 112 | 36 | 55 |
| 4 | 1.38 | 1.54 | | | | | 138 | 154 | 81 | 97 |
| 5 | 1.66 | 1.81 | 21 | 22 | 74 | 72 | 166 | 181 | 109 | 124 |
| 6 | 1.91 | 1.93 | | | | | 191 | 193 | 134 | 136 |
| 7 | 2.05 | 2.11 | | | | | 205 | 211 | 148 | 154 |
| 8 | 2.16 | 2.30 | | | | | 216 | 230 | 159 | 173 |
| 9 | 2.19 | 2.46 | | | | | 219 | 246 | 162 | 189 |
| 10 | 2.25 | 2.50 | 28 | 30 | | | 225 | 250 | 168 | 193 |
| 2% sewage in mixture, 20° C incubation, 8.01 p. p. m. O at start | | | | | | | | | | |
| 1 | 0.41 | 0.44 | | | | | 21 | 22 | 0 | 0 |
| 2 | 0.83 | 0.86 | | | | | 42 | 43 | 13 | 14 |
| 3 | 1.14 | 1.12 | | | | | 57 | 56 | 28 | 27 |
| 4 | 1.68 | 1.57 | | | | | 84 | 79 | 55 | 50 |
| 5 | 1.92 | 1.80 | 24 | 22 | 69 | 56 | 96 | 90 | 67 | 61 |
| 6 | 2.01 | 2.26 | | | | | 101 | 113 | 72 | 84 |
| 7 | 2.25 | 2.54 | | | | | 113 | 127 | 84 | 98 |
| 8 | 2.48 | 2.82 | | | | | 124 | 141 | 95 | 112 |
| 9 | 2.53 | 3.01 | | | | | 127 | 152 | 98 | 123 |
| 10 | 2.80 | 3.22 | 35 | 40 | | | 140 | 161 | 111 | 132 |
| 1% sewage in mixture, 37° C. incubation, 8.30 p. p. m. O at start | | | | | | | | | | |
| 1 | 2.54 | | | | | | 254 | | 94 | |
| 2 | 3.62 | | | | | | 362 | | 172 | |
| 3 | 4 85 | | 58 | | 93 | | 485 | | 265 | |
| 4 | 4.88 | | | | | | 488 | | 268 | |
| 5 | 5.24 | | 63 | | | | 524 | | 304 | |

NOTE—A and B are duplicates. Above tests on one sample of sewage.

each other and with the 3 per cent value on Fig. III at 5 days. These percentages feel the effect of the loss of oxygen least and approach nearer to the prescribed conditions in the English test. The English method specifies 30 to 60 per cent consumption of oxygen in five days. However, little prediction can be made as to results when starting a test. In the nine sets charted in Figs. II and III, only the two starred curves on Fig. III met this condition. Only a few of the results turned out as expected.

Although the results on Fig. III are all corrected, there is no agreement between the different percentages. This uncertainty of result by the English method militates greatly against its usefulness. It appears to offer the simplest of technique, but is exceedingly disappointing.

In Fig. IV are shown results at 37° C. and at 20° C. on three different sewages by the English method, 1 per cent dilution, corrected values. More consistent results appear to be obtained at 37° C., as well as quicker results, than at 20° C.

We believe that the standard methods for oxygen demand should be made at 37° C. More reliable results and quicker are thus obtained, and as the results in any case are empirical, comparison between laboratories will be closer. The results at 20° C.

TABLE V OXYGEN DEMAND ENGLISH METHOD

| Days of incubation | O absorbed in diluted sewage P. p. m. | Ratio of oxygen absorbed in 5 Per cent | 10 days Per cent | P. p. m. oxygen absorbed expressed as to sewage Uncorrected | Corrected |
|---|---|---|---|---|---|
| 1½% sewage in mixture, 20° C. incubation, 8.05 p. p. m. O at start | | | | | |
| 1 | 0.95 | | | 285 | 162 |
| 2 | 1.35 | | | 405 | 234 |
| 3 | 1.75 | | | 525 | 354 |
| 4 | 2.05 | | | 615 | 444 |
| 5 | 2.12 | 26 | 94 | 636 | 465 |
| 6 | 2.16 | | | 648 | 477 |
| 7 | 2.18 | | | 654 | 483 |
| 8 | 2.20 | | | 660 | 489 |
| 9 | 2.20 | | | 660 | 489 |
| 10 | 2.25 | 28 | | 675 | 504 |
| 1% sewage in mixture, 20° C. incubation, 8.05 p. p. m. O at start | | | | | |
| 1 | 0.95 | | | 95 | 54 |
| 2 | 1.45 | | | 145 | 88 |
| 3 | 2.05 | | | 205 | 148 |
| 4 | 2.53 | | | 253 | 196 |
| 5 | 2.82 | 35 | 84 | 282 | 225 |
| 6 | 3.03 | | | 303 | 246 |
| 7 | 3.25 | | | 325 | 268 |
| 8 | 3.33 | | | 333 | 276 |
| 9 | 3.35 | | | 335 | 278 |
| 10 | 3.35 | 42 | | 335 | 278 |
| 3% sewage in mixture, 20° C. incubation, 8.05 p. p. m. O at start | | | | | |
| 1 | 1.23 | | | 41 | 27 |
| 2 | 1.75 | | | 58 | 39 |
| 3 | 2.05 | | | 68 | 49 |
| 4 | 2.50 | | | 83 | 64 |
| 5 | 2.81 | 35 | 79 | 94 | 75 |
| 6 | 3.31 | | | 110 | 91 |
| 7 | 3.45 | | | 115 | 96 |
| 8 | 3.52 | | | 117 | 98 |
| 9 | 3.55 | | | 118 | 99 |
| 10 | 3.57 | 44 | | 119 | 100 |
| 1% sewage in mixture, 37° C. incubation, 8.05 p. p. m. O at start | | | | | |
| 1 | 2.63 | | | 263 | 103 |
| 2 | 3.63 | | | 363 | 173 |
| 3 | 4.42 | 55 | 100 | 442 | 222 |
| 4 | 4.43 | | | 443 | 223 |
| 5 | 4.43 | 55 | | 443 | 223 |

should be made special as applying to any particular stream, possibly, as Hoover recommends, using open bottles or otherwise striving to approach natural conditions, but for comparison between laboratories 37° C. seems far more advantageous.

## SUMMARY

I—We believe that the Dilution Method using methylene green, or methylene blue, is at present the only reliable method for determining oxygen required to prevent putrescibility. The results of other methods if rightly interpreted and corrected coincide.

II—Five days at 37° C. are preferable to ten days at 20° C.

III—Ground glass stoppers are preferable to any other type.

IV—The English method as at present practiced is subject to grave and uncertain errors, among them loss of oxygen, and is therefore exceedingly unreliable. Apparently other unexplainable variations occur.

V—The Nitrate Method should be thoroughly investigated in comparison with the Dilution Method in order to determine the amount of oxygen available from the nitrate both at 37° C. and at 20° C. It appears possible to develop considerable accuracy and obtain comparable results by this method under proper conditions.

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## MOLYBDIC ACID RECOVERY

By C. Ammerman

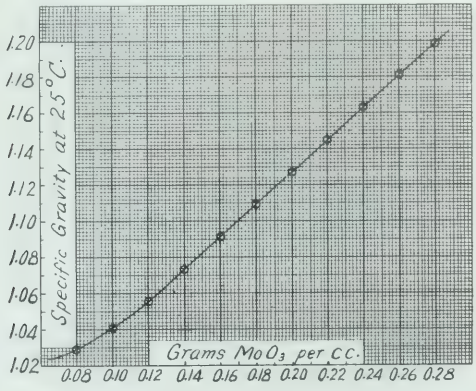
Received March 16, 1915

The large waste of molybdic acid and the difficulty experienced in obtaining the reagent pointed out the great need of a process for its recovery. Numerous methods were tried and cast aside on account of their impracticability or the unnecessary consumption of expensive reagents but finally a method, which is herewith described, was found, which is practical and simple: namely, the precipitation of the acid in $HNO_3$ by concentration, and its solution in $NH_4OH$, whereby the molybdic acid is obtained in a condition to be readily used for the preparation of a new stock solution for phosphorus.

### PROCESS

On account of the fact that phosphomolybdate precipitates are often added to the waste molybdic acid residues in steel analysis, these should be filtered before the recovery process is commenced. This is most conveniently accomplished by means of an asbestos suction filter.

The filtered solution is then placed in a five-liter German flask and supported inverted over a large evaporating dish on a sand bath, allowing but a small




amount of the solution in the dish. This method allows a large amount of liquid to be evaporated with little attention. The flask may be refilled until the precipitate of $MoO_3$, which forms in the bottom of the evaporating dish, becomes too bulky. Remove the flask and evaporate the solution in the dish until it begins to foam considerably and there is just enough solution left to cover the precipitate and keep the iron in solution. Cool, dilute with one-half volume of cold water, allow to settle and decant. Wash the precipitate thoroughly a couple of times with water by decantation to remove the iron salts and treat with enough 1 : 1 $NH_4OH$ to fill the dish. A dark brown precipitate will form, due to precipitated iron. The whole is then washed into a large flask, warmed slightly and allowed to stand a couple of hours with an occasional shaking to facilitate solution. When all is in solution, or after two hours, the liquid may be filtered off by a siphon, sand and asbestos, suction filter into another flask. Arrange the suction tube so that the lower portion of the solution, containing the precipitate, will be the last to come upon the filter, thus preventing troublesome clogging of the filter by the iron precipitate. Add 5 per cent of the original amount of $NH_4OH$ to the solution to make up for that used in precipitating the iron.

This solution contains the $MoO_3$ as ammonium molybdate and when the specific gravity of it is taken with a hydrometer at 25° C., by referring to accompanying cu ve the per cent of $MoO_3$ present may be found and then the proper amount of fresh $MoO_3$ added to bring the concentration up to 0.2825 g. per cc., which is the concentration of the precipitating solution for phosphorus.

The solution of $(NH_4)_2MoO_4$ may be evaporated to dryness and then roasted at 600° C. to $MoO_3$, but this is impractical in most cases.

The specific gravity curve was plotted from data obtained by making up solutions of different concentrations and using a pyknometer at 25° C. Various solutions were made up to test the curve and in each case the specific gravity indicated the per cent of $MoO_3$ to within 0.003 g. per cc. excepting in concentrations below 0.06 g. per cc., which concentrations are seldom met with in actual practice.

The solution of $(NH_4)_2MoO_4$ in 1 : 1 $NH_4OH$ when ready to mix with $HNO_3$ has a concentration of 0.2825 g. per cc. with a specific gravity of 1.20 (25° C.). This, when mixed with $HNO_3$ and water, constitutes the regular phosphorus precipitating solution.

The recovery in these tests, which were carried out on large amounts of residues and under actual working conditions, was 93 per cent and the recovered molybdic acid obtained by evaporation and roasting at 600° C. tested chemically pure in all cases (Merck's reagents and their tests).

The cost of recovery is practically nothing except for the gas and time, as no reagents are used which do not go to make up the working solution for phosphorus determinations.

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## THE IODIDE METHOD APPLIED TO THE DETERMINATION OF COPPER IN THE PRESENCE OF TIN

By Robert W. Coltman

Received May 28, 1915

In the determination of copper in a copper-tin alloy, the usual procedures involve a separation of the copper and tin. The most common method is to decompose the alloy with nitric acid, whereby metastannic

acid and copper nitrate are formed. The tin precipitate is filtered off, and the copper determined in the filtrate. This method has the disadvantage that the metastannic acid filters with difficulty; furthermore, the tin precipitate always contains traces of other metals present in the alloy, so that it must undergo further treatment.

Tin and copper may also be separated by sodium sulfide in alkaline solution, whereby the copper separates as sulfide and the tin goes into solution as a sulfosalt. The inconvenience of this method needs no comment.

Having had occasion to investigate the behavior of metallic copper and metallic tin when treated with concentrated sulfuric acid, the writer was struck by the facility with which the tin was held in solution. The fact that tin goes into solution as a stannic salt when treated with concentrated sulfuric acid is made use of in Low's method for antimony in babbitt metal;[1] the hydrochloric acid added after the decomposition of the alloy ensures the tin and antimony remaining in solution after dilution. It was found that the solution of tin in sulfuric acid alone was fairly stable, and with the knowledge that stannic salts do not liberate iodine from a solution of potassium iodide, the question naturally arose as to whether copper might not be determined by the iodide method in a solution containing tin. Further experiments showed that this was quite feasible; by proper treatment of the alloy a solution of stannic and cupric sulfate in sulfuric acid may be obtained that may be titrated for copper with the same accuracy as a copper sulfate solution alone.

Although hydrochloric acid holds tin in solution much more readily than sulfuric, its use was not considered, as copper is not readily soluble in hydrochloric acid and thus would necessitate the use of aqua regia to effect solution of the alloy. The nitric acid would then have to be removed by repeated evaporations with hydrochloric, consuming much time, and making the method much less simple than in its present form.

Preliminary work showed that the best method of preparing the solution was to treat the finely divided alloy with nitric acid until decomposed, and then fume with sulfuric acid over an open flame (using a Jena Erlenmeyer). The metastannic acid dissolves to stannic sulfate, and the copper nitrate is converted into copper sulfate. On taking the cold residue up with water, a clear solution is obtained that may be titrated directly for copper by the iodide method.

The use of sulfuric acid alone to decompose the alloy is not satisfactory, as a small residue of copper remains even after repeated fuming. A large excess of acid must be used, otherwise the pasty mass will spatter. It is practically impossible to control the amount of free sulfuric acid present, and this is important, as in using a mineral acid in the copper iodide method, the acidity must be low.

The allowable amount of tin present under given conditions of acidity was determined as follows:

[1] *J. Am. Chem. Soc.*, **29** (1907), 66.

The volume of the solution to be titrated having been chosen as 75 cc., and the amount of concentrated sulfuric acid as 3 cc., increasing quantities of metallic tin were dissolved in nitric acid, evaporated with 3 cc. of concentrated sulfuric,[1] diluted to 75 cc., and the stabilities of the different solutions compared.

| Tin Grm | Vol. Cc. | Conc. $H_2SO_4$ Cc. | Remarks |
|---|---|---|---|
| 0.05 | 75 | 3 | No change in one hour |
| 0.1 | 75 | 3 | Slight turbidity in 15 minutes |
| 0.2 | 75 | 3 | Would not dissolve to clear solution |

It is evident that not more than 0.1 gram of tin may be present, otherwise hydrolysis and precipitation of stannic hydrate take place in a short time.

The weight of copper titrated may be as high as 0.25 gram (= 39.3 cc. $N/10$ $Na_2S_2O_3$). This weight of copper in the presence of 0.1 gram tin would be equivalent to 71.43 per cent Cu. There would then be 28.57 per cent Sn. As the amount of tin in a bronze is seldom so high as this, there is no danger that the sample taken for analysis will contain more than the allowable weight of tin, provided the amount of copper present is not much over 0.25 gram.

## EXPERIMENTAL DATA

**STANDARDIZATION OF THIOSULFATE SOLUTION AGAINST COPPER FOIL**—The sample was dissolved in nitric, fumed with 3 cc. conc. $H_2SO_4$, allowed to cool, 25 cc. water added, and evaporated again to fuming. The solution was allowed to cool, diluted to 75 cc., 10 cc. of 40 per cent KI solution added, and titrated with the thiosulfate solution.

| No. | Grams copper | Cc. $Na_2S_2O_3$ | 1 cc. = Grams Cu |
|---|---|---|---|
| 1 | 0.2655 | 42.37 | 0.006266 |
| 2 | 0.2648 | 42.24 | 0.006269 |
| 3 | 0.2684 | 42.83 | 0.006267 |
| Average value 1 cc $Na_2S_2O_3$ | | | 0.006267 |

**TITRATION OF COPPER IN PRESENCE OF TIN**—The solution was prepared as before, but metallic tin was added to the copper samples:

| No | Weight Grams Cu | Weight Grams Sn | Per cent Cu | Per cent Sn | Cc $Na_2S_2O_3$ | Gram | Cu Found Per cent | Difference Per cent |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.2526 | 0.0311 | 89.04 | 10.96 | 40.31 | 0.2526 | 89.04 | |
| 2 | 0.2507 | 0.0804 | 88.26 | 16.74 | 40.02 | 0.2508 | 88.30 | −0.04 |
| 3 | 0.2455 | 0.0799 | 75.45 | 24.55 | 39.15 | 0.2454 | 75.41 | −0.04 |

These differences lie entirely within the limits of error.

## ANALYTICAL PROCEDURE

Weigh out a sample containing not over 0.25 gram copper and boil with 15 cc. of 2 : 1 nitric in a 500 cc. Jena Erlenmeyer provided with a small funnel to prevent loss. When the alloy is thoroughly decomposed, add dilute sulfuric acid equivalent to 3 cc. of concentrated acid, remove and rinse the funnel, and evaporate over an open flame. As the evaporation progresses, the solution becomes more and more clear. After the nitric acid is all driven off, and the sulfuric begins to fume, the stannic and cupric sulfates suddenly separate out, forming a very characteristic crystalline mass of pearly scales somewhat resembling manganese ammonium phosphate. The flask must be removed from the flame immediately after this

[1] Three cubic centimeters of concentrated sulfuric acid is the maximum amount which may be present in the copper iodide method, according to Gooch and Heath, *Z. anorg. Chem.*, **55** (1907), 129.

crystallization takes place or the mass will spatter. After cooling, take up with about 25 cc. water, shake until dissolved, and again evaporate just to fuming in order to remove the last traces of lower oxides of nitrogen. Allow to cool, take up with 50 cc. cold water (the stannic sulfate dissolves more quickly by using less water at first) and when all is in solution, add 25 cc. more water, 10 cc. of 40 per cent KI, and titrate immediately with the $N/10$ thiosulfate. If the alloy contains a small amount of lead, some lead sulfate remains undissolved, and the solution at the end point is yellowish (owing to the lead iodide) instead of the creamy white of cuprous iodide, but the presence of lead has no effect upon the titration, at least in moderate amounts.

A copper-tin alloy containing about 10 per cent of tin and 8 per cent lead analyzed as follows:

| No. | Sample Gram | Cc. $Na_2S_2O_3$ | Cu Found Gram | Cu Found Per cent | Average Per cent Cu |
|---|---|---|---|---|---|
| 1 | 0.3127 | 39.49 | 0.2474 (8) | 79.14 | |
| 2 | 0.3227 | 40.79 | 0.2556 (3) | 79.22 | 79.16 |
| 3 | 0.3303 | 41.70 | 0.2613 (4) | 79.12 | |
| 4 | 0.3108 | 39.21 | 0.2457 (4) | 79.06 | 79.11 |
| 5 | 0.3327 | 42.02 | 0.2633 (4) | 79.15 | |

In the analyses indicated as 4 and 5 above, the alloy was decomposed with nitric, the metastannic acid filtered off, and the copper determined in the filtrate after evaporation with sulfuric.

Too much stress cannot be laid upon the fact that a second fuming of the solution is necessary: 0.05 gram of metallic tin, treated with nitric, fumed *once* with sulfuric, and diluted to 75 cc., gave a blue color with KI and starch requiring 0.55 cc. to discharge it. When this same amount of tin was fumed *twice*, potassium iodide and starch gave no color in the diluted solution.

As regards the time necessary, determinations 1, 2 and 3, cited above, were run in one hour. The filtering, washing and evaporating necessary when the ordinary method was used, made the time about five hours. (In this, no correction was made for any copper remaining with the metastannic acid.)

The method proposed is simple, accurate, and rapid; the advantages of carrying out the analysis in the same container are obvious.

In conclusion, it must be remembered that no metals which separate iodine from potassium iodide may be present, such as antimonic or ferric salts; the method has naturally the limitations of the iodide method in this respect. It is simply the desire of the writer to show an extended use of this excellent method, thus making it available under apparently adverse conditions.

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## TITRATION OF NITRATES WITH FERROUS SULFATE

By Fred C. Bowman and W. W. Scott

Received May 29, 1915

The great variety of methods of determining nitrates found in chemical literature shows the need felt by chemists for simpler ways of making this important analysis. Most methods now in use involve distillation or evaporation or the use of special apparatus, all of which take a good deal of time and attention.

The method proposed by the authors is as easy and quick as any ordinary titration, has a wide range of usefulness and is accurate enough for most purposes.

### BIBLIOGRAPHY

The first mention of the method was made by Grossart[1] in 1847. He titrated nitrates in boiling 60 per cent sulfuric acid with a ferrous sulfate solution, using ferricyanide as an outside indicator. He gives no details or test analyses. No doubt his results were less accurate than he thought.

Mohr[2] announced the discovery of the method in 1861. He dissolved the sample in sulfuric acid (diluted 1 to 9) and titrated at 70° to 80° C. with a ferrous sulfate solution containing 200 grams of the salt per liter, using as the end point the appearance of a brownish color. He declared that it was a good technical method, but Fresenius[3] and Eder,[4] who examined it later, condemned it strongly.

In 1899 van Deventer[5] carried out the reaction over mercury in a Crum tube with exclusion of air, using fairly strong sulfuric acid as a medium and a weak ferrous sulfate solution as reagent. The process was awkward to handle.

No comment on these methods was found in the journals, and evidently they failed of acceptance. They were all based on the reduction of the nitrate to NO and not to $N_2O_3$, as in the method given below, for estimations in presence of sulfuric acid. No mention of acids other than sulfuric was found in the literature.

### ESTIMATION OF NITRIC ACID IN PRESENCE OF ARSENIC ACID

The writers devised the method given below, originally, for the purpose of estimating nitric acid in arsenic acid. The original form of the method was as follows:

Dilute the sample to be tested to 100 cc. with nitre-free arsenic acid of such strength that there is not more than 20 per cent water in the mixture. Then titrate with a ferrous sulfate solution, containing 264.7 grams $FeSO_4.7H_2O$ and 50 cc. strong sulfuric acid per liter (1 cc. = 0.02 g. $HNO_3$). Standardize the solution on a known amount of nitric acid.

The following reaction occurs:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 2NO + 3Fe_2(SO_4)_3 + 4H_2O$$

The ferrous sulfate forms a dark brown color, which disappears on stirring as long as any nitric acid remains. The end point is the first permanent brown and is readable to 0.03 cc. During the first two-thirds of the titration, the ferrous sulfate is taken up very quickly; then a lively evolution of NO commences and continues to the end. It would be thought that the oxygen of the air might reoxidize the NO

[1] "Sur un nouveau dosage de l'acide azotique et des azotates," Grossart. *Compt. rend.*, **1** (1847), 21.

[2] Dingler's *Polytechnisches Journal*, **160** (1861), 219.

[3] *Zeitschrift fuer anal. Chemie*, **1** (1862), 32

[4] *Ibid.*, **16** (1877), 267.

[5] *Zeitschrift fuer physik. Chemie*, **31** (1899), 50

and cause error in the titration, but this does not occur.

The presence of too much water in the solution makes the reaction "hang," *i. e.*, refuse to begin. If the solution is warmed with a few cc. of the ferrous sulfate solution, the reaction begins abruptly and runs easily thereafter. Heating even to boiling does not change the reaction, but may volatilize some of the $HNO_3$. There should not be more than 25 per cent of water present at the end of the titration. Water added in the ferrous sulfate solution must be taken into account.

In the light of subsequent knowledge, it would seem better to make up the standard solution without any sulfuric acid. The proportion of sulfuric acid present in a titration was, however, so small that its influence could not be detected.

A few analyses will show the accuracy of the method.

PER CENT $HNO_3$ IN ARSENIC ACID

| | | | |
|---|---|---|---|
| Nitrometer | 0.25 | Ferrous sulfate method | 0.27 |

Nitric acid was added to nitre-free arsenic acid and the mixture analyzed:

| Grams nitric acid | (1) | (2) | (3) |
|---|---|---|---|
| Taken | 0.6610 | 0.5968 | 0.0661 |
| Found | 0.6608 | 0.5984 | 0.0660 |

A small excess of ferrous sulfate is necessary to give a good color at the end point. Usually, this does not amount to more than 0.1 cc., but for small quantities of nitrates the correction is greater. In this case a little nitric acid should first be added to the arsenic acid and titrated with ferrous sulfate to a brown tint; then the sample to be tested may be added and titrated accurately.

### ESTIMATION OF NITRIC ACID IN PRESENCE OF PHOSPHORIC ACID

The same reaction between ferrous salts and nitrates occurs in phosphoric as in arsenic acid, but titrations are even more satisfactory. No heating is required to start the action and the end point is a little sharper than in arsenic acid, being readable to about 0.02 cc. with the ferrous sulfate solution described above. Practically no excess is required at the end point, except for very small amounts of nitrate. As with arsenic acid, the concentration of water present at the end of a titration should be less than 25 per cent and better results will be obtained with 20 per cent.

Below are a few test analyses made in phosphoric acid:

| Grams $HNO_3$ | (1) | (2) | (3) |
|---|---|---|---|
| Taken | 0.6610 | 0.5968 | 0.5968 |
| Found | 0.6618 | 0.5984 | 0.5966 |

### ESTIMATION OF NITRIC ACID IN PRESENCE OF SULFURIC ACID

Both arsenic and phosphoric acids have the drawback that they are too expensive for general use in titrations. Sulfuric acid is the only strong acid available in the laboratory at a reasonable price. When this was tried the surprising fact was discovered that the reaction proceeds only two-thirds as far as in arsenic and phosphoric acids. Nitrates are reduced, not to NO, but to $N_2O_3$. Strong heating will, however, drive the reaction somewhat further. The reaction that occurs in the cold is, therefore:

$$4FeSO_4 + 2HNO_3 + 2H_2SO_4 = N_2O_3 + 2Fe_2(SO_4)_3 + 3H_2O$$

The end point is a delicate pinkish brown, not so sharp as with the other acids, but as easy to read as the usual methyl orange end point in acid titrations.

EFFECT OF WATER—Experiments showed that water slows down the reaction and weakens the color of the end point, so that a considerable excess of ferrous sulfate is required to give a readable tint. Larger quantities of water stop the reaction entirely in the cold.

| Per cent water at end point | 15 | 20 | 20 | 25 | 35 |
|---|---|---|---|---|---|
| Gram $HNO_3$ taken | 0.4963 | 0.4963 | 0.4963 | 0.4963 | 0.5968 |
| Gram $HNO_3$ found | 0.4935 | 0.4923 | 0.5024 | 0.4973 | 0.6808 |

These figures are not of high accuracy, but they show that 25 per cent of water is permissible as a maximum, though it makes a rather difficult end point.

EFFECT OF TEMPERATURE—The temperature of titration should be low. Too high a temperature acts in two opposite ways: (1) it causes volatilization of $HNO_3$, which leads to low results; (2) it causes a slight reduction of $N_2O_3$ to NO, which makes for high values.

| Maximum temperature during titration | 40° C. | 50° C. | 60° C. | 90° C. | 110° C. |
|---|---|---|---|---|---|
| Gram $HNO_3$ taken | 0.4963 | 0.4963 | 0.4963 | 0.4963 | 0.4963 |
| Gram $HNO_3$ found | 0.4960 | 0.4947 | 0.4940 | 0.5038 | 0.5460 |

The lowest temperature gives the best results; at medium temperatures the compensation of errors is fair but irregular; at high temperatures the results are high and the end point is very bad. The conclusion is that the temperature should be kept as low as possible, and should not exceed 60° C. So much heat is generated by running the ferrous sulfate solution into the sulfuric acid that the test beaker must be cooled in a bath of water during titration.

CORRECTION FOR END POINT—It was found that ferrous sulfate attacks $N_2O_3$ slowly under the conditions of the titration, but that it has so marked a preference for $HNO_3$ that no reduction of $N_2O_3$ occurs while $HNO_3$ is present. As the brown color of the end point is due to the formation of a compound of $FeSO_4$ and NO, some slight reduction to NO must occur always. The results of many experiments show that about 0.2 cc. excess of ferrous sulfate solution (1 cc. = 0.02 g. $HNO_3$) is required to give the brown tint of the end point in a volume of 100–150 cc. This holds for titrations ranging from 0.5 cc. to at least 80 cc.

EFFECT OF COMMONLY OCCURRING IMPURITIES—The effect of impurities ordinarily occurring in nitrates was investigated by adding them to a known amount of nitric acid and titrating the latter. The table at the top of p. 768 gives the results.

The table shows that nitrite has little effect; chloride, iodide and bromide cause low results in quantities as little as 2 per cent, and chlorate, bromate and iodate cause high results. Elsewhere in this paper it is shown that ammonium salts have no effect.

[illegible] SUBSTANCES FURNISH [illegible] TITRATION FOR NO3 IN PRESENCE OF SULFURIC ACID
Amount of $HNO_3$ taken, 0.3039 g.

| Substance added to $HNO_3$ | Weight Gram | Percentage mixture tested | Titration Cc. $FeSO_4$ solution | Remarks |
|---|---|---|---|---|
| Blank | None | | 15.8 | |
| $KNO_3$ | 0.08511 | 21.9 | 15.71 | |
| $KNO_3$ | 0.4356 | 58.7 | 16.06 | |
| $KNO_3$ | 0.8511 | 73.0 | 16.76 | Odor of $N_2O_3$ evident |
| $NaNO_3$ | 0.05846 | 16.0 | 14.96 | |
| $NaNO_3$ | 0.2923 | 49.0 | | No distinct end point |
| NaCl | 0.00585 | 1.9 | 15.65 | |
| KI | 0.166 | 33.2 | 11.4 | |
| KI | 0.017 | 5.3 | 15.25 | |
| KI | 0.0057 | 0.57 | 15.8 | |
| $KIO_3$ | 0.1190 | 28.0 | | No distinct end point |
| $KIO_3$ | 0.0119 | 3.8 | 15.66 | |
| $KIO_3$ | 0.3039 | 50.0 | 45.0 | No good end point |
| KIO | 0.10701 | 26.0 | 17.36 | |
| KIO | 0.01070 | 3.4 | 15.96 | |
| $KBrO_3$ | 0.0835 | 21.6 | | No distinct end point |
| $KBrO_3$ | 0.00835 | 2.7 | 16.06 | |

PROCEDURE RECOMMENDED

Based on the foregoing results, the following standard procedure is recommended for the analysis of nitrates with concentrated sulfuric acid as the medium:

FERROUS SULFATE SOLUTION—Dissolve 170.5 grams $FeSO_4.7H_2O$ in 400 cc. water. Stir into this gradually 500 cc. of dilute sulfuric acid, made by mixing equal volumes of water and concentrated acid. Cool the mixture and make up to 1000 cc. The order of mixing given above should be followed, for a different order is apt to cause precipitation of an iron sulfate that cannot be redissolved.

1 cc. = 0.02 g. $HNO_3$ and contains 0.8 cc. water

STANDARDIZING—Either potassium bichromate or nitric acid[1] may serve for a standard. With the former, estimate the strength of the iron solution by Penny's method. Remember to allow 0.2 cc. for the end point in titrating nitrates.

1 gram $K_2Cr_2O_7$ = 0.6426 g. $HNO_3$

A more satisfactory method of standardizing is to titrate a nitric acid solution of known strength under the exact conditions in which the iron solution is to be used. For this, dilute 41 cc. of the usual 70 per cent laboratory nitric acid to 1000 cc. and titrate with normal caustic alkali. Use 10 cc. of the dilute nitric acid to standardize the ferrous sulfate solution in the manner described above.

A certain solution standardized carefully by both methods gave the following results, showing that the methods agree well:

1 cc. = 0.02068 g. $HNO_3$ ($HNO_3$ as standard)
1 cc. = 0.02073 g. $HNO_3$ ($K_2Cr_2O_7$ as standard)

TITRATION—The sample should be chosen to contain 0.3 to 0.6 g. $HNO_3$. For the most accurate work, the titration should be on practically the same quantity of $HNO_3$ as was used in standardizing the solution.

Place 100 cc. concentrated sulfuric acid, free from nitrates, in a 250 cc. beaker set in a large porcelain casserole full of cold water. Run the sample in slowly from a 10 cc. pipette to the bottom of the acid, stirring meanwhile with the pipette; this procedure is designed to prevent loss of nitric acid fumes. Run in the ferrous sulfate solution slowly in a fine stream with constant stirring until the solution turns from yellow to faint brown or pink. Then rinse out the pipette[1] by sucking it full of the acid and draining it and continue titrating cautiously to the first color change. The end point is clear to 0.05 cc. and different operators should agree within 0.1 cc.

The casserole of water serves the double purpose of cooling the acid and making the end point much clearer. It is sometimes necessary to halt the titration and let the solution cool. The temperature should never exceed 60° C. and is better kept below 40° C.

Let the burette stand five minutes before taking the reading, as the ferrous sulfate solution drains very slowly.

SOME INDUSTRIAL APPLICATIONS OF THE METHOD

NITRIC ACID IN OLEUM (FUMING SULFURIC ACID)—Weigh about 10 grams of the oleum in a pipette and titrate according to the scheme given above. A pipette of known content may be used for routine work, so that weighing is unnecessary. This method does not estimate nitrous acid in the oleum.

The accuracy of the ferrous sulfate method was given a rigid test by two laboratories by analyzing the same lot of samples independently and afterward comparing the results.

PER CENT NITRIC ACID IN OLEUM

| Analyses | Method | I | II | III | IV | V |
|---|---|---|---|---|---|---|
| Seller's | $FeSO_4$ | 2.40 | 2.82 | 3.23 | 3.35 | 3.52 |
| Buyer's | Nitrometer | 2.35 | 2.79 | 3.26 | 3.39 | 3.57 |
| Difference | | +0.05 | +0.03 | −0.03 | −0.04 | −0.05 |

| Analyses | Method | VI | VII | VIII | IX | X |
|---|---|---|---|---|---|---|
| Seller's | $FeSO_4$ | 3.50 | 3.48 | 3.57 | 3.53 | 3.56 |
| Buyer's | Nitrometer | 3.53 | 3.50 | 3.58 | 3.57 | 3.56 |
| Difference | | −0.03 | −0.02 | −0.01 | −0.04 | 0.00 |

The ferrous sulfate method is the quickest and probably the most accurate way of determining nitrates in oleum.

AMMONIUM NITRATE—A test on pure salt showed:

Taken..... 0.5000 Gram Found..... 0.5004 Gram

The method has been used extensively in one laboratory for the rapid determination of nitrates in the presence of nitrites and ammonium salts. This would be a laborious analysis by the usual methods.

SODIUM AND POTASSIUM NITRATES—Samples of chemically pure potassium nitrate and a sample of commercial nitrate of soda were tested with the following results:

| Gram $KNO_3$ | | Commercial $NaNO_3$ | | |
|---|---|---|---|---|
| Taken..... | 0.7000 | 0.3500 | By Devarda's method | 97.62 per cent |
| Found..... | 0.6997 | 0.3510 | By $FeSO_4$ method.... | 97.65 and 99.13 |

In the latter case the end point was bad, and the impurities present caused poor agreement between duplicates. This method is only roughly correct for impure nitrate of soda.

"MIXED ACID" (NITRIC AND SULFURIC ACIDS)—Samples of mixed acid weighing 6 to 7 grams were diluted to exactly 100 cc. with concentrated sulfuric acid and 10 cc. portions were titrated. The ferrous sulfate solution used was only one-half as strong as is recommended above; it was made up by diluting one volume

[1] Potassium nitrate may be used for standardizing, but it involves more work than the use of nitric acid. To dry a sample of potassium nitrate and test it for impurities, particularly sodium, is more troublesome than to titrate a nitric acid solution. The writers met trouble in using a supposedly pure sample of potassium nitrate for standardizing, and for that reason abandoned it in favor of nitric acid.

[1] The pipette used for measuring the sample should be graduated to contain, not to deliver.

of the standard solution with one volume of 60 per cent sulfuric acid. The temperature of titration was kept down to 70° F. by the use of an ice bath. The acids used were most carefully analyzed by the evaporation method and the ferrous sulfate solution was standardized against a mixed acid of known analysis.

| Per Cent $HNO_3$ | (1) | (2) | (3) |
|---|---|---|---|
| By $FeSO_4$ method | 50.32 | 50.16 | 49.49 |
| By evaporation method | 50.15 | 50.02 | 49.35 |

These analyses represent the limit of accuracy attainable by this method. Reasonable care to observe constancy of conditions permits an accuracy of 1 in 300, where large amounts of nitrates are present.

SUMMARY

I—The authors have devised a method based on the well-known ferrous sulfate test for nitrates, by which large amounts of nitric acid may be titrated directly.

II—The accuracy of the method is shown by analyses of known amounts of nitric acid combined and free, comparison being made with the usual standard methods. With care the error does not exceed $^1/_{300}$ of the quantity of nitric acid estimated. The method is not suitable for traces.

III—Constancy of conditions is important. The water content should not exceed 25 per cent of the sample titrated and the temperature should be kept below 60° C. Chlorates, bromates, iodates, chlorides, bromides and iodides interfere, but nitrites do not when sulfuric acid is used as a medium.

IV—A detailed procedure for analysis is given.

V—Some applications of the method to technical analysis are included: these are now in regular use in several technical laboratories.

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New York, N. Y.

## A DEVICE FOR THE SUCCESSIVE DETERMINATION OF THE SOLIDS AND FAT IN MILK AND OTHER FLUIDS

By Armin Seidenberg

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A large number of methods for the accurate gravimetric determination of fat in milk have been developed. In one class of methods of which the Rose[1]-Gottlieb[2] and the Werner-Schmidt[3] are examples, the proteids are first brought into solution by the proper reagent, after which the fat is extracted by agitation with a solvent. These methods require a considerable amount of manipulation on the part of the analyst, thus demanding a good deal of his time and attention. On the other hand, the direct extraction of the dry residue of the milk in a Soxhlet or modified Soxhlet apparatus, although the results are not obtained as quickly, consumes practically no more of the analyst's time than is required to make the necessary weighings.

[1] *Zeitschrift angew. Chem.*, **1888**, p. 100; *Milch Ztg.*, **18** (1888), 264.
[2] *Landw. Vers. Sta.*, **40** (1892), 6.
[3] *Zeitschr. f. analyt. Chem.*, **27** (1888), 464.

In order that the solvent may act effectively on the dry milk residue, it is of advantage to have it in a finely divided state. To bring this about a number of materials have been suggested, thus: sand, pumice stone, asbestos, copper sulfate, plaster of Paris, wood pulp, absorbent paper, etc. Of all these substances the Adams[1] fat-free paper offers probably the conditions that are most favorable to the complete extraction of the fat since the pores of the paper absorb the water in the milk very readily, leaving the fat on the surface where it is most exposed to the action of the ether. However, there is always some difficulty in transferring a weighed quantity of the milk on to the paper, a weighing flask being desirable for most accurate work; also a slight amount of extractable matter remains in the paper commonly supplied to analytical laboratories.

When a material is chosen that is not itself hygroscopic, the possibility is presented of making successive determinations of the total solids and fat on the same original weighing. In this case the fat can also be determined by difference and the solids-not-fat, when these are desired, can be directly weighed instead of being computed from the results of two different determinations. For the determination of total solids and fat (by difference) and of solids-not-fat, only four weighings are then necessary instead of seven, where separate quantities are weighed out for solids and for fat. The Adams fat-free paper is of course not adapted to the determination of fat by difference since it is intensely hygroscopic. The material that has gained most favor for this purpose is asbestos, first proposed by Babcock for the determination of total solids and developed by Richmond[2] and also by MacFarlane[3] for the determination of fat by difference. As adopted by the Association of Official Agricultural Chemists,[4] 1.5 to 2.5 grams of asbestos are loosely packed into a perforated sheet-metal cylinder 60 mm. long and 20 mm. in diameter, closed 5 mm. from one end by a perforated disc of the same material. The total solids are first determined and then the fat either by difference or by weighing directly. The asbestos must be prepared first. Freshly ignited woolly asbestos is used from which all grit and small particles must be carefully removed.

### DESCRIPTION

Whatever medium is chosen to hold the milk, its function is to permit the ready access (1) of heat at a uniform temperature and (2) of the solvent used for extraction. This is accomplished by using a material that distributes the milk solids in a finely divided state over as large a surface as is possible and which, while permitting ready access to both the solvent and heat, is acted upon by neither of these. It was with these considerations in mind that it occurred to the writer that a fine meshed wire gauze seemed to meet all the conditions enumerated, while at the same time it offered some advantages in respect to sim-

[1] *Analyst*, **10** (1885), 46.
[2] *Ibid.*, **17** (1892), 225.
[3] *Ibid.*, **18** (1893), 85.
[4] U. S. Dept. of Agr., Bureau of Chemistry, *Bull.* **107**, 117.

plicity and reliability not possessed by any of the substances so far employed. The particular modification finally adopted by the writer is as follows: An oxidized copper wire gauze of 40 or 60 mesh is used, ridged (or pleated) laterally with about 18 to 20 ridges. The two long sides of the gauze are bent up for 2 mm. in such a way as to close the opening of the grooves formed by the ridges. The dimensions of the gauze are 7 × 10 cm., the ridges being about 2 mm. high and about 2 mm. apart. The gauze is placed upon two ridges 2 mm. high running the length of a dish made of heavy tinfoil on whose surface are numerous cross-sectional indentations. The dimensions of the dish are 7 × 10½ cm.; three of the sides are 4 mm. high and the fourth (a long side) is 8 mm. high. The sides are not joined at the corners.

In making determinations of solids and fat the wire gauze and dish are first weighed accurately and then 4 or 5 grams (or other weighed quantity) of milk are evenly distributed drop by drop by means of a pipette over the entire gauze. In some respects the most satisfactory amount to use is 4 grams. If too great an amount of milk has been added to any one portion of the gauze it can readily be withdrawn with the pipette and redistributed. The milk is then dried to a constant weight in an air bath at 100° C. and the device again weighed to find total solids. Particular attention must be given to see that the liquid is well distributed and that the gauze is held level throughout and not subjected to any jolting. For the determination of fat the gauze is rolled into a conical form along with the dish, the high side and the ridges of the dish being first flattened out. After the gauze and dish have been rolled up the high side at one end is folded up, the other end being left open. The device is now introduced into a Soxhlet or other extraction apparatus and subjected to the action of the extracting medium. It is then dried again to constant weight, the loss in weight being fat.

## DISCUSSION

An oxidized or a well-flamed copper gauze was used, because it was found that with an unoxidized gauze the milk tended to gather in drops, but when the gauze was oxidized the milk spread out over the surface of the gauze and entered the interstices of the meshes without, however, going through even when the grooves formed by the ridges were well filled with liquid. The bent up edges of the gauze close the grooves at each end and prevent the milk from flowing out there. However, should a few drops go through the meshes, they would be caught on the containing dish. The amount would be so small that it would be well spread out and not affect the results. The gauze is placed upon two ridges running lengthwise on the bottom of the containing dish. The object of these ridges is to prevent direct contact between the gauze and the bottom of the dish as in this case some of the milk is at times drawn into the dish by capillary attraction. After drying, the solid matter will be found to be distributed quite uniformly over the surface of the gauze, and will adhere firmly to it as though forming an integral part of it. There is no evidence of cracking as when milk is evaporated in a dish; nor is there any charring as would be shown by a yellowish or brownish discoloration. When the device is placed in the extraction apparatus, the end closed by the one long side is placed toward the bottom. After using once it is best to discard the containing dish; the wire gauze, however, may in some cases be used again. To do this the milk solids are first burned off, the ash washed out with water and the gauze then dried thoroughly in the flame. It would seem that by repeating this process the wire gauze could be used indefinitely, but the writer has found that after the third and at times after the second use a very few particles of the oxide become loose and are washed out by the ether. This danger does not exist at all with a new gauze oxidized the first time and usually not with one used but twice. However, for most accurate work it would seem best to use only a new gauze. For the determination of total solids alone the gauze can be used repeatedly after burning off the matter from the previous determination. The wire gauze makes certain the wide and uniform distribution of the milk solids over a large horizontal surface, while in the case of material consisting of small particles or fibers held in a vertical cylinder or dish, the liquid may, if the packing is imperfect, gather largely in one part of the apparatus without the observer knowing it. The gauze, while permitting the free passage of the extracting medium, is not in any way affected by this, either chemically or when a newly oxidized gauze is used, by the washing out of any loose particles.

For the purpose of this investigation the wire gauze and dishes used were made in the laboratory. For the milk, a 60 mesh copper wire gauze was used, the same that is employed in combustion work; for cream a 40 mesh copper gauze is more desirable. Where a large number of determinations of this character are to be made the device can be turned out, ready for use, by a manufacturing concern. As opposed to the asbestos and other material so far suggested, no preliminary work of preparation is then necessary; *i. e.*, no other than is required before using a lead or platinum dish in determining total solids. Instead of using a Soxhlet extraction apparatus the writer found it practicable to use a Landsiedl extraction apparatus with a siphoning tube that held four gauzes rolled into the cylindrical form. The Landsiedl extraction apparatus is in many respects similar to the Soxhlet extraction apparatus except that the siphoning tube instead of being held in a special adapter placed between the flask and the condenser, is suspended in the enlarged neck of the flask which is directly connected to the condenser. The height of the siphoning tube should be slightly greater than the height of the wire gauze used and the neck of the flask should be adapted to this. An apparatus with a wider siphoning tube capable of holding an even larger number of gauzes might well be used. The fat, of course, can be determined only by difference. The saving of time and

trouble of manipulation in using one Landsiedl apparatus in place of four or more Soxhlets is evident.

DETERMINATIONS

In order to ascertain the reliability and accuracy attainable by using the wire gauze as described, the writer made a large number of determinations, under varying conditions, of both the fat and the solids of milk. First of all, tests were made to determine to what extent, if any, the device was affected either by heat at the temperatures employed or by the extracting medium. No change of weight that could be due to either of these two causes was noticeable. The gauze and dish were heated in the air bath at temperatures from 100° C. to 110° C. for prolonged periods of time without there being any significant gain or loss of weight. The same can be said when 5 cc. of distilled water were added and heating carried on under the same conditions. There is therefore no danger of oxidation of the copper when heated under the conditions described. The ether also had no perceptible effect on the weight of the gauze and dish.

The determinations made with the wire gauze for total solids were checked by making determinations under exactly the same conditions in lead dishes, of 5.5 cm. diameter and which have always been used in this laboratory for this purpose. The fat determinations were checked with the Adams fat-free paper as supplied by the firm of Schleicher and Schüll. The extractions were made with ether in an Adams modification of the Soxhlet apparatus. On evaporating the ether alone, spontaneously, no residue remained. However, when the ether was boiled with a reflux condenser for about 4 hrs. it left a slight residue; on prolonged drying this was considerably reduced. The writer found that the fat-free paper used by him gave an extract after 4 hrs. treatment with ether, amounting to from 0.0041 to 0.0062 g., an average of 0.0051 g. Siegfeld[1] states that he found the Schleicher and Schüll fat-free paper to give an extract amounting to from 0.006 to 0.009 g.; in some cases to 0.012 g. Leffmann[2] and some others, however, give a much lower figure, namely 0.001 to 0.002 g. When 5 grams of milk are used originally, and the results expressed in percentages, an error of from 0.120 to 0.180 per cent would be introduced on the basis of Siegfeld's determinations and of 0.082 to 0.124 per cent on the basis of the writer's determinations. This error can be corrected for either by subjecting the paper to several hours treatment with ether previous to using, or by subtracting in each case the amount due to the extract from the paper. In the determination of fat made by the writer with the Adams fat-free paper a uniform amount of 0.10 per cent was subtracted from all the results obtained.

TOTAL SOLIDS—Determinations for total solids were made on 39 different samples of milk; in most cases two series of determinations were made in a lead dish and two on a wire gauze; weighings were then made after the drying of both the lead dish and the wire gauze containing the same samples under similar conditions at 100° C. at intervals of 2 to 4 hours. In some cases the solids were subjected to temperatures varying from 60° C. to 80° C. for from 16 to 18 hours. In all, 461 weighings were made on the 39 samples. The drying was carried on entirely in an electric oven automatically regulated to maintain a temperature of within 2° to 3° of 100° C. Milk solids lose weight almost continuously at 100° C.; when, however, according to Blythe[1] the loss for 5 grams of milk is at the rate of 1 milligram or 0.02 per cent or less per hour, the residue can be considered to have reached constant weight. The rates of evaporation in the various cases, even where the same device was used, were not uniform. Where the drying is continuous, constant weight is usually reached after about 5 hours heating at 100° C. in an air bath. When drying is interrupted, however, a longer time is necessary. After constant weight has been reached the rate of loss of weight is almost always the same, where the solids are dried in the same device. On several occasions there was a slight gain instead of loss of weight on heating the solids both on the wire gauze and in the lead dish. The cause to which this is due is not entirely clear. It seems, however, in most cases to be due to a slight oxidation of the fat in the milk, rather than to absorption of moisture or any other cause. The amount at which the solids in the lead dish reached constant weight was almost in every case lower than that at which constant weight was reached when the wire gauze was used. Of the 39 samples on which determinations were made for total solids there were 35 in which the results obtained with the wire gauze were higher than those obtained with the lead dish by an average difference of 0.07 per cent. In no case was the difference as much as 0.2 per cent and in only 5 was it between 0.15 per cent and 0.20 per cent. In only 4 out of the 39 samples were the solids obtained by using the wire gauze equal to or lower than those obtained when using a lead dish. In these cases the differences were much less than in the former case, namely, on an average of 0.04 per cent—the greatest difference being 0.052 per cent. Taking the averages of all the determinations at constant weight made on the 39 samples—*i. e.*, 83 determinations at constant weight with the wire gauze and 63 check determinations at constant weight with the lead dish—it was found that the average of all the results obtained with the wire gauze was 0.06 per cent above the average of the results obtained with the lead dish. In a number of instances heating was continued after constant weight had been reached. While the solids lost weight in both cases, the rate at which the solids in the lead dish lost weight was much greater than that at which the solids on the wire gauze lost weight. Thus in 3 of the samples the losses of weight of the solids in the lead dish due to heating for a prolonged period of time after constant weight had been reached amounted to 0.25 per cent, 0.19 per cent and 0.08 per cent, respectively, or an average of 0.17 per cent. During the same periods of time the drops in weight

[1] *Zeitschr. f. Untersuch. d. Nahrung- u. Genussmittel*, **6** (1903), 259.

[2] "Anal. of Milk and Milk Products," Ed. **1908**, p. 12.

[1] "Foods: Their Composition and Analysis," Ed. **1903**, p. 215

from constant weight of the corresponding solids on the wire gauze were 0.12 per cent, 0.03 per cent and 0.02 per cent, respectively, or an average of 0.06 per cent. It will thus be seen that on the wire gauze the milk solids reached constant weight at an average of 0.06 per cent above the point at which constant weight is reached by the solids in the lead dish, and that this weight changes considerably less during a continued period of heating than is the case when a lead dish is used. This, of course, substantiates the statement made as to the uniform heating and resultant absence of disintegration of the solids on the wire gauze.

FAT—Fat determinations were made on 11 samples of milk. On each sample two determinations were made by the Adams method and two or more with the wire gauze, the fat in the latter case being determined in each instance both by direct weight in the flask and by difference on the wire gauze. Practically all the fat is extracted after 2 hours extraction; however, extraction was carried on in every case for 4 hours. The Adams modification of the Soxhlet apparatus used made from 15 to 20 extractions per hour. The fat flasks were allowed to stand in the air 10 to 15 minutes before weighing since when perfectly dry they gain weight very rapidly. This is similar to the procedure recommended by Siegfeld[1] who suggests, however, that the flasks be wiped off with a fine silk cloth before weighing. This latter was omitted by the writer as of rather dubious value. Siegfeld states that the errors of weighing the fat flasks amounted to from 0.008 to 0.012 g., or where 5 grams of milk are used to from 0.160 to 0.240 per cent. However, where the procedure described is pursued, these errors are considerably reduced. After the fat has all been extracted, $2^1/_2$ to 3 hours drying at 100° C. are sufficient to bring the solids-not-fat to constant weight. Since the loss in weight after the total solids or solids-not-fat have reached constant weight is less than 0.02 per cent per hour, the determination of the fat by difference can be secured with a high degree of accuracy. This is particularly true in view of the fact that the weighings can be made before an appreciable amount of moisture is absorbed from the air, thus presenting an advantage over the determination of fat involving the weighing of fat flasks. The extent to which the total solids and the solids-not-fat are hygroscopic amounts according to the writer's determinations to no more than a gain of 0.05 per cent in 10 minutes. After correction has been made for the extractable matter from the Adams fat-free paper the results obtained by this method and where the fat is determined by means of the wire gauze, both by difference and by direct weight, are in practical agreement. The average of all the corrected results by the Adams method, and the corresponding averages obtained by the wire gauze method, both by difference and by direct weight, are respectively 2.854, 2.868, and 2.859 per cent.

Very satisfactory results were also obtained in making determinations of fat and total solids of creams, skimmed milks, and of homogenized milks and creams. For sweetened condensed milks it was found that unless a very dilute solution was used, the sugar present prevented, somewhat, the complete extraction of the fat. However, for the determination of total solids of sweetened condensed milks the wire gauze may be employed to particular advantage. The charring of the large amount of sugar present in condensed milk introduces a serious error when a dish is used for the determination of total solids. It makes the attainment of constant weight at 100° C. practically impossible. When 5 grams of a 40 per cent solution of sweetened condensed milk, which is about twice to three times the consistency of ordinary milk, are evaporated on a wire gauze, constant weight, as previously defined, is obtained in the usual time and there is no discoloration of the residue to show charring. Richmond[1] found that the Adams method gave low results when used for determining the fat in homogenized milk or cream. This he ascribed to the fact that the subdivided fat globules of the homogenized milk were drawn into the cores of the Adams fat-free paper and there, being surrounded by the fibers of the paper, did not come into effective contact with the extracting medium. The determinations made by the writer would seem to confirm these conclusions. The wire gauze is not open to these objections and the results obtained by it in determining the fat in homogenized milk and cream were higher than those obtained when the Adams method was employed.

## CONCLUSION

Besides milk and milk products it would seem as though the wire gauze, by using an appropriate modification, is well adapted for the determination of the solid matter of a large number of other substances such as: glues, varnishes, shellacs, some oils, tanning materials, etc.; syrups, flavoring extracts and other saccharin products; and for the extracts of vinegars, beers, wines and distilled liquors. Thus for liquors and other thin fluids an 80 mesh wire gauze was found suitable. The device has been used lately with very satisfactory results by J. Wiener of this laboratory in the determination of the solid matter in medicinal preparations containing considerable amounts of sugar and glycerine. The solids reached constant weight without charring at a percentage in quite close agreement with that found from the summation of the individual constituents contained in the preparation. When a dish was used there was always charring, even though the results were considerably too high, and it was impossible to establish at what point constant weight had been reached. In conclusion it may be said that the device gives particularly reliable results in the determination of total solids of milk and of other substances that tend to char easily. The results for fat and for solids-not-fat of milk are also in every way accurate and reliable and compare favorably in this respect with those obtained by other methods, no corrections or blank determinations being necessary. While care is demanded in the manipulation of

[1] "Food—Their Composition and Analysis," Ed. **1903**, p. 215.

[1] *Analyst*, **31** [1906], 318

the device a means is provided that can be kept ready for use in the laboratory and that permits the successive determination of solids and fat of milk and the direct determination of the solids-not-fat, thus effecting a very considerable saving of time on the part of the analyst.

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## THE DETERMINATION OF FAT IN ICE CREAM BY THE BABCOCK METHOD

By C A A Utt

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The determination of fat in ice cream by the Babcock method is simple, desirable, and accurate, if properly conducted. In this laboratory the hydrochloric-acetic acid method has not been found satisfactory in most cases. If much gum thickener, gelatine, or condensed milk, has been added, a white precipitate comes up in the neck of the bottle on the last addition of water, obscuring the fat column, thus preventing an accurate reading.

The following method, making use of a mixture of sulfuric and acetic acids, was developed in this laboratory. It has been in use over a year and has given excellent results on commercial ice cream. It has also been checked against ice cream mixtures of known fat content. Since developing the method the author has been told that there is such a method in existence but he has been unable to locate it. The details are offered for what they may be worth.

### PROCEDURE

A—MIXING THE SAMPLE—Warm the sample to 40° C. and mix by pouring and stirring. If the fat has separated, a few granules of powdered sodium hydroxide may be necessary to aid in the emulsification.

B—WEIGHING—Weigh 9 grams of the well-mixed sample into a 10 per cent Babcock milk bottle. A pipette, with a large outlet, but sufficiently small to fit in the neck of the bottle, is desirable. Nearly the required amount can be added to the bottle by blowing and the remainder by dropping.

C—THE BABCOCK PROCESS Make up a mixture of equal parts by volume of commercial sulfuric acid (sp. gr. 1.83) and glacial acetic acid.[1] Allow this mixture to cool before using. Add 12 to 15 cc. of this mixture to the ice cream in the Babcock bottle at about the same temperature. Shake the mixture, using a rotary motion. Place the bottle in a steam bath or hot water, and heat with occasional shaking until it turns a dark chocolate color. Remove the bottle from the steam bath and allow it to stand 10 minutes. Place in a centrifuge (preferably a steam centrifuge) and whirl 10 minutes. Shake the bottle again, using a whirling motion. Fill to the neck with hot water and mix. A precipitate sometimes forms on the addition of hot water. This can usually be destroyed by adding a few cc. of the acid mixture. Whirl 3 minutes and add boiling water to bring the fat column in the neck of the bottle. Whirl 2 minutes. Read from the bottom of the fat column to the extreme top of the meniscus and multiply the reading by 2. If a centrifuge without a heating device has been used, the bottle should be held in water at 55° C. for 10 minutes before reading. Chalk, powdered calcium carbonate or talc rubbed on the graduated neck of the bottle facilitates reading the fat column.

A few examples will illustrate the value of the method:

| Ice cream mixture containing | | Per cent butter fat found | | | | Av. | Diff. |
|---|---|---|---|---|---|---|---|
| No. Thickener | Butter fat (%) | A | B | C | D | Per cent | Per cent |
| 1 None | 13.60 | 13.40 | 13.50 | 13.70 | ..... | 13.53 | 0.07 |
| 2 None | 15.67 | 15.60 | 15.60 | 15.60 | 15.60 | 15.60 | 0.09 |
| 3 Gum tragacanth | 13.54 | 13.50 | 13.40 | 13.60 | 13.60 | 13.50 | 0.04 |
| 4 1 Rennin tablet | 12.22 | 12.20 | 12.00 | 12.30 | ..... | 12.15 | 0.07 |
| 5 Condensed milk | 16.20 | 16.00 | 16.00 | 16.20 | ..... | 16.07 | 0.13 |
| 6 Condensed milk and gelatin | 16.60 | 16.40 | 16.40 | 16.60 | 16.40 | 16.45 | 0.15 |

### SUMMARY

The method as outlined, using a mixture of sulfuric and acetic acids, gives good results in the determination of fat in ice cream. Checks were obtained in ice cream mixtures made up according to various formulas within from 0.04 to 0.15 per cent of the amount occurring in the mixtures.

The above method has been in constant use for over a year in this laboratory and uniformly good results have been obtained on commercial samples of ice cream.

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[1] We use Grasselli Chemical Co. glacial acetic acid 99½ per cent strictly C. P.

## BETTER BREAD BY MEANS OF NATURAL LACTIC ACID[1]

By Arnold Wahl

### HISTORICAL

Corup-Besanez made the first experiments in 1847[2] to demonstrate the presence of a proteolytic enzyme. These results were published in the *Berichte* and later confirmed by the work of Neumeister.[3]

Langley in 1886 found that pepsin which is secreted by the glands of the stomach as a pepsinogen needs a specific acid to activate it, which acid he showed was hydrochloric. R. Wahl in 1893[4] pointed out that similar to the manner in which starch is dissolved during the mashing process and by means of diastase converted into dextrine, iso-maltose and maltose, so the insoluble proteins of barley, partially during malting but more extensively during mashing, are by means of peptase, a proteolytic enzyme of malt and a counterpart to pepsin, converted into three different proteins: albumoses, peptones and amides, the process of peptonization progressing as long as the mash is held at a temperature favorable to the operation of the peptic enzyme.

Nilson showed in 1903[5] and again in 1904[6] that the peptonizing of proteins by peptase was dependent to some extent on the acidity of the mash. He ex-

[1] Presented at the 51st Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

[2] *Ber.*, **7** (1847), 1478; **8** (1875), 1510; **9** (1876), 673.

[3] *Amer. Brewer Rev.*, **7**, 188, 301.

[4] *Ibid.*, **7**, 185, 201.

[5] *Ibid.*, **17**, 294–7.

[6] *Ibid.*, **18**, 294–7.

pressed the view that the germ and endosperm of the barley does not contain free enzymes in sufficient quantity to make germination possible, and that the enzymes are set free by chemical action of the acids produced by the living bacteria of the barley corn, which bacteria, in exchange for the soluble carbohydrates and proteins extracted by the steeping water from the barley, send back into the germ and endosperm the lactic acid which dissolves the insoluble proteins and thereby sets free the enzymes.

R. Wahl in 1912[1] published extensive researches on the proteolytic enzyme of malt, in which he showed conclusively that the peptic enzyme contained in malt becomes active through liberation by bacterial acidity.

The researches of H. L. White[2] bear out the fact that acid extracts of bran when added to the dough in breadmaking effects an improvement in the bread.

The author spent the summer of 1914 studying in Copenhagen, Denmark, with Dr. S. P. L. Sorensen and Dr. H. Jessen Hansen in the Carlsberg Laboratories of Biological Research, in order to become thoroughly familiar with Dr. Sorensen's[3] method of measuring the concentration of hydrogen ions and the researches of Dr. H. Jessen Hansen in applying the principles of this science to extracts of flour.

Dr. H. Jessen Hansen showed, in 1911,[4] that a definite relation exists between the concentration of hydrogen ions of water extracts of flour and its baking value.

Prof. L. D. Bushwell[5] gave an address in 1915 showing that acids added to the dough have certain germicidal tendencies therein.

## SCOPE OF PRESENT INVESTIGATION

The investigation here described is concerned mainly with the improvement of bread as influenced by the presence of lactic acid produced by *Bacillus Delbruecki*. No details of operation are given, it being my intention to publish them at some later date.

The scope of the work from the results of which my conclusions were reached included:

1—The investigation of the effect of various kinds and concentrations of acids in breadmaking when added to the dough.

2–4—The investigation of the effect in breadmaking of the various lactic acids produced by different microörganisms when added in various concentrations to the dough.

3—Researches on the diastasis and peptonization of the starch and proteins contained in the flour as influenced by the natural lactic acid produced by *Bacillus Delbruecki*.

4—The investigation of the influence of this bacterial lactic acid on the basic phosphates and insoluble proteins of flour.

5—Researches to determine the value of the products of the flour made soluble by bacterial lactic acid as nourishment for bakers' yeast.

6—Researches on the effect of various acids on the mucilaginous coating surrounding the yeast in an attempt to produce a non-cluster forming yeast type.

7—The measurement of the hydrogen ion concentration of bacterial lactic acid extracts of flour.

8—The investigation of bacterial lactic acid extracts of bran for their value as yeast food.

9—Researches on the bacterial lactic acid extracts of various malted cereals for proteolytic and diastatic strength.

## DISCUSSION

The results of my researches lead me to believe that the lactic acid produced by a certain type of lactic acid microörganism known as *Bacillus Delbruecki* found in germinating barley when added to bread in the dough stage acts to liberate and activate the proteolytic enzymes contained in very small quantities in the flour, besides itself acting enzymatically in splitting up the insoluble proteins into soluble peptones and amino bodies. This bacterial lactic acid also effects the solution of the basic phosphates and these soluble phosphates together with the soluble peptones and amino bodies provide the food required by the yeast to build up its protoplasm, much of the required yeast food being contained in the flour in an unassimilable because insoluble condition, but which the lactic acid transforms and makes soluble and assimilable. The acidulation does not become markedly noticeable, either in taste or otherwise, because the lactic acid is neutralized by the alkali of the basic phosphates. The potassium, calcium and magnesium phosphates, which are present as bases, are in turn changed from basic to acid phosphates.

It is also to be noted that the production of yeast food by the effect of lactic acid on the phosphates and protein substance of the flour aided by the activated proteolytic enzymes has a marked stimulating and invigorating effect on the yeast, whereby the latter is caused to produce within a given time a much larger amount of carbonic acid gas, so that in the period of making bread during the time of dough fermentation as well as in the "proofing," the gas generated is in dependably large quantities. The increased nourishment afforded the yeast with its resultant invigoration produces increased yeast growth and a constant tendency to separate the yeast into individual cells and thus avoid cell aggregations, whereas if the individual yeast cells comprising them be undisturbed or insufficiently nourished, they remain intact and through combined action of the aggregated cells, cause the production of holes in the crumb, or a lack of uniformity in its texture. The lactic acid itself has a tendency to dissolve the mucilaginous coating surrounding the individual yeast cell membrane, which renders the yeast sticky and forms the non-readily dispersible cell aggregations already referred to, the yeast thus yielding more readily to thorough mechanical mixing with the dough.

The greater volume of the loaf is due to the increased distribution of the invigorated yeast cells combined with a larger number of the latter so that each particle of the dough becomes, as it were, aerated,

[1] Communication 8th Intern. Congress App. Chem., XIV, 215.
[2] THIS JOURNAL, **5** (1913), 990.
[3] Meddelelser Carlsberg Labor., 1909, Vol. 8.
[4] *Compt. rend.*, Carlsberg Labor., 1911, Vol. 10.
[5] *Bakers' Weekly*, Vol. XXXII, No. 8.

each cell being surrounded by gluten (gliadin and glutenin) modified by the lactic acid in the direction of greater elasticity.

Bread made by usual methods has often the alkaline taste of the basic phosphates of the flour from which it was made. By the transformation of these basic phosphates, by the lactic acid, to acid phosphates with their palatable qualities, together with the agreeable taste of the lactic acid itself, a much sweeter and more pleasant flavor is imparted to the resulting bread.

The crumb of the bread is at the same time rendered whiter by the bleaching effect of the lactic acid on the bran specks, oil and other coloring matter of the flour.

The change of the tribasic alkaline phosphates of calcium and magnesium to soluble acid phosphates, and the partial change of the insoluble nitrogenous substances to soluble peptones and amino bodies renders the bread more wholesome and more readily digestible.

Moreover, the acid, be it the added lactic acid or the acid phosphate produced, has a general retarding influence on the development of the foreign ferments, or other microörganisms, the growth of which would tend to produce bad odor, discoloration, ropiness or sourness in the bread.

The organisms *Bacillus Delbruecki* can be propagated in almost any media containing soluble phosphates, proteins, and sugars, such as crushed wheat, rye, corn, or the flours therefrom; fresh, stale, or defective bread; or bran. The organism will not grow in milk without added sugar in the form of saccharose, maltose, or glucose, since the organism cannot ferment the lactose of the milk.

When propagated in milk, whey, or similar milk products and the whole added to the dough, the resulting bread is much improved for reasons similar to those given above.

A bran mash is the most desirable propagation media, since the highly nutritious soluble phosphates and soluble proteins contained in relatively large quantities therein, are dissolved out by the acid, and are thus incorporated into the dough which adds materially to the effectiveness of the propagated acid. This lactic liquor of an acid strength of 1–2 per cent may be employed with crushed wheat or rye malt flours, thus liberating the proteolytic enzyme, peptase contained in the malt or malt flour, which enzyme goes into solution together with the diastase of the malt flour. Thus the acid-extracted substances of that flour containing, in addition, this activated peptase and diastase, besides the free lactic acid, will, when added to the dough, effect an inversion not only in the protein and basic phosphates, but also of that form of starch which is in a gelatinized condition. Starch, in a gelatinized condition, may be added conveniently to the dough which thus provides not only for the yeast food that forms the protoplasm of the yeast cell, *viz.*, amino bodies and soluble phosphate salts (potassium phosphates and acid phosphates) but also malt sugar and dextrin through the splitting up of which into carbon dioxide and alcohol the vital energy of the yeast necessary to carry on its life function is supplied. The malt sugar so produced and not used by the yeast, adds color to the bread when baked, due to the low caramelization temperature of the sugar.

While commercial lactic acid may be used with improved results in all cases, it is preferable to use bacterial lactic acid on account of its greater effectiveness since this acid with the extractive substances in it, contains a much greater concentration of hydrogen ion, upon which the effectiveness of the acid largely depends.

## CONCLUSIONS

In the main it was found that:

I—The general appearance of a loaf of bread is greatly improved by the use of bacterial lactic acid; a larger loaf results per weight of bread with improved bloom, and color of crust.

II—Through the chemical influences of the bacterial acidity, there results a greater whiteness of crumb with improved texture consisting of a more uniform distribution of the fermentation gas cells which are of smaller size in augmented number, with avoidance of large holes, thus eliminating crumbleness and producing a more velvety crumb.

III—By the addition of bacterial lactic acid to the dough there results a finer flavor and increased palatableness in the bread by virtue of a chemical combination with the phosphates of the flour. Due to its physical condition, it produces a more pleasant taste, and adds zest and appetizing qualities to the bread.

IV—By using bacterial lactic acid produced by propagating *Bacillus Delbruecki* in a bran mash, all the highly nutritious extractive substances of the bran are thus incorporated into the dough, while the lactic acid renders soluble the proteins and basic phosphates of the flour which results in a more wholesome product by reason of its increased digestibility.

V—The employment of bacterial lactic acid insures better bread since the "microbi-cidal" tendencies of lactic acid check the growth of those undesirable microörganisms which tend to cause a disagreeable taste, bad odor, ropiness and other bread diseases.

VI—Bacterial lactic acid extracts of malted cereals at low temperatures contain in addition the activated proteolytic and diastatic enzymes, peptase, and diastase, which act during dough fermentation to effect a partial digestion of the dough, the resulting soluble proteins, phosphates, and carbohydrates serving as a most desirable nourishment for the yeast.

VII—Milk, whey, buttermilk, and similar milk products containing either added or developed bacterial lactic acid, when added to the dough, also effect a similar improvement in the bread.

VIII—Commercial lactic acid may be used with improved results but bacterial lactic acid is preferable and that bacterial lactic acid which is produced by the organism *Bacillus Delbruecki* is the most desirable, since this lactic acid with the extractive substances in it contains a much greater concentration of hydrogen ions upon which the effectiveness of this acid largely depends.

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## THE EFFECT OF GRINDING THE SOIL ON ITS REACTION AS DETERMINED BY THE VEITCH METHOD

By P. E. Brown and H. W. Johnson

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In the course of some recent studies of Iowa soils, it became necessary to ascertain their reaction or need of lime and inasmuch as previous tests had been carried out by the Veitch method and comparisons had indicated it to be quite satisfactory, it was decided to use the same method in this work.

It was soon noted, however, that the results which were being secured were in most cases the direct opposite of those obtained by previous tests of samples of the same soil types taken from approximately the same localities. For instance, practically all the samples from Bremer County were found to be basic in reaction, whereas previous tests of the soils of that county had shown that almost all were acid. The test had been carried out in exactly the same way in both cases. Every step in the operation and every detail in manipulation was carefully checked but no difficulties were encountered with the method. The soil samples were taken in the same way, and both lots were chosen as representative of soil types. Furthermore they were taken *by the same man* so that there was every reason to expect that the reaction of the samples would be very similar. At least it was felt that the same tendency of the soils to react acid or basic should have been observed with both lots of samples.

There was only one difference in the two lots of samples: the first was secured especially for acidity tests and the soils were tested in an unground condition, while the second lot was obtained in connection with the soil survey of the county and the samples were finely ground before being tested. This grinding was necessary in order to prepare the samples for the chemical analysis which was to be made of the soils.

It seemed probable, therefore, that the difference in the reaction of the two lots of samples was due to the grinding. The questions then arose—Does the grinding of soils increase their basicity according to the Veitch test? If so, what causes the production of a basic reaction?

In a critical study of the method which he devised, Veitch[1] observed that the length of time the treated and dried soil was allowed to stand in contact with water had a considerable effect on the apparent acidity as determined by the method. He noted that when solution was allowed to go on from 48 to 72 hours the pink color with phenolphthalein was developed with less added lime water than when the solution was allowed to stand 16 hours or less. The increase in basicity was so pronounced in some cases that soils which were acid when allowed to stand 16 hours gave a basic reaction upon standing 24 to 48 hours longer.

In discussing the cause of this increase in basicity, Veitch concluded that it was not due to the failure of $CaCO_3$ to go into solution in partially carbonated water in the shorter time and he suggested that the cause might probably be found in the slower solubility and hydrolyzation of the neutral lime compounds that are formed with the added lime water or to the solution and hydrolyzation of neutral compounds already present in the soil.

He called attention to the fact that in 1845, Rogers Brothers[1] showed that many of the common minerals, "particularly the zeolites and feldspars when reduced to fine powder and treated with carbon dioxide-free water, gave a more or less strong reaction with phenolphthalein." Since that time the solution of minerals in water has been studied by a large number of investigators[2] and it has come to be quite generally accepted that the observations of Rogers Brothers were correct. Minerals are known to be present in soils in considerable amounts, and their solution to proceed very slowly. The development of a basic reaction when soils are subjected to long standing in the lime-water test may, therefore, be due to the solution of silicates.

The directions for carrying out the Veitch test based on these experiments by the author of the method and numerous other investigators prescribe, therefore, that the samples shall stand only over night in contact with the water. In this way it is deemed that there is not sufficient time for the solution of any of the silicates in the soil to occur and make the test basic.

It seemed probable that the same reason which Veitch advanced for the development of a basic reaction by soil upon long standing with water might account for the production of basicity in a ground soil, that is, the solution and hydrolyzation of silicates.

As the point raised is of some interest and the question of the condition in which the soil should be when tested for acidity is of considerable importance, some tests have been carried out along this line. No previous investigations, as far as the authors are aware, have specified what the condition of the soil should be when the Veitch test is applied, and these results indicate that it is of importance because of the development of a basic reaction when soils are ground before being tested.

### EXPERIMENTAL

In order to determine definitely whether grinding occasioned a development of basicity in soils, four samples of soil from Bremer County were secured and each sample was thoroughly mixed and divided into four portions. The first portion was unground and unsieved, the second was put through a 20 mesh sieve, the third through a 40 mesh sieve and the fourth portion through an 80 mesh sieve: grinding was done wherever necessary.

In the case of the Bremer fine sandy loam and the Carrington sandy loam very little grinding was necessary to put the soils through the 20 mesh sieve but considerable grinding was needed to put them

[1] *Am. J. Sci. and Arts*, **5** (1845), 5.

[2] F. K. Cameron and J. M. Bell, Bur. of Soils, *Bull.* **30** (1905).

[1] *J. Am. Chem. Soc.*, **26**, 63.

through the 40 and 80 mesh sieves. With the other two soils, considerable grinding was required for them to pass the 20 mesh sieve.

Examining the results given in Table I, it is found that all the soils showed acidity when tested in an unground condition and all showed a basic reaction when they were ground and put through an 80 mesh sieve before being tested. With three of these samples enough basicity was developed, when the soils were ground to pass the 40 mesh sieve, to change the reaction from acid to basic. Even the slight grinding necessary to put the soils through the 20 mesh sieve reduced the lime requirements of two of the soils.

These results indicate clearly that grinding increases the basicity of soils and those normally having an acid reaction by the Veitch test may show a basic reaction.

Table I—Reactions and Lime Requirements (Lbs. per 2,000,000 Lbs. of Surface Soil) of Four Sandy Loams

| Condition of Soil when Tested | Soil No. 14 Bremer fine sandy loam(a) | | Soil No. 51 Bremer coarse sandy loam (b) | | Soil No. 57 Bremer sandy loam(b) | | Soil No. 24 Carrington sandy loam (a) | |
|---|---|---|---|---|---|---|---|---|
| | Reaction | Lime | Reaction | Lime | Reaction | Lime | Reaction | Lime |
| Unground and unsieved | Acid | 2816 | Acid | 3520 | Acid | 5280 | Acid | 3168 |
| Through 20 mesh sieve | Acid | 2816 | Acid | 3520 | Acid | 3168 | Acid | 1760 |
| Through 40 mesh sieve | Acid | 2116 | Basic | .... | Basic | .... | Basic | |
| Through 80 mesh sieve | Basic | .... | Basic | .... | Basic | .... | Basic | |

(a) Very little grinding to pass 20 mesh. (b) Considerable grinding to pass 20 mesh.

In order to test the point further and also to ascertain to what extent the sand affected the development of a basic reaction when a ground sample was tested, five samples of the Lintonia series of soils from Muscatine County, Iowa, carrying different contents of sand and all reacting acid in the natural condition were tested in the same way as the previous soils. The results appear in Table II.

The coarse sand needed a little grinding to put it through the 20 mesh sieve and this reduced the lime requirement somewhat but when ground and put through the 40 mesh sieve the reaction became basic. Very little grinding was required to put the fine sand through the 20 mesh sieve and while more was required for it to pass the 40 and 80 mesh sieves the grinding was not sufficient to make the reaction basic; a gradual reduction in the lime requirement of the variously treated samples, however, was noted.

Table II—Reactions and Lime Requirements (Lbs. per 2,000,000 Lbs. of Surface Soil) of Lintonia Sands and Sandy Loams

| Condition of Soil when Tested | Soil No. 32 Coarse sand(a) 92.2% sand | | Soil No. 37 Find sand(b) 92.0% sand | | Soil No. 18 Sand(c) 91.1% sand | | Soil No. 8 Coarse sandy loam(a) 86.2% sand | | Soil No. 42 Fine sandy loam(d) 79.2% sand | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Reaction | Lime | Reaction | Lime | Reaction | Lime | Reaction | Lime | Reaction | Lime |
| Unground and unsieved | Acid | 5280.0 | Acid | 3345.0 | Acid | 2341.5 | Acid | 3010.5 | Acid | 5017.5 |
| Through 20 mesh sieve | Acid | 4224.0 | Acid | 3010.5 | Acid | 2341.5 | Acid | 3010.5 | Acid | 5017.5 |
| Through 40 mesh sieve | Basic | .... | Acid | 1672.5 | Acid | 1672.5 | Acid | 1338.0 | Acid | 5017.5 |
| Through 80 mesh sieve | Basic | .... | Acid | 1338.0 | Basic | .... | Acid | 1338.0 | Acid | 4348.5 |

(a) Little grinding to pass 20 mesh. (b) Very little grinding to pass 20 mesh. (c) No grinding to pass 20 mesh. (d) Very little grinding to pass 40 mesh.

With both the coarse sandy loam and the fine sandy loam the lime requirement was changed by grinding, but the soils still tested acid even when ground to pass the 80 mesh sieve. The reduction in lime requirement was noted sooner in the coarse sandy loam as might be expected, very little grinding being necessary to put the fine sandy loam through the 40 mesh sieve.

According to these results there seems to be a direct relationship between the sand content of the soil and the effect which grinding the sample exerts on the reaction by the Veitch test. The larger the amount of sand present and the coarser the condition in which it exists, the less grinding is required to alter the reaction of the soil according to the Veitch test. Where the percentage of sand is low the effects of grinding are small although the influence in reducing the lime requirement of acid soils is still noticeable.

It is evident, therefore, that "silicates when finely ground lead to the development of a basic reaction" in soils and the observations of Rogers Brothers and others, as noted above, are confirmed. Veitch's suggestion regarding the cause of the development of a basic reaction in the soil upon long standing with water is likewise confirmed.

In order to test soils for their reaction by the Veitch method it is obviously necessary, therefore, that the soil be in its natural condition and unground.

It may be argued that calcium silicate and other silicates lead to the production of basic compounds in the soil through the action of carbon dioxide produced in the decomposition of organic matter but this production of basic material is much too slow to remedy acid conditions in the soil and hence the soil reaction should be determined without consideration of the presence of silicates.

## SUMMARY

The results of these tests lead to the following conclusions:

I—When acid soils are ground before being tested by the Veitch method the acidity is reduced and frequently the reaction becomes basic.

II—The development of basicity increases with the grinding of the soil.

III—The increase in basicity depends upon the amount of sand present and is greater in coarse sandy soils than in fine sands.

IV—Soils should not be ground previous to testing their reactions by the Veitch method.

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# LABORATORY AND PLANT

## INVESTIGATIONS ON THE NATURE AND ELIMINATION OF ODORS AND DUST FROM A GARBAGE REDUCTION PLANT

By Hermann W. Mahr and Alvin C. Kraft

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Plants and processes for treating garbage to recover grease and manufacture tankage give rise to odors and sometimes to dust of an unpleasant nature. Within the confines of New York City the nuisance from several plants for waste disposal led to protests and legal action by the health department. The municipality appointed Mr. Irwin S. Osborn, consulting waste-disposal engineer, to investigate the trouble. Mr. Osborn decided to supplement the engineering investigation with a chemical study of the nature of the odors and dust, and the present and possible means of treating them. With the coöperation of this laboratory the chemical investigation was carried out.

The odors from a reduction plant originate from the raw "green" garbage, from the processes of manufacture, and from the buildings becoming permeated with garbage and liquors. Odors from the green garbage and from some of the operations are of a local nature. Those from some treating methods are capable of causing discomfort several miles away.

Most of the work described in this paper was carried on at a works located on an island within the boundaries of New York City. The greatest inconvenience was felt by those districts on a peninsula, whose nearest point was about one mile from the disposal plant. The latter is the largest of its kind in the world, and has most of the processes typical of the smaller reduction works, and also modifications obligatory because of its size.

### DESCRIPTION OF REDUCTION PROCESS

Garbage reduction may be characterized industrially, as one economically handling large quantities of very low-grade materials. The garbage arrives at the docks of the works on open scows, and is transferred to conveyor hoppers by scoop-shovels. On the conveyor it receives a rough sorting to eliminate some of the tin cans, bottles, rags, etc. The odors arising from the transportation, conveying and sorting are of a local nature, and the operations are carried on in the open air.

Conveyors deposit the garbage in large iron, brick or fire-clay lined tanks in which the material is cooked, with the addition of water, by live steam for from 10 to 12 hours. These digesters are vented from time to time, and the vent gases have considerable odor of more than local importance. Apparatus for treating these gases has been installed by the company, and a study of the odors and action of the treating appliances was a part of this investigation. The cooked garbage and liquor are run into receiving tanks and held for the presses. These receiving tanks are also vented into the devices mentioned above.

The liquor, fat, and garbage are run from the tanks to presses. The latter are of three types: flat hydraulic, in which the garbage is pressed in sacking, torpedo-shaped steam presses, in which steam pressure is depended upon, and continuous roller presses, which carry the material on metal belts through several sets of squeeze rolls. Liquid known as "stick liquor" and the grease from the presses is run to a system of settling tanks located in the open. Here the grease is skimmed off and the "stick liquor" run into the bay. "Stick liquor" has an odor probably of only local importance. At some reduction works it is evaporated in vacuum apparatus, and when of sufficient consistency mixed with the tankage. The material thus recovered adds considerably to the value of the latter.

The pressed garbage is further treated to recover the residual grease by taking it to the primary direct-heat dryers, where the remaining water is removed. The direct-heat dryers are necessary in large scale garbage treatment, steam dryers being used in many small plants. Considerable odor and dust are caused by the drying, and the odor is perceptible miles from the plant. A scrubber for the dryer gases had recently been installed. As the dryer nuisance was of great importance, it required considerable investigation in the present work. The dried garbage is conveyed to a naphtha percolating or extraction plant, where the grease is dissolved out. The naphtha solution of the grease is evaporated, first under a vacuum by means of closed steam coils and then with live steam. Extracted tankage in the percolators is treated with steam to remove the retained naphtha and then dried in a second set of direct-heat dryers known as the secondary dryers. Here, too, the drying gives rise to odor and dust which is led to the scrubber for treatment.

The dried tankage is sent to the screen house where the glass, cans, rags and bones are taken out and sorted. Considerable dust arises from the screens, but at this plant it settled within the boundaries of the works. Tankage is then stored for shipment, and its odor, which is quite mild, is confined to the store-house.

### RAW MATERIAL AND LOCAL PLANT ODORS

In the above description certain odors, such as those from handling the raw garbage, from the grease separating tanks, from pressing, and from conveying garbage in the process of treatment, are characterized as of only local importance. In many reduction works, located nearer to inhabited sections, these would have to be eliminated. The transportation of garbage in open scows or cars would, in this case, be obliged to give way to closed conveyances. The handling of the garbage, both raw and in process, and other obnoxious treatments, would necessarily be carried on inside. To dispose of the odors in buildings, they should be provided with ventilating systems drawing the air through scrubbers and afterward through de-

vices for perfuming it with wood-tar oils. Systems similar to this are successfully used in treating packing-house air.

DIGESTER-VENT ODORS AND GASES

During the cooking of garbage the digesters are vented through a by-pass around the valve of the main outlet pipe. This operation has two objects: (1) to drive out air at the beginning of the cooking, and (2) to insure good circulation of the cook. The receiving tanks are also vented, and the gases from both operations treated in the same sort of apparatus. Fig. I is a diagrammatic representation of digesters, tanks and vent-odor eliminating appliances. The steam and gases pass to tanks *E* and *F*, which serve as catch tanks in the event of a digester boiling over. They are then conducted to barometric condensers, fed with sea water, where the steam and the condensable constituents are condensed. The end of the condensers, from digester vents, runs into a tank, *G*, the water and uncondensable gases here separating; the former escape through a sealed overflow to the bay, and the gases are conducted to behind the bridge wall of the boiler furnaces for heat treatment. The water and gas from the receiving-tank condensers are conducted directly to the bay.

The investigation of the digester-venting included a study of the chemical nature of the condensable substances and odors eliminated by the barometric condensers. These condensable constituents fall into two classes: (1) substances mechanically entrained by steam, and (2) those volatile in the form of vapor. Closely connected with the proceeding was a determination of the chemical nature of the gases escaping condensation in the treating apparatus. Experiments on deodorizing the water from the condensers and the uncondensable vent gases were also made.

THE CHEMICAL NATURE OF CONDENSABLE VENT SUBSTANCES

Information regarding the condensable substances in the vent gases was obtained from samples of condensate of the vapors taken at a point before entering the barometric condensers, as shown in Fig. II.

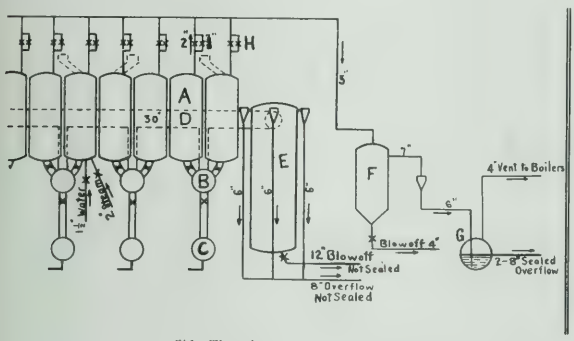



FIG. I DIGESTERS AND VENT TREATING APPARATUS

A—Digester, with Feeding Chutes
B—Receiving Tank
C Steam Presses
D—Receiving Tank Vent
E—Vent Tank with Condensers
F—Digester Vent Tank with Condensers
G—Blowoff Tank
H—Digester Vent By-Pass

At the beginning of the sampling, bottle *D*, filled with water, was connected to the condenser, and the uncondensable gases allowed to displace the water through the siphon. When the water had been completely displaced the siphon was shut off, and the bottle *E*, full of water, connected to *D*. Condensate from the vent line was then collected in *D*, and the uncondensable gases in *E*. During the sampling the average temperature in the vent line was found to be 101° C.

SUBSTANCES CARRIED OVER MECHANICALLY—An examination of the solids in the condensate was carried out by evaporating in a platinum dish, drying and igniting, with the following results:

| PER CENT SOLIDS | In unfiltered condensate | In solution | In suspension |
|---|---|---|---|
| Total | 0.0224 | 0.0102 | 0.0122 |
| Inorganic | 0.0083 | 0.0067 | 0.0016 |
| Organic | 0.0141 | 0.0035 | 0.0106 |

These results show that two-thirds of the soluble materials carried over mechanically with the vent steam are inorganic. It will be shown below that a large part of the organic matter, thus taken from the digesters, consists of fats and fatty acids. None of the substances carried over mechanically are of importance from the odor standpoint.

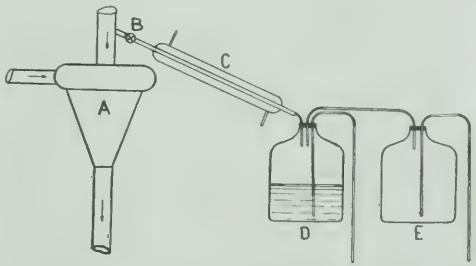



FIG. II—SAMPLING APPARATUS, ABOVE BAROMETRIC CONDENSERS

A—Barometric Condenser
B—Sampling Control Valve
C—Condenser
D—Condensate Sample
E—Gas Sample

CONDENSABLE VOLATILE SUBSTANCES, on the contrary, are of considerable importance as odor pro-

ducers. The condensate was filtered, and the specific gravity taken and found to be 0.9967, thus pointing to the presence of *ethyl alcohol* to the amount of 1.87 per cent by weight. On distilling, to concentrate, the characteristic bead-like drops caused by alcohol condensation were noticed in the condenser and the distillate gave the iodoform reaction for alcohol.

ACIDS in the condensate were determined by titration with alkali, using phenolphthalein as an indicator, and found to be equivalent to 0.0851 per cent, calculated as acetic acid. A 100 cc. sample of condensate was placed in an apparatus for determining carbon dioxide in carbonates by the evolution method, and boiled while a current of air was led through the apparatus. The steam and steam-volatile acids were condensed by the reflux condenser of the apparatus, while any carbon dioxide was conducted through drying tubes to a weighed potash absorption bulb. It was found that the amount of carbon dioxide present was practically *nil*.

ACETIC ACID AND OTHER STEAM-VOLATILE ACIDS were found by steam-distilling the condensate and titrating the distillate. The results gave 0.0792 per cent of steam-volatile acids, calculated as acetic. Part of this was acetic acid and part steam-volatile fatty acids. The remaining non-volatile acidity was probably due to non-volatile fatty acids carried over mechanically.

The acidity of the vent gases has an important bearing on the corrosion of the vent pipe lines.

SAPONIFIABLE SUBSTANCES in the condensate were estimated by neutralizing a portion of it, and then saponifying with standard alcoholic potash; 100 cc. of condensate required 103.6 mg. of potassium hydrate for saponification. Some of the neutralized condensate was then steam-distilled. The surface of the distillate was covered with oily drops, and the distillate from 100 cc. of condensate required 79.5 mg. of potassium hydrate for its saponification. The volatile saponifiable substances were therefore apparently *essential oils*. This supposition was confirmed by a test for aldehydic constituents of essential oils in the distillate, by means of fuchsine reagent. The residue from the steam distillation was extracted with ethyl ether, and after evaporating off the latter, a fatty residue remained. The saponifiable substances in the condensate were thus proven to be steam-volatile essential oils and mechanically entrained fats.

On boiling the condensate and passing the vapors through lead acetate paper a test for sulfur compounds was obtained.

The *indol* test for bacterial decomposition products gave negative results.

CONCLUSIONS. The mechanically carried over substances removed by the condensers are principally mineral matter, fats and fatty acids. The volatile substances in the vent gases which are condensable, or absorbable in water include alcohol, acetic acid, carbon dioxide, essential oils and sulfur compounds. Of these constituents, the two latter are important from the odor standpoint, and impart their smell to the condensing water passing through the jet condensers.

### UNCONDENSABLE VENT GASES

The uncondensable vent gases were examined before and after passing the barometric condenser. Samples of the former were obtained at the same time the condensate was sampled. The gases after passing the condenser were sampled from the vent pipe to the boiler by displacement (*G*, Fig. I). Simultaneous samples before and after passing the barometric condensers gave the following results:

UNCONDENSABLE VENT GASES AT BAROMETRIC CONDENSERS

| | Before passing | After passing |
|---|---|---|
| Carbon dioxide | 45.2 per cent | 6.2 per cent |
| Oxygen | 10.8 per cent | 18.0 per cent |
| Sulfur compounds | Large amount present | Large amount present |

The sulfur compounds were tested for in a solution of bromine water through which the gases had been conducted. The decrease in the carbon dioxide content, as a result of passing through the barometric condenser, is an indication of the efficiency with which the condensers are absorbing the condensable gases. The extremely nauseating odor of the uncondensable vent gases appears to be due to sulfur compounds and other non-sulfur containing substances, possibly essential oils. It will be shown below that the presence of the sulfur compounds is important in determining the method of treatment for the gases.

### EXPERIMENTS ON THE ELIMINATION OF VENT ODORS

The *water leaving the barometric condensers* has considerable smell. Water containing the condensable odorous vent substances was quickly deodorized by small amounts of sodium and calcium hypochlorite. The location of the reduction works in question, on the sea, makes possible a practical application of this treatment. Sea water could be electrolyzed and run into the condenser water before it enters the condensers.

To investigate the efficiency of water in eliminating the uncondensable gases by further scrubbing, some of the gas from tank *G* was led through 100 cc. of water in a small Erlenmeyer flask at the rate of about five bubbles per second. The gas was metered through a wet test meter and after about 0.2 cu. ft. of gas had passed through the water the odor of the vent gas was noticeable.

Some of the gases were then led through sodium hypochlorite solution containing 4 parts of available chlorine in 1000. The rate was also about five bubbles per second, and the volume of solution 150 cc.; 10 cu. ft. of uncondensable vent gas were passed through the solution before its odor was apparent. Calcium hypochlorite (chloride of lime) solution was also found to be a good deodorizer.

The strength of sodium hypochlorite necessary to deodorize was determined by leading the gases through solutions containing various amounts of available chlorine. A strength of 1 part of available chlorine in 1,000 was necessary for a decided deodorizing action.

In applying to condenser water the treatment with electrolyzed sea water, mentioned above, the uncondensed vent gases would be deodorized as they

passed through the condenser and vent tank *G* (Fig. I). Of course, steps would have to be taken to insure the presence of sufficient hypochlorite.

A possible method of combining the condensing and deodorization treatment would be by means of surface condensers. The volume of odorous liquids requiring treatment with chemicals would be reduced greatly in comparison with that at present passing through the jet condensers.

HEAT is a favorite agent for eliminating odors, and uncondensable vent gases from garbage digesters are often treated thus. As was mentioned above, this method is in use at the plant under consideration.

Mr. Osborn[1] and Prof. Crowe studied the action of heat on the uncondensable vent gases from the Municipal Reduction Works at Columbus, Ohio, in 1911. They led the gases through a heated copper tube provided with a temperature-recording device, and then through the water jet pumps, which furnished suction.

They concluded that heating the vent gases to 1600° F. completely destroyed the odor.

In the present study the uncondensable vent gases were led from tank *G* to a bottle for equalizing and observing the pressure and thence to a Hoskins electric tube furnace containing a heated silica tube. The furnace was provided with a rheostat and the temperature determined by means of a pyrometer. The couple of the latter was inserted so that the hot junction was in the center of the heated gas. Pressure in the vent tank made the use of suction unnecessary. The odor of the gases after heating was observed at the end of the silica tube with the results given below:

EFFECT OF HEATING ON THE ODOR OF DIGESTIVE VENT GASES

| Temp in furnace | Temp. of gases at point where odor was noted | NATURE OF ODOR |
|---|---|---|
| 40° F | 40° F. | Sweet, slightly nauseating, essential oil like |
| 150 | 66 | |
| 250 | 86 | |
| 350 | 118 | Sweet, slightly nauseating, slightly acrid |
| 450 | 114 | Sweet, slightly acrid, slightly irritating |
| 550 | 169 | Less sweet, acrid, slightly irritating |
| 750 | 176 | No sweetness, quite acrid and irritating |
| 850 | 194 | Acrid, irritating, |
| 950 | 201 | $SO_2$ odor apparent |
| 1050 | 205 | More acrid and irritating, $SO_2$ odor very |
| 1100 | 233 | distinct |
| 1150 | 230 | Very acrid and irritating, $SO_2$ odor very |
| 1200 | 239 | distinct |
| From 1200 to 2000 | .. | Increase in irritating, pungent, $SO_2$ odor |

The presence of sulfur dioxide in the heated gases was confirmed by passing them into bromine water and adding barium chloride.

To ascertain whether the copper tube used by Osborn and Crowe was a factor in destroying the vent gas odor, a heating experiment similar to the first was run and a layer of copper oxide was placed in the heated zone of the silica tube. The results were practically the same as those when the plain silica tube was employed. Osborn and Crowe's conclusion regarding the effect of heating on the vent gases was therefore not substantiated by these experiments.

All garbage digester odor was shown to disappear at a temperature of 700 to 800° F., giving place to the odor of sulfur dioxide, formed from the sulfur compounds in the gas. The vent odor was apparently completely replaced by that of sulfur dioxide at temperatures of 1100 to 1200° F. A study of the apparatus used by Osborn and Crowe led to the conclusion that the action of water, in their jet suction pump, had been an important factor in eliminating the sulfur dioxide in the gases after heating.

An experiment in which the gases were heated to about 1200° F. in the silica tube and then bubbled through water showed the washed gas to be without odor of any sort.

These experiments show that the generally used heating method (without subsequent scrubbing with water) for treating uncondensable digester-vent gases is inadequate. It results in forming a gas which is almost as obnoxious and probably more harmful than that from which it originated. One practical method of treating the gases at the present plant would be to send them through the fires of the direct heat dryers and then to the scrubber for washing the dryer gases.

A method of deodorizing packing-house air by means of sulfur dioxide has been said to give good results. It is possible that the sulfur dioxide, formed by heating the vent gases, could be reconducted to the jet condensers, and in this way a deodorization of the condenser water brought about.

That the sulfur compounds are the interfering factor in preventing deodorization by simple heating of the vent gases was confirmed by similar heating experiments on "stick" roll gases at a plant for treating offal, located near the garbage plant. The "stick" rolls are steam-heated drums on which concentrated liquor, obtained by evaporating the water from offal digesters, is dried. When the gas from these rolls was heated to 1200° F. the odor was completely destroyed and a test showed it to be free from sulfur compounds.

Objectionable odors are often masked by treatment with *coal-* or *pine-tar*. The odor of uncondensable vent gases, when led through a bottle containing pine tar oil, gave way completely to that of the tar oil.

## GASES, DUST AND ODOR FROM THE DRYERS

When the reduction process was outlined, mention was made of the far-reaching effect of the odors from drying garbage and tankage in direct heat dryers. At this disposal works the process required two dryings, one of the cooked garbage, known as the primary drying, and a drying of the degreased material, which contains water from the steam used to displace the naphtha residues. The latter is designated as secondary drying. The dryers are cylindrical, about 25 ft. long, 5 ft. in diameter, and made of sheet steel. They are rotated in a manner similar to a tube furnace, but at a much greater speed. The heating is by means of hand-fed coal fires with a forced draft, each dryer having its own furnace.

The garbage is fed into the furnace end of the dryer from a room located above it. On arriving in the dryer the garbage at once comes into contact with the

[1] Private communication.

flame, resulting in a quick drying, with some burning, which gives rise to a large part of the dryer odor. The object of feeding at the heated end of the dryer is to obtain a fairly well dried material, which will not stick to the dryer as it proceeds to the outlet end. As the garbage becomes dried, the fast rotation, aided by the high draft, carries off considerable dust, which, with the dryer odor, was a source of annoyance to the surrounding communities.

The gases and dust leave the end of the dryers in the dust rooms shown in Fig. III and then pass through a brick flue. The dust rooms have many openings through which air enters to dilute the dryer gas, and the amount of this dilution has a bearing on the treatment of the gases. From the flue the gas is diverted into a scrubber which has recently been installed, and after being washed returns to the flue and thence to the chimney. Fig. III also shows the arrangement of the scrubber. The nozzles form a spray curtain through which the gas passes. Sea water is used in the scrubber, after it has been used for cooling in the naphtha recovery plant. Considerable care is exercised to keep the scrubber water free from mechanical impurities which would clog the nozzles.

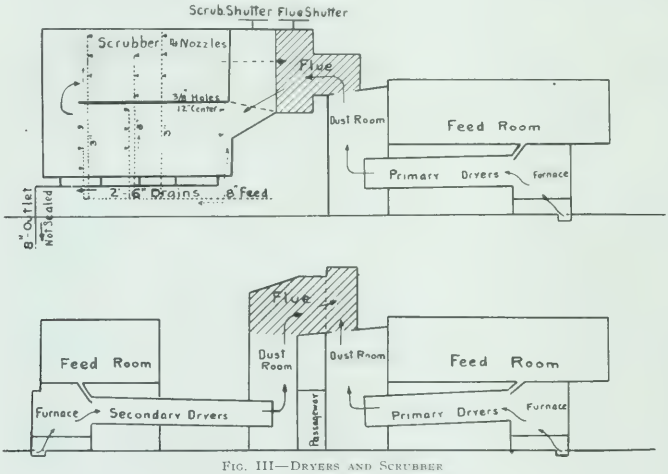



FIG. III—DRYERS AND SCRUBBER

The first determination in this section of the work was one of the velocity and volume of the dryer gases passing to the stack. To ascertain if the amount of gas treated by the scrubber could be decreased, an estimation of the dilution of the gases by leakage was made. The value of the scrubber in removing dust was found by dust determinations before and after scrubbing the gases. The chemical nature of the odor of the dryer gases was investigated in order to select constituents which could be determined before and after scrubbing, in this way testing the efficiency of the scrubber as an odor eliminator. The dryer studies were completed with experiments on methods of deodorizing the gases.

THE VELOCITY OF THE DRYER GASES was determined in the main flue, opposite the scrubber entrance. The latter and the scrubber exit were walled off from the flue for the purpose of the determination. Use was made of the standard pitot tube of the American Blower Company and the method described by Rouse.[1]

Owing to the large size of the flue (width 5 ft. 9 in.; depth 17 ft. 2 in.), means of lengthening the tube were necessary. The end section of the pitot tube was soldered into a reducer on the end of an iron pipe. The pitot tube connections were soldered to copper pipe, which ran through the iron pipe to rubber connections from the manometer. In order to keep the pitot cool, water could be conducted through the iron casing pipe. Fig. IV is a photograph of the pitot tube and observation station.

The width of the flue was divided into 5 and the depth into 10 equal parts; readings were taken at the center of each of the fifty rectangles thus formed. During the tests observations on the number of dryers in action, revolutions per minute of the blowers, draft in the latter, in the flue, in the dust chambers, and flue temperatures were made. Moisture determinations on the flue gas were also run by drawing it through the steam-jacketed tube, described below, and absorbing in calcium chloride. Results of two runs showed a velocity of 30.446 and 27.705 ft. per second under flue conditions of temperature. From the latter results the volume of gas passing through the flue was found to be 2735 cu. ft. per second.

The question of whether the gas leaving the dryers was diluted by leakage from the air, entered into the engineering study. This had a bearing on the amount of gas which could be efficiently scrubbed by the present apparatus. Analyses were made of the gas leaving the dryers and of that entering the scrubber. Calculations based on the carbon dioxide content showed the dilution to vary from 1–1.9 to 1–3.9 volumes.

### EFFICIENCY OF THE SCRUBBER IN REMOVING DUST

To determine the amount of dust being removed by the scrubber, estimations of the amount in the flue gases before and after scrubbing were required. Because of the size of the dust particles, and particularly the amount of moisture in the gas, considerable study and experimentation were necessary to evolve a satisfactory method. It was decided to use the principles and apparatus of Brady and Touzalin,[2] and the latest form of their apparatus was first employed. The sampling tube was found to be of too small a bore for this work; it soon clogged because of the moisture, large amount of dust and size of the dust particles.

[1] *J. Am. Soc. Mech. Engrs.*, Sept., **1913**, see also Fairlie, THIS JOURNAL, **1914**, 583.

[2] "The Determination of Dust in Blast Furnace Gases," THIS JOURNAL, **3** (1911), 662.

A much larger bore tube ($^3/_8$ in.) was made and steam-jacketed (see Fig. V) to avoid condensation. To obtain correct results, according to the above authors, the velocity of the gas withdrawn through the sampling tube must be the same as that in the flue proper. In their original method the flue velocity was ascer-

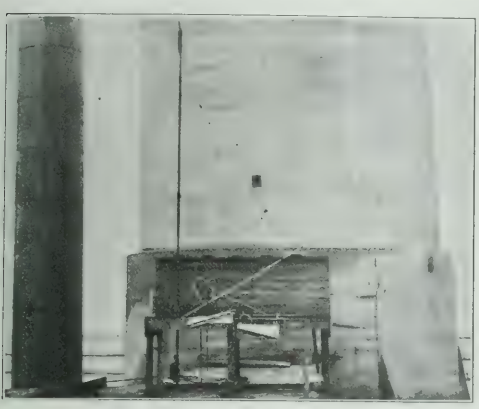


FIG. IV—MODIFIED PITOT TUBE

tained with a pitot tube, and the sample metered so as to maintain this velocity in the sample tube. In their improved apparatus[1] a side tube leads from a point in and near the entrance to the sampling tube to one arm of an Ellison gauge. The other arm of the gauge leads to a tube with its opening into the flue near the intake of the sampling tube. The latter is turned so that the opening is in the plane of the flue gas stream. The pressure on these tube ends is the static pressure of the gas flowing past them. By connecting one to each side of an Ellison gauge, and regulating the speed of sampling so that the levels of the liquids in both arms remain equal, the essential condition of equal velocities in the flue and sampling tube is attained. This modified pitot tube device was added to our new sampling tube.

To maintain equal velocity in the flue and large sampling tube, required the metering of volumes of gas so large as to be greater than the capacity of the wet test meter accompanying the Brady apparatus. A standardized 20-light dry meter was therefore employed. The nature of the dust, and its large amount, soon clogged the Brady paper filters and made impossible the maintenance of the requisite sampling velocity. Filters of 200-mesh wire gauze were therefore used. The filter was enclosed in a chamber heated by steam coils, the electric heater of the original apparatus having proved inadequate under conditions of the present work.

Some dust escaped the gauze filters and this was caught by scrubbing in two large baffle wash bottles[2] (Fig. VI) made from two-liter wide-mouthed bottles, into which were ground stoppers with the entrance and exit tubes. The entrance tube was provided with perforated glass baffle plates extending nearly to its sides. The lower plate was under the water level and helped break up the gas and at the same time kept the water from being lifted too high when large amounts of gas were washed. The upper plate prevented the carrying away of the liquid mechanically.

The dust determining apparatus was set up as shown in Fig. VII. In carrying out the determination a dried and weighed gauze filter was placed on the end of the sampling tube and from 20 to 30 ft. of gas led through the apparatus. The latter was then taken apart, and the connections, from *C* on, washed into the bottle *D*. No dust was ever found in the sampling tube. The filter and dust were dried and weighed, and the dust in the wash bottles determined by filtering on a Gooch crucible. The volume of the gas recorded by the meter was calculated to a temperature of 15.5° C.

The dust was determined in the flue with the scrubber walled off, and in the exit of the scrubber at the left and right side of the damper. Samples were taken at the latter points with the water shut off in the scrubber, and also with water on. The following table gives results of the dust determinations:

DUST DETERMINATIONS

| No of run | Scrubber | Gas(*a*) filtered Cu. ft. | Total dust Grams | Dust per cu. ft. of gas(*a*) Gram | Length of run Min. | Test point |
|---|---|---|---|---|---|---|
| 1 | off | 6.39 | 0.571 | 0.0893 | 11 | |
| 2 | off | 21.28 | 1.625 | 0.0764 | 28 | Left side of scrubber damper facing stack |
| 3 | off | 13.28 | 1.015 | 0.0766 | 27 | |
| 4 | on | 30.08 | 0.272 | 0.0096 | 40 | |
| 5 | on | 38.63 | 0.335 | 0.0087 | 36 | |
| 6 | off | 17.13 | 1.162 | 0.0678 | 19 | |
| 7 | off | 26.06 | 2.203 | 0.0846 | 34 | Right side of scrubber damper facing stack |
| 8 | off | 34.57 | 2.609 | 0.0755 | 43 | |
| 9 | on | 20.63 | 0.122 | 0.0059 | 27 | |
| 10 | on | 23.87 | 0.089 | 0.0037 | 37 | |
| 13 | on | 19.77 | 1.485 | 0.0751 | 20 | In dryer flue just before entering stack (scrubber walled off) |
| 14 | on | 27.87 | 1.989 | 0.0714 | 25 | |

Av. wt. of dust per cu. ft. of gas, scrubber off..... 0.077 g.
Av. wt. of dust per cu. ft. of gas, scrubber on..... 0.007
Av. wt. of dust per cu. ft. of gas, removed by scrubbing..... 0.070

(*a*) Gas at 15.5° C. at 29.92 in mercury pressure.

These results show that 91 per cent of the total dust in the dryer gases is removed by the scrubber.

The amount of dust removed from the gas by the scrubber was also calculated from determinations of the dust in the water entering and leaving scrubber. In order to do this the amount of water delivered to the scrubber was obtained from the number of strokes and size of the pump. Using the volume of gas passing into the scrubber found by the pitot tube observations and the foregoing data, two runs gave 0.0832 and 0.0805 g. of dust removed from a cu. ft. of gas. This is a fair check on the direct determinations, considering the assumptions and possible variables in the second method.

### ODOROUS SUBSTANCES IN DRYER GASES AND EFFICIENCY OF SCRUBBER AS AN ODOR ELIMINATOR

To determine the efficiency of the scrubber as an eliminator of odors, it was necessary first to ascertain the odorous substances present, whose nature would permit quantitative chemical determination. The analysis of the flue gas just mentioned showed car-

[1] Private communication from Mr Brady

[2] These bottles were first used in an investigation of the amount of sulfur dioxide in the air of one of the sections of this city, when a study of nuisance from a number of industrial plants was made. At that time they were found to work without entrainment when 10 cu. ft. of air per minute were washed, although in the present work the rate was only one cu. ft. per minute.

bon monoxide and carbon dioxide, but these substances could not be regarded as important from the odor standpoint.

After a number of attempts to isolate possible constituents, some of the water used for scrubbing in the dust determinations was made acid with phosphoric acid and distilled. The distillate was condensed, the end of the condenser tube dipping into water in the receiving vessel. The distillate had a sharp burnt odor. On titrating with alkali considerable acid was found. The carbon dioxide in the neutralized distillate was determined by evolution. It was found that about 80 per cent of the acidity of this distillate was due to carbon dioxide. The presence of so much of this odorless gas in the distillate

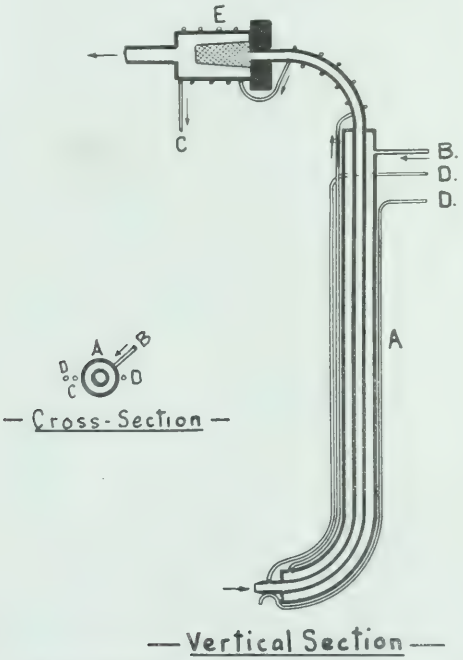



FIG. V—SAMPLING TUBE AND FILTER, SHOWING STEAM JACKET
A—Sampling Tube B—Feed Steam C—Exhaust Steam
D—Pitot Connections to Ellison Gauge E—Wire Gauze Dust Filter

of the volatile acid substances made the determination of the efficiency of the scrubber by this means inadvisable.

Some of the dust scrubber water was then made alkaline with sodium hydrate and distilled in the same manner. The distillate containing the volatile alkaline constituents of the dryer gas had a strong pyridine odor and was alkaline. The number of cc. of $N/10$ acid necessary to neutralize these substances were obtained by titration, using methyl orange. On Nesslerizing, ammonia was also found in the distillate. The amount of volatile alkaline constituents in the dryer gas was selected as a means of ascertaining the performance of the scrubber as an odor eliminator.

Efficiency determinations were carried out by drawing the gas through dilute sulfuric acid, using the dust determining apparatus. In this case a gauze dust filter was placed over the entrance of the sampling tube. An aliquot part of the total volume of the acid solutions from both bottles was taken for distilling. This was made alkaline with sodium hydrate and distilled from a Thompson flask, used for determining acetic acid in white lead. The end of the condenser dipped into water containing standard acid. Methyl orange was used as an indicator in titrating back. All results were expressed in cc. of $N/10$ acid required to neutralize the volatile alkaline constituents in 100 cu. ft. of gas.

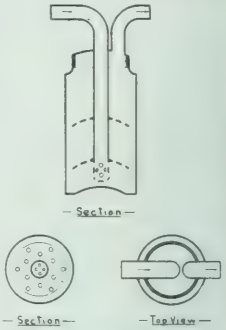



FIG. VI—BAFFLE WASH BOTTLE WITH GROUND JOINT

A test with the scrubber off required 89 cc. $N/10$ acid per 100 cu. ft., and with the scrubber working under the most perfect conditions 26 cc. $N/10$ acid. From this it follows that the scrubber has an efficiency of about 70 per cent in eliminating odorous substances from the dryer gases.

CONCLUSIONS—The scrubber under present conditions of working eliminates practically all the dust in the dryer gases. By excluding the air now leaking into these gases the volume of gas to be scrubbed could probably be much lessened and all the dust removed. Considerable dryer odor now escapes with the scrubber at its utmost capacity. It will be shown

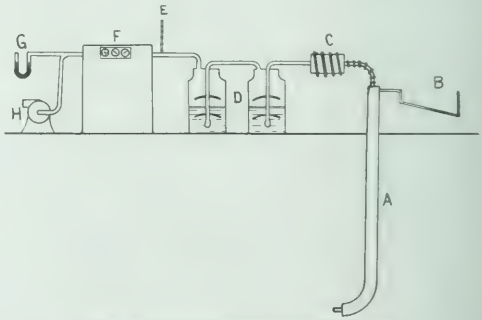



FIG. VII—DUST DETERMINATION APPARATUS
A—Sampling Tube *See Detail* E—Thermometer
B—Ellison Gauge F—Gas Meter, Dry Type
C—Dust Filter *See Detail* G—Pressure Gauge
D—Baffle Wash Bottles *See Detail* H—Centrifugal Fan

below that the odors can be completely removed by water. Decreasing the air leakage, as mentioned, would allow a more efficient scrubbing under the present working conditions. To thoroughly eliminate the dust and odor it would be advisable to increase the efficiency of the scrubber.

### EXPERIMENTS ON THE DEODORIZATION OF DRYER GASES

On passing dryer gas through several bottles of water its odor was practically all removed. In the same way the odor was destroyed by means of a solution of calcium hypochlorite (bleaching powder) containing 1 part of available chlorine in 1000. By leading the gas across *pine tar oil* its characteristic smell was replaced by that of the oil. The latter result suggested that mineral oil of the paraffin oil or light engine oil class might have sufficient solvent effect on the odorous substances to make their use in a scrubber possible. The effect of mineral oil was not investigated because of lack of time.

The action of heat on dryer gas was observed using the same apparatus as for the digester gas. It was in this case necessary to draw the gas through the tube furnace. The results are given below:

EFFECT OF HEAT ON THE ODOR OF DRYER GASES

| Temp. in furnace ° F. | Temp. of gases at point where odor was noted | NATURE OF ODOR |
|---|---|---|
| 40 | 40° F. | Slightly burned |
| 150 | 52 | Sweet, slightly irritating, burned |
| 250 | 60 | |
| 350 | 72 | |
| 450 | 86 | Irritating, acrid, slightly burned |
| 550 | 86 | |
| 650 | 86 | |
| 750 | 84 | |
| 850 | 100 | Very irritating, acrid, burned |
| 950 | 95 | |
| 1050 | 93 | Very irritating but not quite so burned |
| 1150 | 116 | |
| 1250 | 120 | |
| 1350 | 116 | Not quite so irritating or acrid, only slightly burned |
| 1450 | 122 | |
| 1550 | 129 | Only slightly irritating and acrid, no burned odor |
| 1650 | 147 | Less irritating than at 1550° F. |
| 1750 | 154 | Practically no irritating odor |
| 1850 | 163 | No odor of any kind |

No sulfur compounds were present in these gases.

Experiments were made to ascertain if dilution with air, before leaving the stack, could be carried to such a degree that the dryer odor would be unperceptible. Gas and air were passed separately through meters and then mixed in a 4 ft. length of $^1/_2$ in. tube, and the odor noted. The data obtained follows:

| Rate of flow, cu. ft. per min. Dryer gas | Air | Dilution of dryer gas to air | Intensity of dryer gas odor |
|---|---|---|---|
| 0.6 | 12 | 1 : 20 | Very strong |
| 0.2 | 12 | 1 : 60 | Strong |
| 0.031 | 12 | 1 : 400 | Distinct |

The results show that no reasonable amount of dilution with air is effective in causing the dryer gas odor to become negligible.

### ODORS ARISING FROM PERMEATION OF THE REDUCTION WORKS STRUCTURE WITH LIQUIDS, ETC.

Brief mention may be made of the odors resulting from the permeation of the buildings of reduction works with liquids, etc. The wind passing over the plant may in this way take up considerable odor, even when no garbage is present or in process. To eliminate this source of trouble garbage plants should be of the most sanitary construction to permit washing and prevent material lodging in crevices. The cement of concrete floors is readily attacked by the stick liquor and garbage, and wooden floors are sometimes put down. As may be easily understood, these soon become of a very objectionable nature and cannot be well cleaned. A concrete floor with a frequently renewed tar coat or one of asphalt would be a great improvement on the wood.

In conclusion, we wish to acknowledge our indebtedness to Mr. Osborn for his invaluable suggestions, advice and inspiring interest in this investigation. We also wish to thank Mr. Thomas D. Banks, Superintendent of the Garbage Reduction Plant of Columbus, O., for valuable assistance, and Mr. George Wood, Assistant Engineer in the Department of Street Cleaning of this city, for aid in carrying out the experimental work and for the sketches accompanying this paper. To Mr. Charles Crew, of this laboratory, we are grateful for the performance of analytical determinations.

CENTRAL TESTING LABORATORY
CITY OF NEW YORK

## TWO CONVENIENT FORMS OF RECEIVER FOR FRACTIONAL DISTILLATIONS UNDER DIMINISHED PRESSURE

By MARSTON TAYLOR BOGERT

Received June 16, 1915

Having had occasion recently to carry out many fractional distillations of two or three liters of liquid at a time, under reduced pressure, the writer could not find upon the market any form of receiver which would permit the taking of a large number of fractions, of varying volume, without interruption of the distillation. To meet this need, the forms described below were devised and have proven very serviceable. Possibly, other chemists confronted with similar problems, also may find them of use.

APPARATUS I is constructed entirely of glass resistant to the action of chemicals, well tempered, and sufficiently strong to withstand the full atmospheric pressure. Ordinarily, the connections with the end of the condenser (or distilling tube), and with the lower vessel into which the fractions are to be drawn, will be made with perforated rubber stoppers; but, if desired, they can of course be made with ground glass joints.

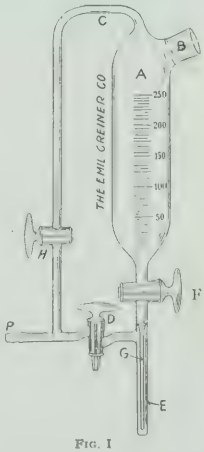



FIG. I

In detail, the apparatus consists of a cylindrical receiving chamber, *A*, graduated in cc. and with a funnel stem through which the distillate collected in *A* may be removed at will by opening the plain cock *F*. On one side of this receiving chamber, near the top, is the opening *B*, for the end of the condenser. From the top of the receiving chamber *A*, the tube *C* passes to the pump *P* and to the outer jacket *E* of the funnel stem. On this tube *C*, there is a plain cock at *H*, and a 3-way cock with offset ports at *D*. By turning this 3-way cock 90°, connection is established by means of a perforation in the stem of the cock, between the

outer air and, through the outer jacket *E*, with the lower receiving vessel. In this way, atmospheric pressure can be restored to the lower vessel without in any way affecting the vacuum throughout the rest of the distilling system. The lower vessel can then be removed, or its contents drawn off, as the case may be. The effect of this arrangement of the 3-way cock, therefore, is that in one position only does it make connection between the pump and the lower receiver; and in one position only, between the latter and the outer air. In all other positions, it merely seals the tube at *D*. The manipulations are as follows:

The end of the condenser (or distilling tube) is inserted through a rubber stopper in *B*, a suitable receiving vessel is attached to the funnel stem, also by means of a rubber stopper, the pump is connected at *P*, and the entire apparatus evacuated, the stopcock *F* being closed, the stopcock *H* open, and the 3-way cock *D* being turned so as to establish connection between the pump and, through the outer jacket of the funnel stem, the lower receiving vessel. When the first fraction has been collected in *A*, and its volume read, it can be run into the lower receiving vessel simply by opening the stopcock *F*. If the first (or any subsequent fraction) proves greater than the graduated capacity of *A*, the latter can be filled and drawn off as many times as may be necessary; or, if preferred, the stopcock *F* may be left open during the taking of the fraction, allowing the distillate to run right on through *A* into the lower receiver.

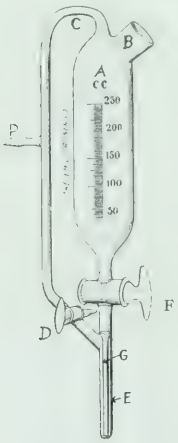


FIG. II

After the first fraction has all been run into the lower receiver, the stopcocks *F* and *H* are closed, and the 3-way cock *D* turned so as to close the connection between the lower receiver and the pump and open that to the outer air. This allows the air to flow into the lower receiver, and the latter can then be removed, emptied and replaced, or a new one attached. Meanwhile, the distillation has not been interrupted in any way nor the vacuum affected, and the distillate is accumulating in *A*.

When the new receiver is connected below, it is first evacuated by turning back the 3-way cock to its original position, after which stopcock *H* can be opened again, and the fraction accumulated in *A* drawn off as before. If the new receiver attached below is large in comparison with the capacity of the pump, and the operator suspects that leaks may be altering the pressure in the distilling system (since the pump is cut off at *H*), he can test this for himself at any moment, without losing any of the evacuation of the lower receiver already gained, by turning the 3-way cock so as to seal the tube at *D*, waiting a moment until the pressure gauge has fallen again to the initial pressure in the distilling system, and then slowly opening the stopcock *H*. Any loss of pressure will then be immediately apparent. In case there have been leaks and the pressure has changed, stopcock *H* is left open until the desired evacuation is restored, after which it is closed and the exhaustion of the lower receiver resumed.

With this apparatus, any number of fractions may be taken, of any desired volume. By using a separatory funnel, or similar vessel, as the lower receiver, the fractions can be drawn off at will without removing it at all.

The writer has found 250 cc. a very convenient size for the receiver. An apparatus of this capacity is about 15 in. high over all, and the diameter of *A* is approximately 2 in., so that it is easily held by an ordinary Liebig condenser clamp.

APPARATUS II is a somewhat simpler form, for use in laboratories which, like that of the writer, happen to be equipped with more than one pump. The 3-way cock *D* may be set as indicated either in Fig. I or Fig. II.

In this type of apparatus, after the removal of the first fraction, the lower receiver is evacuated by connecting the auxiliary pump with the hollow stem of the 3-way cock, after which it is thrown again into the distilling system by turning the 3-way cock back to its original position.

Both forms of the receiver are manufactured by the Emil Greiner Co., 55 Fulton St., New York, N. Y.

COLUMBIA UNIVERSITY, NEW YORK CITY

## A SIMPLE AUTOMATIC-ZERO BURETTE

By A. T. MERTES

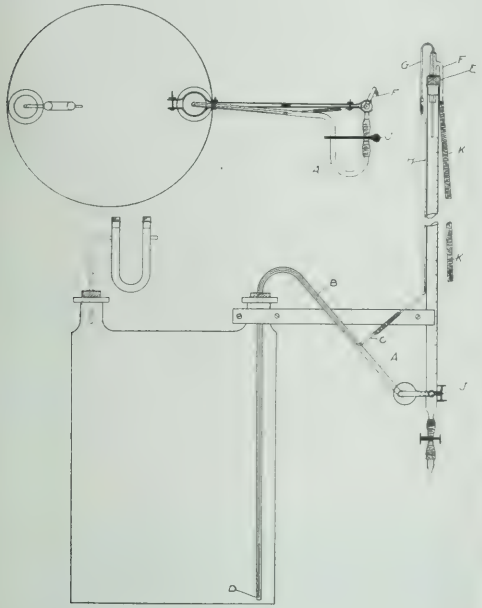
Received May 7, 1915

Most automatic-zero burettes discharge the overflow from the burette into a receptacle separate from the main reservoir, and this excess is either thrown away or is poured back into the main supply. For solutions that have been carefully standardized, this practice is inconvenient and may be a source of error.

The accompanying drawing shows an automatic-zero burette that discharges the overflow back into the main reservoir. It has the advantage that it may be protected from the carbon dioxide of the air, and hence is especially adapted for use with standard acid and alkali solutions.

It consists of a large Woulfe bottle having a burette attached to its neck by a clamp. The burette has a side aperture which connects, by means of rubber tubing, to a goose-neck-shaped glass tubing, *A*, about 5 mm. in bore. This is bent in such manner that the ring of the pinch clamp encircles it and is thus prevented from rotating. Half way between the burette and where the connection tube *A* bends down into the bottle an inner tube, *B*, is fused. This inner tube is about 1 mm. in bore. It connects with a short arm, *C*, forming a T with the main tube. The lower extremity of the inner tube *B* is fused to the outer tube at *D* in such a way that it opens outside this tube. This prevents air bubbles that may be drawn through the inner tube from rising in the main supply tube. The top of the burette is closed by a cork, *E*, through

which is fitted a double tube. The outer tube is connected by a short T tube, *F*, bent downward and fitted with a rubber tube by means of which the operator sucks up solution to fill the burette. The inner or



overflow tube *G* is fused into the outer and bends downward, connecting by means of a short rubber tube, with a small glass tube, *H*. This tube extends down the back of the burette and joins, by means of another short rubber tube, with the tube *C*. The overflow tube *G* may be adjusted by sliding up or down in the cork *E* so that the lower end of it is on the same level as the zero mark on the burette. It is seen that when the liquid above the zero mark on the burette is allowed to siphon back it will drain off all the liquid above the zero mark.

In order to fill the burette, the operator opens the pinch-cock *J* and sucks through the rubber tube *K* till the liquid is above the zero mark on the burette. He then allows the excess to automatically siphon back through the overflow tube into the main supply.

Instead of filling the burette by suction, a rubber bulb may be attached to the bottle so that the burette can be filled by air pressure. For small supply bottles this method is excellent but for larger ones it is not so satisfactory.

6358 Ellis Avenue, Chicago, Illinois

## A KJELDAHL DISTILLATION APPARATUS

By J M Pickel

Received March 6, 1915

Mr. Holmes describes what is evidently an excellent form of Kjeldahl distillation apparatus.[1] We have been using for eight or ten years in the laboratory of the North Carolina Department of Agriculture a distillation apparatus of the writer's designing, which would seem to be simpler, more flexible and less costly than that of Mr. Holmes'. This apparatus has the following features, some of which are, so far as known to the writer, distinctive:

1—The connecting bulbs and condensing tubes are in one piece, thus eliminating annoying rubber connections. (In the case of a copper still, the whole thing is in one piece.)

2—The condensing tubes are not clamped, screwed or attached, in any way, to other parts of the apparatus, and not enclosed within any other part of the apparatus. (To be sure, during distillation, there is connection with flask and receiver.)

3—In consequence of items 1 and 2, any condenser can, without interfering with any other condenser, be instantly removed and another dropped into its place; any condenser can, therefore, without disturbing its neighbors, be repaired, or flushed out with water

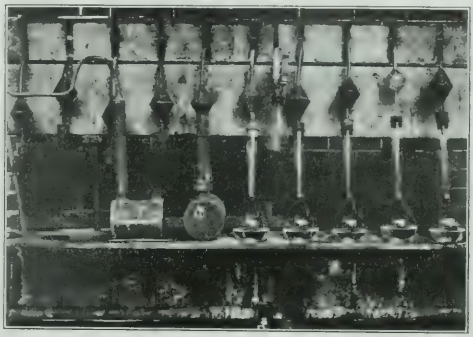


Fig. I Back View of Kjeldahl Distilling Apparatus

under a tap, or air forced into it under water (with a bicycle pump, for example), this latter operation disclosing by air bubbles even the tiniest leak (all of our condensers are thus tested when first put into commission and at suitable intervals thereafter).

4—The condensers adjust themselves automatically to distilling flasks of different lengths.

5—In case one cares to set or hang the apparatus against a wall, thus throwing distilling flasks and receivers on one and the same side, the condensers are easily adjusted to that arrangement; but the receivers are placed *above*, not *below*, the distilling flasks.

6—The distilling flasks, their support and heaters (Bunsen burners) are suspended over a trough.

7—In consequence of arrangement 5 and 6, if, during distillation, a distilling flask breaks, as not infrequently happens, the contents of it drop, not on the table, nor on or into a receiver, but into the trough which can be easily flushed out with water.

8—Regurgitation of liquid from the receiver back into the distilling flask is precluded.

In Fig. II, upper part, are the receivers (flat bottom

[1] This Journal, **6** (1914), 1010

Erlenmeyer flasks of 250 and 300° cc. capacity), connected up with the condensers. The stopper of each receiver carries two bead tubes, in addition to the glass tube that connects, by means of rubber tube, with the condenser. This glass tube and the rubber tube could be dispensed with—the rubber stopper in that case being slipped over the end of the condenser. The condenser, or its glass extension, does not touch the

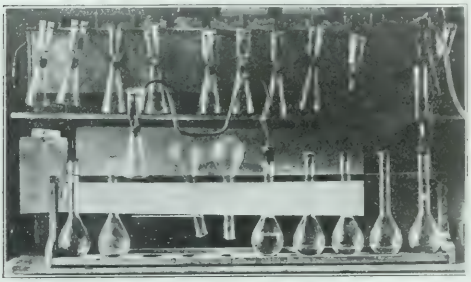


FIG. II—FRONT VIEW OF KJELDAHL DISTILLING APPARATUS

liquid in the receiver. To begin the distillation, introduce the standard acid and indicator into the receiver, but no water. Connect up with the condenser, then fill the interstices of the beads with distilled water.

In lower part of Fig. II are shown:

(*a*) A never-gets-out-of-order carrier, or support, for Kjeldahl flasks.

(*b*) A device (see the flask at the extreme right) which, by mere pressure on a pinchcock, drops into the flask (simultaneously washing its neck) the requisite quantity of water (about 100 to 125 cc.) to dilute the digestate.

(*c*) A distillation flask, marked 10, connected up with condensing tube and receiver. The condensing tube rises from the connecting bulb, passes through a slot (see Fig. I), over the edge of the water tank, into the water, along under the water and rises over the front edge of the tank on which it rests; the only other point of support to the condensing tube is the stopper in the distilling flask. In case one desires to bring the receiver on the same side with the distilling flasks—the condensing tube, after dipping three or four inches into the water, bends back through a slot over the same side of the tank (see the fifth flask from the right in Fig. I, thus connected up with its receiver).

DIMENSIONS OF THE CONDENSING TUBE AND CONNECTING BULB—The bulb (copper or block-tin), greatest diameter 6 or 7 cm., height 8 to 10 cm.; soldered to the lower end of bulb so as to give good drainage back into the flask, is a tube (preferably block-tin) about 6 mm. (1/4 inch) inside diameter, length 7 to 8 cm.; projecting 2 to 3 cm. into the top of the bulb, is the condensing tube (block-tin), diameter inside about 6 mm. length from bulb to top of first bend, 10 to 12 cm. top of first bend to middle of second bend about 20 cm., thence to middle of third bend about 14 cm., thence to middle of fourth bend about 18 cm., thence to end about 6 to 7 cm.; all of these measurements, except those of the bulb, of the tube below the bulb and of the tube above the bulb to the first bend, can, without detriment, be diminished by about half, *provided* that, in order to use interchangeably flasks of different lengths, there must be sufficient length of tube between the first and second bends to prevent lifting too much of the tube out of the water in using flasks with extra long necks. With plenty of cooling water, a block-tin tube 1/4 inch inside diameter and 8 or 10 inches (20 to 25 cm.) under water affords ample condensing surface.

The cooling tank has the following measurements: length (for twelve condensers), 153 cm.; depth, 20 cm.; width at top 26.5 cm., at bottom 21 cm. In case receivers and distilling flasks are on the same side, the tank need be only 4 or 5 cm. wide.

But after the distillation is over, these condensers cannot be easily steamed out? If the steaming out is intended to clean out traces of ammonia, it is entirely superfluous in the case of these condensers—there is no ammonia to clean out; if it is intended to clean out any fixed alkali, that is something steam cannot do; that is a function of water; and these condensers can easily be carried to a tap, water run in at the receiver end and out through the bulb end. However, if one insists on steaming out, each of these condensers can easily and cheaply be furnished with its individual tank, each little tank with a stoppered

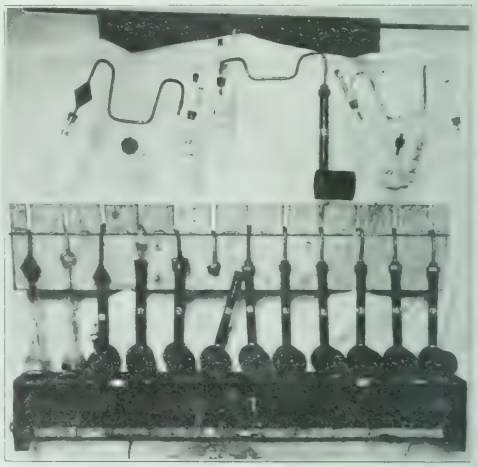


FIG. III MODIFIED APPARATUS

hole in the bottom, through which the water can be drained into a trough running underneath and supporting all of the individual tanks. The writer has used experimentally and successfully for several years a similar little tank and condenser, interchangeably with the other condensers of this apparatus.

In Fig. I is shown at 6 and 7 an end and a side view of two of a set of twelve copper Kjeldahl stills. The parts are: a cylinder 13 cm. long and 10 cm. in diameter; on one end a tubulus; at the other end, and pro-

jecting into it, 2 or 3 cm., a tube about 2.9 cm. in diameter (inside) and 25 cm. long; projecting into the end of this tube is the connecting bulb, and into the connecting bulb the block-tin condensing tube. All parts are soldered together with ordinary tin solder, still and condensing tube forming one continuous piece. The connecting bulb, however, may be dispensed with, as it is of not much use. These stills are as easily charged, discharged and cleansed as a Kjeldahl distilling flask; these operations are performed, of course, through the tubulus. The tubulus may be stoppered with a cork; but a rubber stopper is preferred—either inserted or clamped on. The clamped-on stopper shown on still 6 was used two years, and could doubtless be used several years longer. One of the advantages of these stills is that they practically eliminate the trouble that stoppers cause in the case of Kjeldahl distilling flasks; their chief drawback is the time (about 15 minutes to a set of ten) consumed in transferring the digestage. Only the lower part of these stills is corroded; new bottoms and ends are then soldered on. The writer designed and used a still of this kind six or eight years ago. Five or so years ago he put into use a set of twelve. They were used with entire satisfaction for two years, undergoing repairs several times in the meanwhile. The use of them was discontinued, because they were thought to be no longer economical in view of the cheapness and durability of Jena glass, and in view of the time wasted in transferring.

Fig. III shows another method of connecting these copper stills with the condensing tube, namely, by means of an ordinary pipe coupling with rubber washer between. Despite the fact that this method renders the tubulus unnecessary, it was abandoned in favor of the tubulus. At 22 is shown a disc (copper or block-tin) that is used in some of our connecting bulbs. These discs are slightly less in diameter than the greatest inside diameter of the bulbs; are laid in loose, not soldered; they should have numerous notches, about 0.5 mm. deep, around the edge. The steam impinges against this disc, passes around it and out into the condensing tube.

Many thousands of nitrogen determinations have been made with this apparatus by the writer and by others (in the case of the copper stills, by the writer only). But you cannot see what is going on in the copper stills? You do not need to. But if there is frothing? There will be no frothing, except as the result of bad management; and bad management ought not to occur oftener than once or twice per thousand determinations. Moreover, when frothing does occur, it will manifest itself at the receiver end of the condenser, and the determination is lost. But the stills sometimes get dry and melt apart? Yes, through gross carelessness, once in perhaps, a thousand cases, for there is, to start with, about 250 to 300 cc. of liquid in the still; the distillation is stopped when about 100 cc. of distillate has accumulated in the receiver.

LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE
RALEIGH, N. C

# ADDRESSES

## CHEMICAL PATENTS—I

By SEABURY C. MASTICK[1]

Received May 14, 1915

The subject of chemical patents and of patents for processes relating to industrial chemistry is one of the oldest, if not the oldest, in the realm of patents. As early as 1467 a patent was granted in Berne for the manufacture and sale of paper and in 1507 the Council of Ten in Venice granted an exclusive privilege for twenty years for the introduction of a secret process of mirror-making.

During the first ten years at the beginning of the patent policy in England (1561–70) twelve of the eighteen patents granted were for various chemical products and processes. The chemical patents related to such subjects as soap, saltpeter, alum, sulfur, oil, salt, glass, and cloth- and leather-dressing. In the course of the next decade three of the ten patents granted related to chemistry, *viz.*: those for earthenware, glass and sulfur.

The marked increase in the study and development of the arts relating to chemistry in the United States during the past decade and more has made it imperative for all having to do with the subject to give careful attention to patents, to the ascertaining of what is patentable, how to properly protect inventive ideas and how to enforce the protection so given, as well as how to avoid trespassing upon the rights of those holding patents with which the thing you are considering developing may conflict.

The importance and development of chemistry in the arts in the United States is shown by the following comparative figures relating exclusively to the manufacture of chemicals without reference to allied arts such as fertilizers, petroleum products, rubber manufacture, etc., all of which involve chemical processes to a greater or less degree.

| | 1899 | 1909 |
|---|---|---|
| CAPITAL INVESTED | $89,069,000 | $155,144,000 |
| MANUFACTURED PRODUCT | 62,637,000 | 117,689,000 |
| SALARIES AND WAGES PAID | 12,316,000 | 20,222,000 |
| | 1901 | 1911 |
| EXPORTS | $14,866,035 | $ 23,077,414 |

Such figures and such growth as this in a decade in an art in which invention has played a conspicuous part indicates the necessity the chemist is under of having some knowledge of patents.

It is the purpose of these lectures to give those who have adopted the science of chemistry as their profession some guiding principles which will enable them to form an intelligent opinion concerning such questions of patentable invention, rights of inventors, infringement of patents and related subjects as may come to them for consideration.

As these lectures are primarily addressed to chemists, the illustrations and applications of the patent law have, as far as possible, been drawn from patents and cases relating to chemical compositions of matter and chemical processes, as it is thought that concrete examples, pointing out the principles involved, will not only prove more interesting but more instructive than a mere statement of abstract principles. Furthermore, in elaborating this latter idea, a single series of important cases, those relating to the industrial development of the production of aluminum, has been chosen for study in connection with the more detailed examination of certain phases of the subject: in this connection the basic patent of the late Charles M. Hall for the electrolytic production of aluminum has been followed from the time of the filing of the application in the Patent Office

[1] Special lecturer on Chemical Patents, Department of Chemical Engineering, Columbia University, 1915.

through the Courts to its final adjudication and to the results flowing therefrom.

The subject of the lectures[1] will be discussed under the following heads:

I—Theory and statement of the law relating to patents generally and to patents for compositions of matter and chemical processes specifically.

II—The application for and prosecution of applications for United States Letters Patent.

III—Contractual rights relating to Letters Patent.

1—Assignments.

2—Licenses, express and implied.

3—Employer and employee.

IV—Actions for Infringement.

1—The case in the Lower Court.

2—The case on appeal

## I THEORY AND STATEMENT OF THE LAW RELATING TO PATENTS GENERALLY AND TO PATENTS FOR COMPOSITIONS OF MATTER AND CHEMICAL PROCESSES SPECIFICALLY

The historical development of the theory of patent law begins with and grows out of the history of Monopolies.

A monopoly, in its strict sense, is an exclusive right, granted by the sovereign or the State to an individual or to a few persons, of something which was before of common right. Blackstone defines a monopoly as "a license or privilege allowed by the King for the sole buying and selling, making, working, or using of anything whatsoever, whereby the subject in general is restrained from that liberty of manufacturing or trading which he had before."

In all the definitions of true monopolies there are embraced two leading principles: (*a*) an exclusive right or privilege on the one side, and (*b*) on the other a restriction or restraint which operates to prevent the exercise of a right or liberty which was open to the public before the monopoly was secured.

It is thus seen that a patent for a new and useful invention, never known or used before, is not a true monopoly patent because it does not restrict the exercise of a right which was open to the public before the patent was issued.

It is the failure to realize this difference between a true monopoly and a patent for a new and useful invention which has caused so much confusion with legislators and others in discussing and sometimes condemning patents for inventions.

This distinction was recognized as early as the time of Queen Elizabeth and was put into statute form in the famous Statute of Monopolies passed in the 21st year of King James I, A. D. 1623–1624. This statute is the fountain head of our law relating to patents for inventions and especially excepted from the penalties of the act "letters Patent and grants of privilege..... of the sole working or making of any manner of new manufactures.....to the first and true inventor or inventors of such manufactures, which others at the time of making such letters patent and grants did not use."

The United States Constitution recognized the rights of such inventors and Congress was given the power in Article I, Section 8, "to promote the progress of science and useful arts, by securing for limited times to.....inventors the exclusive right to their respective.....discoveries." In accordance with this power Congress has, from time to time, enacted certain statutes. The principal enactment now in force is Section 4886 of the Revised Statutes which reads as follows:

"Any person who has invented or discovered any new and useful art, machine, manufacture, or composition of matter, or any new and useful improvements thereof, not known or used by others in this country, before his invention or discovery thereof, and not patented or described in any printed publication in this or any foreign country, before his invention or discovery thereof, or more than two years prior to his application, and not in public use or on sale in this country for more than two years prior to his application, unless the same is proved to have been abandoned, may, upon payment of the fees required by law, and other due proceeding had, obtain a patent therefor."

Section 4886 thus provides that patents may be granted for four classes of things, *i. e.*, arts, machines, manufactures, and compositions of matter, and that to be a proper subject of a patent they must each be able to stand the tests of invention, novelty and utility.

Of these four classes of things we are more particularly concerned with "arts" and "compositions of matter." "Processes" come within the definition of "arts" and to be proper subjects of patents should be (*a*) "operations which consist partly or wholly in the employment of heat, light, electricity, magnetism, chemistry, pneumatics, hydraulics, or some other non-mechanical science" or (*b*) "operations which consist entirely of mechanical transactions, but which may be performed by hand or by any of several different mechanisms or machines." "Composition of matter" covers all compositions of two or more substances. "It includes, therefore, all composite articles, whether they be results of chemical union, or of mechanical mixture, or whether they be gases, fluids, powders or solids."

"Patents are granted for things *invented*, and not for things otherwise produced, even when the production requires ability of a high order. Novelty and utility must indeed characterize the subject of a patent, but they alone are not enough to make anything patentable, for the statute provides that things to be patented must be *invented* things, as well as new and useful things. The Courts have therefore declared that not all improvement is invention, and entitled to protection as such, but that to be thus entitled, a thing must be the product of some exercise of the inventive faculties."

### INVENTION

"Invention" may be defined as the result of the exercise of something more than the expected skill of the average intelligent workman in the particular art to which the invention belongs.

While the Courts have never been able to give a concise definition by the application of which things *invented* may be clearly distinguished from things produced merely by the exercise of such expected skill, they have, from time to time, defined what comes within "expected skill" and thus, by a process of exclusion, we can arrive at a fairly definite idea of "invention."

Some of the definitions of "expected skill" are as follows:

(*a*)—It is but expected skill to substitute superior for inferior materials, in making one or more or all of the parts of a machine or manufacture

However, it may or may not be more than mere expected skill to substitute one material for another, as an agent in performing a process, or as an ingredient of a composition of matter. The question in such case, is to be decided by some other rule than this of "mere substitution of materials."

If the substitution of materials developed new properties and uses of the article made it may amount to more than mere expected skill, as in the substitution of vulcanized rubber for guttapercha in the manufacture of plates for false teeth,[1] where the Court found that the new product differed in kind from the art, having new uses and properties. Or in the substitution of fusel oil for alcohol as a solvent of camphor in conjunction with nitrocellulose in the manufacture of pyroxyline[2] thereby giving a better result than the *menstrua* previously used, and at less expense. In this latter case the Court said: "The fact that alcohol had been used for many years as a menstruum, when a cheaper solvent could have been used, and would have been,

[1] In preparing these lectures I have made free use of Walker on Patents (4th Edition) as well as of the publications of the U. S. Patent Office, especially of Principal Examiner A. M. Lewer's paper on "Composition of Matter."

[1] Smith *vs.* Goodyear Dental Vulcanite Co., 93, U. S. 486,496

[2] Celluloid Co. *vs.* Amer. Zylonite Co., 35, F. R. 301.

if the availability of fusel oil as a substitute had been obvious to those skilled in the art, is inconsistent with the suggestion that nothing but the mere exercise of judgment was involved in selecting it as a substitute." Or in the substitution of hydrate of lime for powdered marble in a mixture with glue to form a material to restrain the too-rapid setting of plaster of Paris,[1] the difference between the results accomplished being that between a partial and a complete success.

(*b*)—It is but expected skill to change the size or degree of a thing, or of any feature or function of a machine or manufacture.

For example, it has been held that grinding up flakes of glue into finely comminuted form was the exercise of mere expected skill,[2] the Court saying:

"Two principal suggestions are made, to show that the comminuted glue may be patentable as a new manufacture:

"1—That the mass or particles are more soluble when wanted for practical use than the glue in flakes, as purchased in market, before the flakes are subjected to the patented process

"2—That the patented product may be more conveniently put up into small packages for domestic use and for the retail trade than the glue in flakes, and with less danger of loss.

"Grant all that; still the suggestions are not sufficient to show that comminuted glue is patentable as a new manufacture, as the properties of the glue in flakes are not improved, and for the reason that the change effected by the described process does not involve the exercise of any invention or discovery. Refined sugar, when pulverized, is more readily soluble in water than when in the lump or loaf; and it is matter of common knowledge that small particles of any soluble substance are more readily dissolved in liquids than large lumps or loaves of the same substance. Like many other substances, glue, when comminuted into small particles, whether the operation is effected by breaking, pounding, rasping, grating or grinding, is more readily soluble in water than when the attempt is made to dissolve it in flakes or other large bodies. Common experience is sufficient to verify that proposition, and the remark applies with equal truth and potency to many other articles, such as salts, refined sugar, gypsum, alum, camphor, gums of various kinds and to many other substances in common use. Small particles present, comparatively, a larger portion of surface to the liquid into which they are put than more bulky ones, in consequence of which the substance, if permeable to liquids and soluble, will be more readily dissolved. Beyond doubt, comminuted glue is more readily soluble than glue in flakes; but the admission affords no support to the theory that comminuted glue is patentable, as the fact that small particles of soluble substances are more readily dissolved in liquids than larger ones is matter of common knowledge, and has been known for ages, whereof the memory of man runneth not to the contrary.

"Mere additional convenience in packing the comminuted article, as compared with the flake glue, proves nothing to support the theory of the complainants, as the fact has been matter of common knowledge for centuries."

On the other hand, it may or may not require more than expected skill to change the degree of heat, or other agent, used in a process, or to change the amount of an ingredient used in a composition of matter. For example, it has been held that it was more than mere expected skill to produce a paper board formed from printed newspaper, ground to a pulp and having the permanent particles of the printers' ink minutely subdivided and uniformly distributed throughout the body of the board, the product differing from antecedent paper board in that it contained oils, commonly found in ink, which give to the board a toughness and elasticity theretofore unknown and where in the prior art of making paper board from newspapers the effort was made to separate the carbon of the ink from the oil—the oil being taken out by alkali and bleaching, leaving the carbon for coloring matter,[1] the Court saying:

"It is manifest that in practical operation, under the process mentioned in the patent in suit, the oils cannot be entirely retained; a small portion will be lost in the boiling and heating process calculated to minutely subdivide and distribute the oils throughout the fibers. It is manifest, also, that in the process employed in the previous art, a small portion of the oils was not eliminated; no amount of boiling or bleaching could completely purify the pulp. But in the process under the patent, the purpose is to lose as little as possible; in the previous art, the purpose was to eliminate as much as possible. The processes are in purpose, and in effect, so far as is practicable, the opposites of each other. And though the purpose of each partially fails, the results are so widely different that both the process and the paper board are commercially distinct."

A classic exception to the rule that change in size is but the result of the exercise of expected skill is found in the case of the Edison incandescent light patent[2] where the reduction of the diameter of the filament from $^1/_{32}$ of an inch to $^1/_{64}$ increased the resistance fourfold and reduced the radiating surface twofold, thus increasing eightfold the ratio of resistance to radiating surface and permitting the use of electricity of comparatively high electromotive force and comparatively low current, instead of contrariwise.

(*c*)—It is but expected skill to omit one or more of the parts of a machine or manufacture with a corresponding omission of function, unless that omission causes a new mode of operation of the parts retained.

For example, where the patent was for the process of crushing oleaginous seeds and extracting the oil therefrom, consisting of the following successive steps, *viz.*: the crushing of the seeds under pressure, the moistening of the seeds by direct subjection to steam, and finally the expression of the oil from the seed by suitable pressure, and differed from the old art only in that the first step, the crushing of the seeds under pressure, had been formerly accomplished by means of rollers and muller stones, whereas the inventor dispensed with the mechanical operation performed by the muller stones in the crushing step and employed the rollers alone, having found that the tearing and pulverizing action of the muller stones on the seeds was injurious. The Court held[3] that the omission of the muller stones was more than the exercise of mere expected skill because after such omission more oil was produced and a better quality of oil cake, whereby great improvement was effected in the result.

Again where the patent claimed a process of working bituminous rock by softening it by application of hot water or steam and then immediately compressing the softened material on the road or pavement, under heated rollers without the expulsion of moisture, and the prior art had required rigid exclusion or evaporation of the moisture, the Court held[4] that such process was the result of the exercise of more than mere expected skill because it produced a better result than before, made the material immediately available and greatly simplified the preparation of the same. It was held "that although the idea of the application of hot water or steam to a substance for the purpose of rendering it soft and pliable was undoubtedly old, yet that the idea of such application to bituminous rock in the course of preparation for roofing or paving purposes involved an element of invention from the fact that it was opposed to the generally accepted theory of the treatment of that substance, and the universal belief of those engaged in using the same, which was that the material must be kept waterproof, and must be heated only by dry heat, to the exclusion of moisture, and that the presence of water or steam tended to its disintegration and destruction. Even though it

[1] King *vs.* Anderson, 90, F. R. 500.

[2] Milligan & Higgins Glue Co *vs.* Upton, 97, U. S. 3.

[1] National Newsboard Co. *vs.* Elkhart Egg Case Co., 123, F. R. 431.

[2] Edison Co. *vs.* U. S. Electric Lighting Co., 52, F. R. 300.

[3] Lawther *vs.* Hamilton, 124, U. S. 1.

[4] Pacific Contracting Co. *vs.* Bingham, 62, F. R. 281.

was known that bituminous rock could be softened by steam and that such treatment was not injurious provided the moisture so introduced was expelled before compressing and using the material, nevertheless the patentee had exercised more than mere expected skill in omitting the drying step which had hitherto been considered essential but which the patentee had proved to be useless. The discovery was not that bituminous rock could be softened by steam but that the presence of the moisture in the substance thus treated did not tend to destroy and disintegrate the finished product—the pavement.

(*d*)—It is but expected skill to change a process, machine, manufacture or composition of matter, by substituting an equivalent for either of its parts, unless the new part not only performs the function of the part for which it was substituted, but also performs another function, by another mode of operation, or develops new uses and properties of the article formed.

An equivalent has been defined as a thing which works in substantially the same way to accomplish the same result or perform the same function as the thing for which it is substituted.

As an example of what has been held[1] to be an equivalent and the substitution of which is therefore the result of the exercise of mere expected skill, attention is called to the case where it had been disclosed in the art of forming plates of secondary electric batteries that peroxide of lead ($PbO_2$) was the best oxide of lead to use in the preparation of the plates and the patent claimed the use of red lead or minium ($Pb_3O_4$). The Court held that "after the invention of a support primarily coated with mechanically applied oxide of lead (such as peroxide of lead), merely coating the plate with the commonest, cheapest and best known form of lead oxide did not require the exercise of the inventive faculties..... It would seem that the use of red lead would at once occur to anyone who had even a superficial knowledge of the art." It was shown also that the results obtained by using the red lead were not as good as those when the peroxide was used.

Again where the use of water as a fluid tamping in deep oil wells of small caliber was known, the intended effect of which was to give a lateral direction to the force of the explosion, it was held[2] to be but the exercise of mere expected skill to substitute benzine for the water, the distinctive feature being the use of a fluid possessing the fluid property of water and not the use of any particular fluid.

And again where a flour paste comprising flour, sodium chloride, alum and bichloride of mercury was known, it was held[3] to be but the exercise of expected skill to substitute chloride of zinc for the sodium chloride. The function of the sodium chloride was to increase the solubility and assist in the diffusion through the mass of the bichloride of mercury. The Court held that while sodium chloride and zinc chloride were not equivalents under all possible conditions, nevertheless for the purposes of manufacturing flour paste they practically produced the same results and any chemist would know that the one could be used in this process in place of the other with like results.

(*e*)—It is but expected skill to use an old process, machine, manufacture, or composition of matter for a new and analogous purpose.

For example, in the manufacture of hydrogen peroxide by the addition of a solution of barium peroxide to a suitable diluted acid, such as sulfuric, where the reaction had been facilitated by stirring by hand, it was held[4] to be mere expected skill to adapt a mechanically driven screw having helicoidal blades to perform the stirring. The Court said that the patentee had not "discovered hydrogen peroxide, or the method of adding barium, mixed with water, from time to time, to the diluted acid, or the necessity for stirring or agitating the liquid. Neither did he invent the obliquely bladed screw..... All this was old and well known..... Does it constitute invention to stir, by a well-known and simple mechanical device what had before been stirred by hand? The patentee desired to manufacture in large quantities what had before been produced chiefly in the laboratory. He knew how hydrogen peroxide had been made, every step in the formula was familiar. A mixture that needed stirring, and a vessel provided with a revolving stirrer, were ready at his hand. He put the former into the latter. This was all. The object of agitating the liquid, while making hydrogen peroxide, is to keep the barium, which is three times as heavy as water, suspended in the acid, so that its particles may come in contact with the particles of acid. Whether they come in contact while going round, rising, settling or remaining stationary, can make no difference..... The patentee contends that by the method set out in the patent, a movement is given to the acid which had never before been imparted to it in the manufacture of hydrogen peroxide because the liquid is thrown out towards the circumference of the vessel at the bottom, rises at the sides, returns to the center, and then descends, to be again thrown out at the bottom, while at the same time it is carried round and round. This, being reduced to a simpler language, means that the machine will stir large quantities of the liquid more thoroughly than the hand-worked paddles. The pretense that the patentee had discovered some occult and wonder-working power, in the motion of a screw revolving in the bottom of a tub, is not sustained by the proof. Whether the contents of the tub be oxygenated water, or soap, or lye, or tartaric acid, the action will be the same."

In the case of a patent for recovering precious metals from their solution by the cyanide process wherein the alleged new feature was the use of zinc dust to precipitate the gold and silver from the solution, it was shown to have been old to use zinc dust in a similar process for the precipitation of copper. The Court held[1] that the patented process was nothing more than the application of the old process to analogous matter, producing a result substantially similar in its nature, and was therefore entirely lacking in invention.

On the other hand, where the patent was for a process of tanning leather by subjecting the hides to the action of a bath prepared from a metallic salt, such as bichromate of potash, and then to the action of a bath capable of evolving sulfurous acid, such as a solution of sulfite of soda, in presence of another acid, such as hydrochloric acid, and a similar process had before been used for dyeing fabrics and wools, the Court held[2] that "in dyeing and printing on fabrics and in the treatment of wools, the end finally accomplished is not at all analogous to that of manufacturing leather. The same ingredients may be used to reach the one result as the other, but they are not used for a like purpose. They do not affect the different materials in the same way, and the product evolved in the one case is wholly unlike the change effected in the other. The fact that hides are substituted for fabrics or wool, and that the thing produced is leather, and not dyed fabric or treated wool, distinguishes the two processes. The arts of dyeing and of leather-making are wholly unallied..... To the art of leather-making the patentee supplied a method which was new and highly useful, and which was far from being obvious."

And in the case of a patent for a metallurgical process involving the use of a discrete body of conductive but resistant material rendered incandescent by the passage of an electric current and mixed with the material to be treated, where a similar process had before been used for carbonizing arcs of paper the Court held[3] that the latter process did not "suggest a process for re-

[1] Bauch Electric Co. v. Electrical Accumulator Co., 1 F. R. 18; Robert v. Roter, F. C. No. 11,912.
[2] Woodward vs. Morrison, F. C. No. 18,008.
[3] Marchand v. Emken, 132 U. S. 195.
[4] De Lamar v. De Lamar Mining Co., 97 F. R. 858, 117 F. R. 240.
[1] Tannage Patent Co. vs. Zahn, 70, F. R. 1003.
[2] Electric Smelting and Aluminum Co. v. Carborundum Co., 102, F. R. 618.

ducing ores and highly refractory compounds on any considerable scale, or, indeed, the generation or application of heat for metallurgical purposes at all. The two patents do not relate to the same art nor has the doctrine of analogous use any application as between the processes described therein."

(*f*)—It is but expected skill to change the form or proportions of a machine or manufacture, unless some new mode of operation or function results.

But it is more than the exercise of mere expected skill to change the proportions of the ingredients of a chemical combination, or other composition of matter, where a new product having new properties results.

For example, Charles Goodyear invented soft vulcanized rubber, consisting of crude India rubber and sulfur in the proportion of one part of sulfur to five parts of rubber; and afterward Nelson Goodyear invented hard vulcanized rubber, consisting of equal, or substantially equal, proportions of sulfur and rubber. Here the change in proportion resulted in two entirely distinct articles, having entirely distinct modes of operation and functions and the latter was held[1] to be patentable.

And in the flour paste case previously referred to, it was held to be more than mere expected skill to add bichloride of mercury to flour paste in such small quantities in proportion to the flour that its poisonous and corrosive qualities are neutralized by the flour and the paste thus rendered innocuous, where previously a flour paste had been made in which a larger proportion of corrosive sublimate was used for the purpose of making the paste poisonous and corrosive.

The following definitions do not apply so strictly to chemistry but are added for the sake of rendering the general statement of the rule more complete.

(*g*)—It is but expected skill to produce an article which differs from some older thing only in excellence of workmanship.

For example, where the patent was for a corded fabric in which the cords are elastic and held between the upper and ununder weft threads, and separated from each other by the interweaving of the upper and under weft threads with the warp threads in the spaces between the cords, and only there, and the evidence showed that it differed from the prior art only in greater tightness of weaving, a firmer grasping of the elastic cords by the weft threads half round, above and below, and greater beauty and value of the fabric, the Court held:[2]

"A patentable invention is a mental result. It must be new and shown to be of practical utility. Everything within the domain of the conception belongs to him who conceived it. The machine, process or product is but its material reflex and embodiment. A new idea may be ingrafted upon an old invention, be distinct from the conception which preceded it, and be an improvement. In such case it is patentable. The prior patentee cannot use it without the consent of the improver, and the latter cannot use the original invention without the consent of the former. But a mere carrying forward or new or more extended application of the original thought, a change only in form, proportions or degree, the substitution of equivalents, doing substantially the same thing in the same way by substantially the same means with better results, is not such invention as will sustain a patent. These rules apply alike, whether what preceded was covered by a patent or rested only in public knowledge and use. In neither case can there be an invasion of such domain and an appropriation of anything found there. In one case everything belongs to the prior patentee; in the other to the public at large

"The question before us must be considered in the light of these rules. All the particulars claimed by the complainant, if conceded to be his, are within the category of degree. Many textile fabrics, especially those of cotton and wool, are constantly improved. Sometimes the improvement is due to the skill of the workmen, and sometimes to the perfection of the machinery employed. The results are higher finish, greater beauty of surface, and increased commercial value. A patent for the better fabric in such cases would, we apprehend, be unprecedented. The patent in the present case rests upon no other or better foundation."

(*h*)—It is but expected skill to so enlarge and strengthen a machine that it will operate on larger materials than before.

For example, where circular saws varying in size from ten to thirty inches in diameter had been used for sawing shingles from short blocks of timber and for sawing lath and blinds for windows, the Court held[1] that it was but the exercise of expected skill to produce a circular saw five feet in diameter (the other parts corresponding) for the sawing of logs, saying that such enlargement "is done every day by the ordinary mechanic in making a working machine from the patent model."

And where the prior art showed the use of rotary kilns 60 feet in length and 5 feet in diameter for the purpose of burning a mixture of cement rock and limestone in the manufacture of Portland cement it is but the exercise of the expected skill of one ordinarily skilled in the art[2] to make the kiln upwards of 100 feet in length and more than 12 times the internal diameter thereof, the only real difference between the two being that the larger kiln will produce more product than the small one.

(*i*)—It is but expected skill to duplicate one or more of the parts of a machine or manufacture unless the duplication causes a new mode of operation, or produces a new unitary result.

For example, where the patent was for the combination of a series of evaporating pans for evaporating sugar solutions, to form a multiple-effect evaporating apparatus, a series of surface heaters being also arranged in connection with the pans and operating to use a portion of the vapor from the several pans for heating either a single liquid passed in succession through the several heaters, in the direction from the coolest to the hottest, or for heating different liquids in the several heaters, respectively, and the prior art disclosed the placing of several "single-effect" apparatus side by side, united in such manner that the liquor and vapor, after passing through the first would pass into the second, and so on to and through as many such apparatus as were united, receiving an additional effect from each, it was held[3] that it was but the exercise of expected skill to do what the patent claimed. The fact that the patent in addition disclosed the use of a pump to accelerate the flow of liquor, did not require invention because "any mechanic directed to increase the flow would presumably have added the pump. It is the most common appliance for the purpose."

On the other hand, where it had been customary to place a single turbine, upon a vertical shaft, in such a way that the pressure of the water was partly exerted endwise of the shaft, and that pressure, in addition to the weight of the shaft and the wheel, had to be sustained by the bearing of the shaft, it was held[4] to involve invention to place two such turbines in a pair, face to face, on the same shaft, the water entering between them, so that the downward pressure of the water upon one turbine was balanced by the upward pressure of the water upon the other turbine—the duplication thus causing a new mode of operation.

(*j*)—It is but expected skill to combine old devices into a new machine or manufacture, without producing any new mode of operation.

For example, where in a machine for pebbling leather the pebbled surface was caused by a roller which had the counterpart of that surface engraved or sunk on its periphery, and the

[1] Goodyear *vs.* N. Y. Gutta Percha Co., F. C. No. 5,580.
[2] Smith *vs.* Nichols, 88, U. S. 112.
[3] Phillips *vs.* Page, 65, U. S. 164.
[4] Edison *vs.* Alsens Amer. Portland Cement Works, 219, F. R. 895.
[5] Sugar Apparatus Co. *vs.* Yaryan Co., 43, F. R. 140.
[6] Parker *vs.* Hulme, F. C. No. 10,740.

same kind of roller had previously been used for the same purpose by hand, and the same kind of machine had been previously used for compressing leather, except that the roller in it was smooth, the Court held[1] that the change involved in putting the old figured hand roller in the place of the plain roller of the machine was but the exercise of expected skill.

However, a new combination, with a new mode of operation, may require the exercise of more than expected skill, even though all the parts and the function of the combination as well, be old. Many valid patents have been granted on new combinations of old parts for performing precisely the same function. A combination is not unpatentable merely because its results may also have been produced by other combinations.

(*k*)—Aggregation is but the exercise of mere expected skill, aggregation being the mere assembling in one structure of a plurality of elements, each performing its function without performing any joint function with any of the other elements.

In discussing the distinction between a mere aggregation and a patentable combination the Court has said:[2]

"Another illustration may be found in the frame in a sawmill which advances the log regularly to meet the saw, and the saw which saws the log; the two coöperate and are simultaneous in their joint action of sawing through the whole log—or in the sewing machine, where one part advances the cloth and another part forms the stitches, the action being simultaneous in carrying on a continuous sewing. A stem-winding watch key is another instance. The office of the stem is to hold the watch, or hang the chain to the watch. The office of the key is to wind it. When the stem is made the key, the joint duty of holding the chain and winding the watch is performed by the same instrument. A double effect is produced, or a double duty performed, by the combined result. In these and numerous like cases the parts coöperate in producing the final effect—sometimes simultaneously, sometimes successively. The result comes from the combined effect of the several parts, not simply from the separate action of each, and is therefore patentable."

By the application of these definitions as to what is but the result of the exercise of expected skill, to the problem you have in hand, you will be able to form some idea as to whether the matter in question involves more than expected skill. If it does it is an invention. The law does not concern itself with the question of degree. No matter how slightly the invention may reach beyond mere expected skill, if it does reach beyond, it is an invention.

## NOVELTY

We have found that to be a proper subject of a patent, the subject matter must be able to stand the tests of novelty and utility, as well as of invention.

We have seen that a thing may be new but not be an invention. It cannot be an invention without being new. The question of novelty, however, resolves itself practically into certain rules stating the kind of evidence of the prior art which is required to permit it to be considered relative to the question of invention. If the evidence is of such character that the law permits the prior art subject matter to be considered at all, then it is to be considered in its bearing on the question of invention, unless it should prove to be the exact thing itself when, of course, it would not be invention to do the same thing over again.

Every inventor is conclusively presumed to know what has been already described in the prior patents or printed publications of every country in the world and whatever has been known or in prior public use in this country, and to have borrowed therefrom whatever is shown therein. A printed publication is anything which is printed and, without any injunction of secrecy, is distributed to any part of the public. Exposure for sale is enough to constitute printed matter a printed publication. The mere existence of a printed thing is not sufficient but its deposit in a public library is.

The rules of evidence as to the kind of proof admissible or required in order to permit the prior art to be considered upon the question of invention are substantially as follows:

Prior knowledge or prior use in a foreign country is not to be considered unless the subject matter has been patented (although said patents were never published or printed) or described in some printed publication in that country prior to the making of the invention in question or more than two years prior to the filing in the United States of the application for patent for said invention.

"It may be a hardship to meritorious inventors, who, at the expenditure of much time and thought, have hit upon some ingenious combination of mechanical devices, which for aught they know, is entirely novel, to find that, in some remote time and place, some one else, of whom they never heard, has published to the world, in a patent or a printed publication, a full description of the very combination over which they have been puzzling; but in such cases the Act, none the less, refuses them a patent."[1]

Prior knowledge, possessed in this country, by some person other than the applicant for the patent in question, that the subject of the patent was known and used in some foreign country before its invention here, is not to be considered.

A United States patent issued before the patent in question but applied for after the filing of the application for said latter patent is not to be considered, although if the application for the prior patent was filed before the application for the patent in question, or if a subsequently issued patent was applied for before the application for the patent in question, proof may be submitted of the date and contents of such prior application and the same considered as part of the prior art.

A prior patent or printed publication is not to be considered unless the information contained therein is full and precise enough to enable any person skilled in the particular art to perform the process or make the thing sought to be anticipated. It needs not to have been reduced to practice but may be only a paper proposition. But mere prophetical suggestions of what may be done are not to be considered against a patent which actually accomplishes the result.

A prior abandoned application for a patent is not to be considered unless it has also been embodied in some form of printed publication or, in the United States, proof is submitted to bring it into the category of prior knowledge by others than the applicant for the patent in question.

A prior unsuccessful abandoned experiment is not to be considered if its lack of success was due partly or wholly to any fault of principle.

A thing incapable of fulfilling the function of the subject of the patent, even though apparently similar thereto and alleged to be so capable, is not to be considered. For example, in the case of a patent for the employment of finely powdered flint, quartz or feldspar, mixed with oil, in filling the pores of the surface of wood, where a prior patent set forth the employment of silicious marl or infusorial earth for the same purpose, it was shown that while all five of the substances consisted mainly of silica, nevertheless the first three differed from the last two in being non-absorbent instead of porous and in consisting of angular instead of rounded particles. These differences made the former valuable for wood-filling, whereas the latter were not valuable for that purpose and the Court held[2] that the latter were not to be considered.

And again in a case which was based on a patent for a black dyestuff named "naphthol-black" a prior dyestuff, named "azo-black," was produced which though made from a different

[1] Stimpson *v.* Woodman, 77 U. S. 117.
[2] Reckendorfer *vs.* Faber, 92, U. S. 357.

[1] New Departure Bell Co. *v.* Bevin, 73 F. R. 469.
[2] Bridgeport Wood Finishing Co. *v.* Hooper, 5 F. R. 63.

starting material, was chemically identical with "naphthol-black" or at least chemically equivalent thereto. But the two dyestuffs were not beneficially alike because "azo-black" rubbed off very badly, and "naphthol-black" was so superior thereto that it entirely superseded "azo-black" in actual use. The Court held[1] that the "azo-black" was not to be considered as anticipating "naphthol-black."

A prior accidental occurrence or production of a thing, the character and function of which was not recognized until after the date of application for the patent in question, is not to be considered.

For example, in a case relating to a patent for the manufacturing of fat acids and glycerine from fatty bodies by the action of water at a high temperature and pressure, the Court held[2] that they did not regard as of any consequence the prior accidental formation of fat acids in a steam cylinder from the tallow introduced to lubricate the piston, even if the scum which rose on the water issuing from the ejection pipe was fat acid, saying that "what the process was by which it was generated or formed was never fully understood. Those engaged in the art of making candles, or in any other art in which fat acids are desirable, certainly never derived the least hint from this accidental phenomenon in regard to any practicable process for manufacturing such acids."

And in a case concerning a patent for a stencil sheet consisting of a thin, porous sheet of paper through which ink is readily transmitted, such as Japanese dental paper or yoschino, filled or coated with a substance impervious to ink, as paraffine, where it was shown that prior to the date of application for the patent in suit another party had coated various papers with paraffine, among them yoschino, but that he had never attempted to use this for stencil sheets, and the idea of its adaptability for that use had never occurred to him, the Court held[3] that the product so produced, if it had been capable at all for use as a stencil sheet, was an accidental product, which contributed nothing to the prior art of making such sheets, no knowledge of it or of the method of its employment being derived from it by any one.

A thing which was neither designed nor apparently adapted nor actually used to perform the function of the thing covered by the patent in question, is not to be considered, even though it might have been made to perform that function by means not substantially different from that of the patent. But this rule does not govern except where all three of the conditions mentioned co-exist.

### UTILITY

A very slight degree of utility is sufficient to satisfy the requirements of the statute. If the thing is useful at all for the purpose set forth, the law does not inquire into the degree of utility.

On the other hand, if the thing cannot be used to perform the specified function or if it is injurious to the morals, the health or the good order of society, or injurious to the thing to which it is applied, it is devoid of utility and the patent is invalid.

For example, wherein a patent for treating tobacco leaves consisting in applying an alkali, such as a mixture of potash and glycerine, to the leaves of a growing plant in spots, and the sole object was to counterfeit the leaf spotted by natural causes, the Court held[4] that the patent was void for want of utility, "except to deceive."

### COMPOSITIONS OF MATTER SPECIFICALLY

One of the four classes of inventions named in the Statutes as the subject of patent protection is Composition of Matter. There is no restriction in this country as to the nature of the compositions which may be patented except that they must be new, useful and the result of invention.

Many other countries have restrictions as to the compositions which may be patented. The principal substances which are refused patent protection by them are foods, beverages, medicines or pharmaceutical preparations and the product of a chemical process. Austria, Germany, Japan, Russia and Switzerland will not grant patents on foods, medicines or chemical products though processes of making them may be patented except in Switzerland and as to medicines, in Austria. Denmark will not patent medicines, articles of food nor processes of making articles of food. Sweden will grant patents on processes of making foods or medicines, but not on the product. France, Italy, Spain, Peru and Venezuela refuse patents on medicines and pharmaceutical preparations of all kinds. Portugal will not patent chemical or pharmaceutical products. Great Britain and her colonies grant patents on all the classes of compositions that are patentable in this country.

A patentable composition of matter is one that is produced by the intermixture of two or more specific ingredients and possessing properties pertaining to none of those ingredients separately.

The intermixture of the ingredients in making a composition may be by mechanical or chemical operations or a combination of both.

The properties of the new product may be novel, never before having been possessed by any substance, or they may be old in themselves but new as to that particular association of ingredients and amount to an old result produced by a new means.

In chemical compositions the ingredients, while capable of independent existence, so far lose their identity and individuality when combined as to be no longer capable of being distinguished in the combination. Their mode of operation to produce the composition is also undiscernible. This may be true also in some compositions which are not composed of chemically combined ingredients. Opposed to this class of compositions are those in which the individuality of the ingredients is not wholly obscured and the method by which each ingredient performs its office in the combination is discernible. Between these two extreme classes there are compositions in which the individuality and mode of operation of some of the ingredients may be discernible while that of others may not be. In some compositions it is very difficult to determine whether ingredients have combined chemically or whether they are merely mechanically associated.

Alloys perhaps furnish the simplest and best example of the various kinds of compositions since they may vary all the way from true chemical compounds through mixtures of chemically combined metals with solutions of one metal in another in varying proportions, solutions of metals in each other, mixtures of metals and solutions of metals, to mechanical mixtures of metals.

Where one composition of matter contains ingredients not present nor represented by equivalents in the other the two are essentially different. But the absence of an immaterial ingredient from one, which is included in the other, does not make the two distinct. Though substances contained in two compositions may be different in themselves, yet if they serve the same purpose the compositions may be patentably the same. A composition composed of certain ingredients of a certain quality intermixed in a specified manner and possessing certain properties is not identical with a composition formed of the same ingredients without reference to quality or mode of intermixture and possessing different properties.

The fact that a composition contains an ingredient not contained in another does not necessarily mean that it is not an infringement of the second if the new ingredient does not change the essential properties of the composition. There may be infringement of a combination patent by adding an element or an

[1] Matheson vs. Campbell, 77, F. R. 280
[2] Tilghman vs. Proctor, 102, U. S. 707
[3] Wickelman vs. A. B. Dick Co., 88, F. R. 264
[4] Rickard vs. Du Bon, 103, F. R. 868

ingredient to obtain the same result or substantially the same, but not by leaving out an ingredient or an element of the combination and not substituting an equivalent.

A composition of matter though regarded as a combination is governed by rules peculiar to itself. Elements of a mechanical combination are identical or equivalents only when in their individual character they are the same operative means, not merely furnishing to the combination the same subordinate function but performing this by the same mode of operation. In mechanical combinations the individuality of the constituent parts is not obscured and the mode of operation of each part is discernible. The identity of such a combination is determined by the identity of the individual parts of which it is made up, the identity of the way in which the parts coöperate and the identity of the resultant qualities inhering in the combination as a whole. In a composition of matter such a test is not always possible. In some mechanical compositions in which the identity and individuality of the ingredients is not wholly obscured, the method in which each ingredient performs its part in the combination is discernible. In such a composition the tests of identity are the same as in other mechanical combinations; not only the means must be identical but the manner in which it coöperates with the other elements must be the same. A good example of a composition in which the mode of operation of the ingredients is discernible is one from the art of mixtures for automatically closing punctures in pneumatic tires, called "tire-healers." A typical composition of this kind consists of asbestos fiber, whiting, flour, glucose, water and salt. In such a composition the office of the asbestos fiber is to form a network of fibers in the puncture when forced into it by the escaping air. This network traps and holds the fine particles of whiting, which are insoluble and also the finer particles of flour, thus closing up the openings in the fiber mass. The flour and water and the glucose form a glutinous vehicle for the asbestos and whiting. The salt acts both as a preservative and to lower the freezing point of the mixture. In such a mixture cotton or wood fiber will be the equivalent of asbestos; magnesia, cement, silica, and finely divided insoluble solids generally, the equivalent of whiting; starch will be the equivalent of flour and alcohol will be the equivalent of salt.

In other mechanical and in all chemical compositions, however, the individuality of the ingredients is lost and though it may be known that each ingredient affects the properties of the compound, the operative law by which it produces its effect may be entirely undiscernible.

If the mode of action of the ingredients is discernible, then the coöperative law is perceptible and should be considered in determining identity of compositions. But if the identity of the ingredients is lost and their mode of action to produce their effects in the composition cannot be determined, nothing is then known as to their coöperative law, and it must be regarded as the same in every grouping of the same ingredients which produces the same result.

The logical way of comparing two compositions to see whether they are patentably the same is to compare first their characteristic properties. If these are different the two compositions are, of course, different, but if they are the same then the identity of the constituent elements must be considered. When the character of the composition is such that the mode of action of each ingredient is discernible, then the elements of each are identical only when their mode of action and effect are both the same. But in compositions in which the mode of action of the ingredients is not discernible the elements are considered to be identical if known as being interchangeable without affecting the essential properties of the complete composition. If the ingredients and the properties of the final composition are the same it is safe to assume that the compositions are identical without inquiring into the nature of the reactions between the ingredients.

### CHEMICAL PROCESSES SPECIFICALLY

A process is a mode of treatment of certain materials to produce a given result; it is an act or series of acts performed upon the subject matter to be transformed and reduced to a different state or thing.

Where a result or effect is produced by chemical action, by the application of some element or power of nature, or of one substance to another, such operations are called processes. One may discover a new and useful improvement in the process of tanning, dyeing, making water-proof cloth, vulcanizing India rubber, smelting ores, etc., irrespective of any particular form of machinery or mechanical device. This is a *process*.

Processes have been classified as:

(*a*) Those involving chemical or other elemental action.

(*b*) Mechanical.

A chemical process has clearly and uniformly been held to be patentable.

As to the mechanical process, the decisions hold that if the process consists of a mere function or principle of a *particular* mechanism, and it does not appear that it can be carried out by hand or by any other form of mechanism, it is not patentable. The machine alone, and not its method of operation, should be claimed.

A *principle* cannot be the subject of a valid patent, but as *applied* it may be the subject of a patentable invention.

A principle has been defined as "some natural power or energy which operates with uniformity under given circumstances, and may thus be contemplated as obedient to law."

In O'Reilly *vs.* Morse, 15 Howard, 112, the eighth claim of Morse on the telegraph was construed "to be for the *use* of an electric current for marking signs at any distance, *i. e.*, to be for the exclusive use of one of the powers of nature for a particular purpose and hence void." The Court said:

"He claims the exclusive right to every improvement where the motive power is the electric or galvanic current, and the result is the marking or printing intelligible characters, signs or letters at a distance.

"If this claim can be maintained, it matters not by what process or machinery the result is accomplished. For aught that we now know some future inventor, in the onward march of science, may discover a mode of writing or printing at a distance by means of the electric or galvanic current, without using any part of the process or combination set forth in the plaintiff's specification. His invention may be less complicated—less liable to get out of order—less expensive in construction, and in its operation. But yet if it is covered by this patent the inventor could not use it, nor the public have the benefit of it without the permission of this patentee.

"Nor is this all; while he shuts the door against the inventions of other persons, the patentee would be able to avail himself of new discoveries in the properties and powers of electro-magnetism which scientific men might bring to light. For he says he does not confine his claim to the machinery or parts of machinery, which he specifies; but claims for himself a monopoly in its use, however developed, for the purpose of printing at a distance. New discoveries in physical science may enable him to combine it with new agents and new elements, and by that means attain the object in a manner superior to the present process and altogether different from it. And if he can secure the exclusive use by his present patent he may vary it with every new discovery and development of the science, and need place no description of the new manner, process or machinery, upon the records of the Patent Office. And when his patent expires, the public must apply to him to learn what it is. In fine, he claims an exclusive right to use a manner and process which he has not described, and, indeed, had not invented, and therefore

could not describe when he obtained his patent. The Court is of opinion that the claim is too broad, and not warranted by law."

Another example is found in a case where the patentee had discovered that lead, recently set, would under heat and pressure in a closed vessel, reunite perfectly, after a separation of its parts, so as to make wrought, instead of cast pipe. The Court held[1] that he was not entitled to a patent for this newly discovered principle or quality in lead; and that such a discovery was not patentable, but that he was entitled to a patent for the new process or method in the art of making lead pipe, which this discovery enabled him to invent and employ.

Along the same lines we find that a mere process carried out by nature alone is not patentable. But a patentable process may be had where a force of nature is put into operation under a certain specified condition and then used for a practical purpose, as shown by the decision in Cameron Septic Bank Co. *vs.* Village of Saratoga Springs, 159 F., 453, which involved the process of purifying sewage consisting in:

"Subjecting the sewage under exclusion of air, of light and of agitation to the action of anaerobic bacteria until the whole mass of solid organic matter contained therein becomes liquefied, and then subjecting the liquid effluent to air and light."

This claim was not considered to cover a mere process of nature.

While it has been held that the discoverer of a natural force or scientific fact cannot have a patent for that, yet he may patent a process by which he makes use of a certain effect of one of the forces of nature.

For example, the principle that heat will decompose substances cannot be patented, as involving merely the use of a natural force, but the process involving the decomposition of marble into lime and carbon dioxide by the application of sufficient heat thereto might be patentable if new. This involves the specific application of a principle.

The case of Tilghman *vs.* Proctor discloses the following facts: The celebrated French chemist, Chevreul, discovered in 1813 that fat is a regular chemical compound, consisting of glycerine and three kinds of fat acids. He also discovered that fat can be separated into those, its constituent elements, by causing them to severally unite with an atomic equivalent of water. In 1853 Richard A. Tilghman, a Philadelphia chemist, discovered that those elements of fat can be caused so to unite with an atomic equivalent of water, by mixing the fat with water, and by thereupon subjecting the mixture to a high degree of heat, and to such a degree of pressure as will prevent the conversion of the water into steam. In 1854 Mr. Tilghman obtained a patent, in the specification of which he announced his discovery, and described a suitable apparatus in which to utilize that discovery in connection with the discoveries of Chevreul, and claimed 'the manufacturing of fat acids and glycerine from fatty bodies by the action of water at a high temperature and pressure.' The Supreme Court held that patent to be a patent for a process and to be valid.[2]

A troublesome question is that of Analogous Arts. The rule, simply stated, seems to be that a process claim in an application is anticipated by a patent for a similar process in an analogous art.

The rule is clear, but its application is difficult. The sweeping statement has been made that an old process applied to new material is not patentable. That this statement is too broad may be seen from a remark by one of the Courts to the effect that "Driving cattle off a railroad track with a blast of sand does not anticipate sand blasting for cutting purposes."

The decisions along this line seem confusing until we approach our basic question—Does such an application of an old process in this new art involve something more than expected skill?—by first asking—What is the purpose or the result to be obtained in this new field? If a *new, useful and unobvious result* is obtained, a valid patent should be granted.

To make this clear, we might consider a few guiding decisions. For example: There is no invention involved in the cleansing of chewing gum by the same process used for cleansing rubber. These are analogous materials. On the other hand, a process of manufacturing leather was held to be not at all analogous to a similar process for treating and dyeing fabrics.

In the former case the only process was that of cleansing something, the nature of the thing being immaterial, since the result in the two operations were the same. In the latter case it was held that:

While the process of tanning hides, abstractly considered involving "saturating with acid and then converting this into an oxide by chemical action," must always be the same chemical operation, it does not follow that there is no different process involved when this operation is applied to different materials to accomplish dissimilar results.

In accordance with these decisions, we find the following processes held unpatentable:

No invention is involved in making artificial tooth crowns by the well-known process of striking up metals by means of a die, such as is used in making thimbles, eyelets, etc.

The method of casting stove covers is unpatentable over a similar method for casting wheels, shovels, etc. The process is merely that of casting, irrespective of what is formed thereby.

Painting on canvas with a spray anticipates such on china.

A process for coating carbon paper anticipates the same applied to photographic bromide films.

A method of filling vessels with soda water anticipates the same applied to beer.

The difference between a process of blue-tempering wire clock bells and the process of blue-tempering furniture springs is at most a difference in the articles to which the process is applied, and is not a difference in process.

### AGGREGATION OF PROCESSES

"The addition of one well-known process to another well-known process does not constitute invention unless some different or better result is produced than that which had been previously obtained."

For example, claims for preparing, storing and dispensing a beverage were considered aggregational since each of the steps was complete in itself and independent of the others. In another case the patent was for lixiviating roasted zinc ores by caustic soda, thus producing a zincate solution, combined with a specific process of electrolytically depositing zinc on an electrode from a zincate solution. So far as anything set forth in the claim was concerned the zincate solution made by treating the ores might well have been employed in many kinds of processes, and, again, the zincate solution could have been made by any suitable method other than the one specified. This was held to be an aggregation.

The Court hinted, however, that a claim properly drawn, tying together these different steps to produce a unitary and continuous process with a useful and novel result, would be patentable. And it must be said that it is more often faulty construction of a claim than any defect in the inventive idea that results in claims being rejected as covering an aggregation of processes. In the case last cited, the patentee probably had invented a patentable process involving the manufacture of metallic zinc from ore by the use of caustic soda and the regeneration of the soda with the formation of chlorine as a by-product, all neatly combined in a unitary process; *but the claim did not say so.*

[1] Le Roy *vs.* Tatham, 14 Howard 156.

[2] Tilghman *vs.* Proctor, 102 U. S. 707.

2 RECTOR STREET, NEW YORK CITY

## A PLEA FOR A CHEMISTS' PROTECTIVE ASSOCIATION[1]

By Rollin G Myers

For several years the writer has been studying the conditions under which many of the technical chemists work in the laboratories of this country. More than once he has planned to place his ideas before the American Chemical Society, but other more pressing matters intervened. Now the time is ripe. In the first place it is to be clearly understood that these observations are not second-hand nor the conclusions altogether *a priori* in character. For nearly ten years the writer was connected with different companies: twice as chief chemist, several times as first and second assistants in iron, steel, cement and water laboratories. Besides this he made reports of several technical researches connected with the chemistry of the carbon incandescent lamp. For nearly a year he was assistant in the U. S. Referee Laboratory of Prof. John H. Long, Northwestern University of Chicago. While at the present time and for the past five years he has been a teacher in Chemistry, he has had more than a passing interest in the welfare of the chemist in practical life, more specifically the technical chemist. In view of the writer's experience, he asseverates that his arguments deserve serious attention and the practical part of his thesis a trial.

### LACK OF PRACTICAL ORGANIZATION AMONG CHEMISTS

To the most observing and thoughtful members of the profession, one thing clearly presents itself: the lack of practical organization among chemists. The American Chemical Society and the various alumni associations of the technical schools and universities are organizations, it is true, but their aims are scientific and social rather than practical. The Chemists' Club of New York represents a movement towards practical organization, but its scope is not broad enough to satisfy some of the more fundamental and pressing wants, only vaguely expressed at times by the technical members of the profession. For several years this idea of practical organization has been a recurrent one in the mind of the writer. But for what ends? The first, to increase the financial return of chemists; the second, to raise chemistry to its rightful and just place among the professions. The first end is the more important and cogent. For this reason the writer will make it play a predominant part in the discussion to follow.

### WHAT IS A "CHEMIST?"

In view of the ridiculously small wage chemists receive any attempt to remedy this condition is worth while. Moreover, the practical bearing which this element of social life has on the struggle for existence is of profound significance. Every chemist quickly realizes this. Before dealing with the wage problem and its solution, several questions closely related to it must be discussed. One of these is connected with the common application of the word chemist. There is a manifest dilatoriness on the part of many of the profession, and naturally the public at large, in the use of this word. It is applied indiscriminately to trained and untrained persons. In certain parts of Pennsylvania, for example, a boy who has served for a few days in an iron laboratory, frequently not even a high school graduate, is called a chemist. In many other parts of the country the same custom prevails. Frequently there is a confusion of chemist with druggist. There are people who even look at the chemist as a follower of the "black art," to be respected but to be somewhat feared. In fact, the chemist may be anything or nothing, and he is frequently less respected than a plumber or a mechanic. It is, therefore, imperative to define the word chemist and restrict it to the class which it defines. What then is the definition of chemist? Chemist is applied to that class of persons who have spent four or more years at an accredited technical school or university, in the didactic and laboratory study of all the regular branches of chemistry and who have received formal statements represented by a degree or degrees, that the prescribed courses of study have been satisfactorily completed. A chemist therefore is a trained man. He belongs to a profession which in practical usefulness is unexcelled.

But why do these persons spend four or more years preparing for a profession? First, for a life work; second, for the truly practical object of making a living. They are thoroughly serious in this matter. It is not the result of a passing fancy nor always a pleasing thought. Neither is it for some temporary situation, until something else appear in another line of work which promises greater emolument. These persons train themselves for a purpose and pursue this purpose to the end.

In addition, it canot be denied that the standing of the chemist is equal to that of the other professions. This is true since the requirements for admission, as well as the intellectual ability required to complete a chemical course, are as high, often higher, than those demanded for courses in law, medicine, dentistry, or pharmacy.

Neither can it be denied that the chemist should have a financial return for his services proportionate to his training not only by reason of the cost of his training but on account of his professional standing as well. Since this question of emolument is cardinal to the whole discussion, it is absolutely necessary to decide upon how much the chemist should receive. As a provisional arrangement the writer submits the following estimate of salaries. Assistant chemists who enter laboratories should receive not less than $1200.00 with a yearly increase of $200.00 to a limit of $1800.00 per annum. Chief chemists should receive not less than $2000.00 and be limited to $5000.00 per annum.

Reserving this question of salaries for later discussion and confining the attention to the arguments so far advanced, two principal conclusions and one subordinate conclusion have been arrived at.

I—That the profession of chemistry should be limited to those who have spent a definite period of time in training themselves in a technical school or university for work in practical and research laboratories.

II—That chemists should receive just salaries proportionate to their standing and the high quality of their work.

III—That a just though tentative scale of salaries should be within the limits of $1200.00 to $1800.00 per annum for assistants and $2000.00 to $5000.00 per annum for chief chemists.

These conclusions place all subsequent discussion on firm and definite ground. In addition, they suggest formulated ideals for the chemist to strive for, though it cannot be too greatly emphasized that their realization can come about only by organization. While that conclusion relating to salaries has been given precedence and should be the principal end of any practical organization, the other conclusion relating to the personnel of the chemical profession has an intimate bearing on the attainment of this end and should be always in mind. However, in order to form correct judgments, which have a determining influence on the choice of methods in the attainment of an end, these judgments must not only include the ideal aims, but a knowledge of the actual conditions under which the chemist works. What then are the actual conditions which are common in practical laboratories? To be more specific and clear this question can better be resolved into two: (1) What is the actual rank and file of the workers in the practical laboratories of this country? (2) What are the actual salaries which these workers receive?

Taking these questions in order, it requires but little observation and less practical experience to learn that a large number of these workers are not chemists. They can be divided roughly into two classes, quasi chemists and laboratory boys. The quasi chemists may be placed in three divisions: (*a*) persons who have academic degrees from universities, but who have not

[1] Presented before the Louisiana Section of the American Chemical Society, May 21, 1915.

specially qualified themselves for chemical work; (*b*) persons who have had from one to three years chemical training in an accredited technical school or university; (*c*) persons who have graduated from or who have taken chemical courses in the correspondence schools, and whose training is little better than none at all. The laboratory boys include persons, frequently of immature age, who have had no chemical training and whose knowledge is confined to a few technical methods and some chemical principles vicariously obtained from textbooks and from the chemist himself. Many of this latter class have charge of laboratories, and this is an unfortunate fact.

Compared to the personnel of the professions of medicine, dentistry, pharmacy and law that of the chemical profession is low indeed. Medicine is the only profession which furnishes an approximate parallel, but even here the untrained members are the exception and not the rule. Many of the trade unions have a higher personnel than the chemical profession.

### PRESENT SALARIES OF CHEMISTS

The answer to the second question, *i. e.*, the actual salaries received by the chemical workers, is given on the basis of the writer's personal experience and observation. It represents a mean of the salaries paid to the subordinates and to those in charge of laboratories. The writer is positive that his estimates are correct ones. The assistants in laboratories receive $65 to $75 a month or $780 to $900 per annum. Those in charge of laboratories receive $90 to $200 a month or $1080 to $2400 per annum.

So far the writer has confined his discussions to arguments which emphasize the need of a practical organization among chemists. These arguments have been strengthened by contrasting the ideals of the chemist with the actual conditions met with in chemical laboratories. That the actual conditions are far from ideal is evident in the painfully low personnel and the miserable wage. Before proceeding to the final discussion in respect to the adoption of ways and means for remedying these evils, it is but proper to make a critical study of the interrelationship of these conditions, as well as the causes which are directly or indirectly instrumental in producing them.

### RELATION BETWEEN PERSONNEL AND WAGE

One can hardly question the close relation which exists between personnel and wage. In fact, it may be contended that either one may become the function of the other. If there is a low personnel, there is a low wage. This harmonizes with the general observation that the employer really prefers a trained to an untrained person and consequently may be persuaded to pay more. It is also true that a low wage may produce a low personnel, for a trained man objects to working for nothing and naturally selects a laboratory, if he can find one, where the emolument is greater. But the mere fact that this relationship exists between these prevailing conditions is not satisfying, for there appear to be deeper and more fundamental causes of these effects at work. One of these causes, which to the writer's mind is extremely potent, is the one-sided standard of wages determined for the chemist by business men. This is unfair and unjust: unfair in that the employer takes advantage of the inability of the chemist to raise objections of material aid to himself; and unjust, in that the chemist is not given a voice in the settling of a wage which has such vital meaning to his existence. The judgment of the business man is usually mercenary in character. With him the problem consists essentially in getting as large a financial return as possible for the money invested. What is more, in most cases, he solves the problem successfully. It is easy enough to conclude that a certain employee is worth only so much. The reason that he is worth only so much is because the business man needs to pay him only so much. Besides, it is a very satisfactory thing from the business man's side, for it means that his profits are just that much more. How much more satisfactory it would be, if the employee could be induced to work for nothing!

### RELATION OF BUSINESS MAN TO CHEMIST

To be more particular, the valuation at which the business man rates the chemist is based on amounts paid to chemical employees by other business men. But can the business man judge rightly in respect to a just wage for the chemist? He certainly cannot, for he has no particular training in chemistry and but little understanding of the high quality of the work which the chemist must do to get the proper results. It is hardly possible, then, for the business man to arrive at correct conclusions regarding the proper rating of the chemist's work. *Would not the business man employ similar arguments if the positions were reversed and the chemist decided the financial return for business men?* And right in line with the statement that a chemist is worth only so much, this thing suggests itself: suppose that ten years from now, due to a successful solution of the wage problem, the salaries of chemists had been increased materially, would not the business man say, as he does now, that the chemist is worth only so much? Is it not true after all, that the commercial valuation of the workers largely depends on the mental and physical pressure they can exert on their employers? The average worker cannot press his demands to any great extent and whatever increase he receives is largely governed by the caprice of those above him. Hence, the need of organization. The trade unions resulted undoubtedly from the entirely selfish and tyrannical attitude of the business representatives of capital towards labor. Before the advent of the unions, business men settled the wage scale to suit themselves. Frequently a high-handed policy was pursued. Conditions are different now in this respect, for the business man finds it to his best advantage to consult with the officials of the unions over any prospective changes in wages. It is true that the unions at times have abused their power, but the same statement holds true for the employers of labor. From the writer's point of view, both are necessary in the social organization and both rightly have a voice in the settlement of a question which reacts so profoundly on society. But if untrained labor has a voice in determining a just wage for itself, who shall say that trained labor, in this case chemical labor, should not demand an equal place in the sun? *Is the struggle for existence any the less hard for the chemist at an equal or less salary, than for the laborer?* Perhaps the business man has become deluded into the idea that the chemist is not so necessary to the success of a company or corporation as common labor. If the chemists and chemical workers of the U. S. Steel Corporation or the Swift Packing Company suddenly stopped working, could these organizations still operate? It would seem very doubtful. But assuming that they could adjust themselves to the altered conditions, could they successfully compete with the rival companies employing chemists? In this age it would be impossible. And what would it mean from the financial side? It would mean the daily loss of thousands of dollars. What would be the effect on common labor? A partial or complete laying off of those employed. If there is any doubt, let the officials of any company or corporation employing chemists try the experiment for a month without them. To say the least, these possibilities are well worth considering by the business men as well as the chemist.

The writer's aim is not to antagonize business men, except perhaps in asseverating that their attitude to the wage of the chemist is wrong and unprogressive. It is true they often tacitly or expressly admit that the wages are low, by promising an increase in salary shortly, either from greater efficiency or promotion. So too, the promise is often fulfilled; but the increase in salary is so small and diminishes so rapidly in its approach to the average wage set by business men, that the chemist realizes acutely after several years of hard work that he has barely made a living. In fact, if he is at all cynical, he concludes that in some

manner he has been tricked and deceived. Even in respect to promotion, the extra compensation received is hardly ever commensurate with the added responsibility for the accuracy of thousands of determinations or for the quality of some marketable product. Neither should we at any time lose sight of the fact that many chemists lack the executive capacity for head positions, as well as the particular ambition for them. But to contend, on account of this, that the efficiency of these workers is reduced and their value is lessened as well as their earning power, is decidedly wrong. To say the least, it indicates a very selfish way of looking at things. The chemist in a subordinate position who does his work carefully and conscientiously is deserving of so much financial return that, he, as well as his chief, can obtain enjoyment without unduly skimping himself; and at the same time properly maintain his professional standing.

### LOW STANDARDS IN TECHNICAL LABORATORIES

While the one-sided policy of business men in fixing the wage of chemists has been given the *greatest* weight among causes producing low wages, there are two others, it is believed, which also favor the same effect. One of these is the ease of obtaining positions in technical laboratories, since in most cases nothing is required of the applicant save an ability to learn a few rapid technical methods. The time of apprenticeship is short and in a few weeks the former applicant becomes a laboratory automaton, capable of turning out the required results. Later perhaps this "would-be chemist" hears of a better position. He applies and frequently, by means of credentials from his chief, obtains the situation. If he takes charge of a laboratory he, also, eventually needs an assistant. Sometimes a chemist is selected or, as before, some boy or untrained person is broken in. The general trend of this policy is to supplant chemists by untrained workers. The personnel of the profession suffers in consequence and this in turn has a detrimental effect on the wage as was previously pointed out. There is another aspect also from which this condition of affairs may be viewed. It is in respect to the law of supply and demand. The increased number of persons in the chemical field, due to the continual influx of untrained workers, may produce such a supply of applicants for chemical positions that the demand is equalled or exceeded. This condition would again tend to a reduced wage. The greater sufferer is always the chemist, not only from the lessened return of his four or more years of hard training, but of the money he invests for his training as well. Perhaps the chemist himself can be blamed to a certain extent for these conditions. At least he has been decidedly short-sighted in not maintaining the high standard of his subordinates, by insisting on trained assistants, even in the face of the aggressive attitude of his employer against any increase in expenditure. Still, the business man has set the precedent and can exert the greater pressure, so that the chemist is handicapped in most instances. The business man has also shown a short-sightedness in not realizing the superlative value of the chemist in any respect over the untrained man

### RESPONSIBILITY OF TEACHERS OF CHEMISTRY

The other cause referred to is the skeptical state of mind common to many professors of chemistry in technical schools and universities respecting any increase in the average wage of chemists. Many of them sincerely deplore this condition of affairs, but beyond this they do not go. Whether they reach the conclusion that any amelioration is impossible, or that in any case the chemist will successfully adjust himself to an unsatisfactory environment, does not relieve these men from a certain share of responsibility for the future welfare of their student graduates. The intellectual and ethical standard of the heads of the various chemical departments is admirable. Their lofty ideals and their inspiration in widening the sphere of chemical knowledge by investigation and research have the profound effect of advancing science and of improving social life as well. In view of the elevated standing of these men, they could have great moral influence in bringing about a change of attitude in business men, which would be decidedly favorable to an increase of emolument for the chemists. The student graduates and other chemists could be impressed also with the necessity of encouraging only those applicants for chemical positions, whose training justly entitled them to become members of the profession.

### PROPOSED PLAN FOR PROTECTIVE ASSOCIATION

The power to effect changes of moment for the betterment of the individual is obtained only by the close association and the concerted agreement of the many in respect to formulated and definite policies of action. The objective manifestation of this principle is easily seen in the promotion and existence of protective associations for practical ends and of societies for social and speculative purposes. In the discussion so far the writer has shown the imperative need of a protective association for chemists, by pointing out the small wage paid to these men, the low personnel, and what is more convincing the inability of a chemist alone to remove the causes which actively produce the unsatisfactory conditions. A protective association, then, is the only remedy which has a recognized potency over the evils discussed. According to the principle enunciated its functions must be directed by definite and formulated policies. In respect to wage, it must decide on a just emolument for chemists, to be regulated by the character of the work, the rank and experience of the worker, as well as by a proper regard for the rights of the employer and business man. The length of the working day and the extra fees for work over time, at night and on holidays, should be settled also. In respect to personnel, a *protective association should limit its membership to chemists*, though a special concession might be granted to quasi chemists with at least three years chemical training in a technical school or university. To distinguish them from the graduate members they could be called "chemists by courtesy." In addition the applicants for positions in practical laboratories should be sharply limited to two classes: (1) chemists; (2) quasi chemists who have at least three years of a *bona fide* chemical training and who must pass a compulsory examination over the principal branches of chemistry.

By firmly maintaining the stand taken as to the wage and the personnel, a protective association could widen its policies eventually and take on other functions, the following of which may be suggested: (*a*) to keep an up-to-date register of the chemical laboratories and of the chemists in the United States; (*b*) to keep a daily register of all members seeking positions and to keep them promptly informed of any actual and prospective vacancies in chemical laboratories; (*c*) to aid the applicant for a position in every way possible; (*d*) to keep a careful watch on the supply of chemists and the demand for them in order to control, as efficiently as is possible, any excessive increase or decrease of applicants, by influencing the heads of chemical departments to encourage or discourage students in the study of chemistry when the occasion demanded this; (*e*) to take aggressive action against all companies or corporations which are unfair and unjust to chemists; (*f*) to assume a critical attitude to all chemists who through personal ambition of a mercenary character or in any other way seek to lower the profession and defeat the policies of the association; (*g*) to assist financially when possible all members of the association who have been temporarily or permanently incapacitated through sickness, accident or age.

The policies and functions outlined for a chemists' protective association may be looked upon as parts in a working formula. The supposition that its application will bring about a decided improvement in the financial returns, besides elevating chemistry to its just place among the other professions, is strengthened greatly by two classes of facts.

I—From the standpoint of wage, we have seen the large increase in financial return by the many kinds of untrained labor after organization.

II—From the standpoint of personnel, we know that practicing physicians, dentists, pharmacists and lawyers are limited to those who can pass satisfactory examinations given by the state. It is hardly necessary to add that those applicants who pass the examinations have had several years of training in universities, where they have received degrees. In Germany the "Verband Deutscher Chemiker" (the German Chemists' Association) exists, which limits the applicants for positions in chemical laboratories to those who can pass satisfactory examinations and who have degrees.

Organizations, whether for trained or untrained labor, consciously or unconsciously limit their membership to those who represent the best in the field. In so doing the personnel is raised and this in turn reacts favorably to an increase in wages. There is one thing more: the fact that organizations have clear and definite policies and stand for certain desired ends, produces a profound impression on the public mind. The masses learn to associate certain practical gains with the principles peculiar to a trade or a profession. This means an education of the public and the great moral effect of a favorable sentiment to the just objects of an association.

In respect to the adoption of ways and means required to launch successfully a protective association for chemists the following suggestions are advanced: (*a*) let the American Chemical Society or the Chemists' Club of New York make a careful canvas of the actual number of chemists in the United States, their rank, their salaries, and the companies they are connected with; (*b*) let a straw vote be taken of all the listed chemists in respect to their desire for a protective association; (*c*) have a printed statement, which describes and fixes the functions of the association, the salaries and the standard for applicants for positions in practical laboratories, sent to all chemists, and their comments and suggestions encouraged (this statement to be formulated by a committee of the members of the association which acts favorably on the ideas set forth in this paper).

In conclusion, the writer believes that he has not only shown the need of a protective association for chemists, but he has also shown that it will accomplish all that is necessary in improving the practical conditions of the chemists in this country. If it is argued that there is a certain humiliation for chemists in establishing an association similar to those of untrained labor, it should also be considered *that it is more humiliating* to work for a salary frequently less than that received by untrained labor and to compete with chemical workers whose training is deficient, who have paid nothing for an education and who have taken positions justly belonging to chemists.

Finally, the writer ventures the hope that the chemists of the United States will see fit to take up the idea of practical organization and that in not so many years the chemical profession will stand even with the highest, not only in respect to a just compensation received for services but also to the personnel of its members.

TULANE UNIVERSITY, NEW ORLEANS, LOUISIANA

# CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

## FLUE GASES FOR EXTINGUISHING FIRE IN COAL

At a recent meeting of the Sydney Section of the Society of Chemical Industry, Dr. George Harker described an apparatus which is being successfully used for extinguishing fires in ship's holds by means of flue gases [*J. Gas Lighting*, **130** (1915), 583]. The gases are drawn from the ship's funnels by means of a fan, passed through a special water cooler and cleaner, and delivered to the holds by means of pipes. Mr. Harker remarked that by tests at a plant recently installed in London it had been conclusively proved that coal fires can be so extinguished. The result bears indirectly on the question of the spontaneous combustion of coal. When a confined volume of air is left in contact with coal dust, a large proportion of the oxygen will be removed from the air after several days' contact. In one experiment with a sample of bituminous coal, in which a flask was filled with the finely-ground coal and left to stand in a room at summer temperature for a fortnight, the gas in the flask showed, on analysis, only 4.86 per cent of oxygen and less than 1 per cent of carbon dioxide. The conclusion has been drawn by some authorities, from experiments such as these, that in order to extinguish a mass of coal on fire the atmosphere surrounding the coal must be entirely devoid of oxygen. But the absorption of oxygen by the bituminous compounds of the coal is quite a distinct process from the combustion of the coal, accompanied by the rapid production of carbon dioxide and water. In the experiments in which a large mass of glowing coal was extinguished, the proportion of oxygen in the flue gas was about 9 per cent. Coal when burned under specially suitable conditions can produce a flue gas containing as little as 4 per cent of oxygen; but, as has been pointed out by H. E. Armstrong, the application of a gas containing 10 per cent of carbon dioxide and 10 per cent of oxygen, instead of air with 21 per cent of oxygen, immediately slows down the combustion and produces a cooling effect.

## ELECTRICALLY REMOVING TAR FROM GAS

F. W. Steere, of Detroit, Mich., has taken out three patents for the United States, as Assignor to the Semet-Solvay Company, for removing tar or tarry substances from gas. The specifications are abstracted in the *Journal of the Society of Chemical Industry*. According to the first patent, the gas is passed through an electrical field of alternating polarity, between receiving and discharging electrodes, and is subjected to the action of brush electric discharges from the discharging electrode, which has a pointed surface. The tarry particles coalesce, and are deposited on the receiving electrode. By the second patent, the particles of tar are agglomerated as just described, and are subsequently separated, the gas being passed at such a high velocity that the particles are removed from the electric field with the gas. In the third case the gas is heated sufficiently to liquefy the tar and raise the gas above its water-vapor saturation temperature, and is then passed through an electric field of alternating polarity between opposed electrodes. According to a French patent taken out by H. F. Smith, the gas is passed through a diaphragm of glass wool at such a speed that the fibers are electrified. The very small particles are attracted to the fibers, or are carried through and coalesce into larger drops—being then removed by another filter. Large particles which are retained are removed by the gas stream on reversing the diaphragm.

## SULFURIC ACID IN GREAT BRITAIN

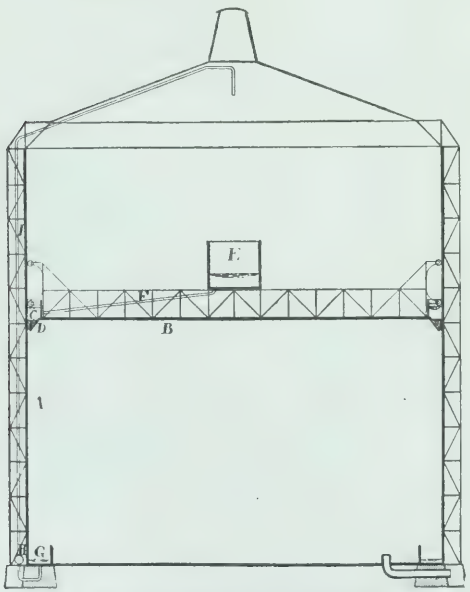
The scarcity and high price of sulfuric acid in Great Britain (in the late spring a contract was closed at $20 a ton delivered) are responsible for the fact that some ammonia producers are considering the advisability of altogether dropping sulfate manufacture for the time being, and putting in its place plants for making strong ammonia or concentrated gas liquor [*J. Gas Lighting*, **130** (1915), 257]. At first sight this latter proposition appears

to have many advantages, since, calculating on ammonia values, and on present prices of acid, labor, etc., it can easily be shown that the manufacture of strong ammonia is more profitable. There are, however, many objections to it, and the most important of these is that the demand is limited. Strong ammonia is used principally for certain trade purposes; and if the supply is increased to any extent, the price will certainly fall, and then the profit is such that sulfate making will pay better. Then, too, the trade in strong ammonia is almost entirely in the hands of one or two large firms, who, if necessary, could easily squeeze out a smaller and less powerful competitor. In the writer's opinion, with acid at $19 per ton, sulfate making is by far the safer proposition.

It is not unlikely that one result of the scarcity will be to encourage the owners of large coke-oven plants to put up their own sulfuric acid plants, and, moreover, to supply their own sulfur requirements largely, if not entirely, by purifying their gas from sulfuretted hydrogen by means of oxide of iron.

## A GASHOLDER WITHOUT A WATER TANK

Early this year a description was given in the *Journal für Gasbeleuchtung* of a type of gasholder having no water tank, which has been designed by the Augsburg-Nuremberg Engineering Works (generally known in Germany by the initials "M. A. N."). The difficulty of keeping a dry seal in sound condition is very great; it does not follow, however, that because a water-seal equal to the holder pressure of 4 to 8 in. cannot well be




A German Gasholder without a Water Tank

A—Wall of Holder B—Partition Travelling Vertically C—Liquid Seal D—Sliding Block E—Liquid Feed Tank F—Feed-Pipe G—Receiver H—Pump I—Rising Main for Liquid

dispensed with, it is necessary to retain a tank having a depth of 30 feet or more. In the tank described the depth of the water-seal is merely slightly greater than the gas pressure.

The illustration shows the design of the new holder, for which a German patent has been obtained. The water-seal C travels with the disc or ring B, and keeps the holder gas-tight in that direction, while the traveling slide or block D prevents the water of the seal escaping through the intervening fissure, or at least reduces the loss to trifling proportions. Any such loss of water from the seal is made good by water flowing from the feed tank E, which again is filled up automatically from the annular receiver G by the pump H and the rising main I.

As there is no loss of the liquid used for the seal, any suitable liquid may be employed in place of water; ordinary gas tar has been found very good for the purpose, and has the advantage that it is unnecessary to warm it to prevent freezing in winter time. Tar and similar liquids pass only to a very slight extent through the very na row slit, especially as the pressure is kept nearly the same on both sides of the holder partition. Measurements have shown that, with a holder of 880,000 cubic feet capacity, the pumping of the tar used as a sealing material would entail an expenditure of only 0.1 H. P. on the average, when it has been calculated that with power costing $0.022 per B. T. U. the annual expense of pumping would be only 3 per cent of the customary expense (in Germany) of heating a gasholder having water-sealed cups.

The cost of erecting the new type of holder on unfavorable ground is very much lower than that of a holder with water tank, as the load on the foundations is comparatively trifling. No inside painting of the holder is required, since the walls on the inside are protected by the tar. The outside also is not exposed to the ill effects of tank-water, and is dealt with in the same way as any exposed iron structure. The holder may be enlarged at any time by merely extending upwards its wall A. In appearance it is better than an ordinary telescopic gasholder.

An experimental holder of the new type has been erected at the Gustavburg works and one of 45,000 cubic feet capacity is in course of erection at the Augsburg works, the contract price being the same as that of an enclosed holder of the ordinary type of half the capacity.

## AMERICAN COPPER

The smelter production of primary copper in the United States last year was 1,150,137,192 lbs., as compared with 1,224,484,098 lb. in 1913, showing a decrease of rather more than 6 per cent. The total value of last year's output, taking an average of 13 1/4 cents per lb., was $152,968,246, as compared with $189,795,035 in 1913. The greatest State production last year was effected in Arizona with 382,449,922 lbs.; Montana came second with 236,805,845 lbs.; Utah third with 160,589,360 lbs.; and Michigan, fourth with 158,009,748 lbs. New Mexico had a production of 64,204,703 lbs. last year, and Nevada produced 60,122,904 lbs. California turned out 29,784,173 lbs., and Alaska 24,985,847 lbs. No other state reached a production of 20,000,000 lbs. in 1914. Refined copper was exported from the United States in 1914 to the extent of 748,902,137 lbs.; the corresponding exports in 1913 were 817,911,424 lbs.

## THE GALICIAN PETROLEUM INDUSTRY

About 80 per cent of the aggregate production of petroleum in Galicia comes from the Drohobys, Broyslav, and Tustanowice concerns, and, perhaps owing to the fact that a great deal of English, French, and Belgian capital is invested in these undertakings, they have not suffered much during the Russian occupation [*Engineering*, **99** (1915), 689]. Considerable stocks, stated to amount to about 1,000,000 tons, which were intended for railway fuel, were found in the stores of the naphtha companies. Some of the petroleum refineries, which, all told, number about sixty, situated in Central Galicia and on the slopes of the Carpathians, notably Limanova and Mariampol, belonging to the Galician Carpathian Petroleum Company, have been entirely or partly destroyed by fire. The mining department of Petrograd recently despatched a commission of experts to Galicia in order to investigate and report on the country's petroleum industry, its value for Russia, and its position, as

against the Baku petroleum industry. Fears had been entertained that more especially Southern Russia might expect a keen competition from the Galician petroleum industry, on account of which protests were already raised against Galician petroleum being imported into Russia free of duty. Although the Galician petroleum industry shows a decreasing yield since the year 1909, the production during the year 1913, the last year of normal working, amounted to 1,063,283 tons, and the exports that year of the different petroleum products were:

| | Tons | Value |
|---|---|---|
| Lighting oil | 244,072 | $4,800,000 |
| Benzine | 49,772 | 2,200,000 |
| Light oils | 41,373 | 685,000 |
| Heavy oils | 154,697 | 4,160,000 |
| Refined paraffin | 42,655 | 3,810,000 |

While formerly only part of the export went to Germany, this country now reckons upon being able to control the entire quantity available after the home demand has been supplied.

## THE MINERAL PRODUCTION OF BRITISH COLUMBIA

*Bulletin* No. 1, 1915, on the mineral production of British Columbia, gives figures covering 1913 and 1914, those for 1914 being estimated. The value of the gold output in 1913 amounted to $6,137,490, and in 1914 to an estimated total of $5,628,126. This is stated first, then come in the following order:

| | 1913 | 1914 |
|---|---|---|
| Silver | $1,908,606 | $1,768,666 |
| Lead | 2,175,832 | 1,834,866 |
| Copper | 7,094,489 | 5,845,910 |
| Zinc | 324,421 | 309,288 |
| Coal and coke | 9,197,460 | 7,802,164 |
| Building materials, etc. | 3,398,100 | 3,000,000 |

From these figures it will be seen that the value of the output of coal and coke in the province far exceeded that of gold, and the extraction of coal and manufacture of coke probably gave work to a larger number of men than the extraction of gold. The gold output probably forms a maximum which is limited either by the labor available, by the extent and richness of the gold-bearing strata, or by both conditions combined. The table also shows that the value of the copper worked in the province also exceeded the value of gold during both years under consideration. In regard to coal, the Bulletin states that a much larger quantity than the estimated total for 1914, 2,172,530 tons, could have been produced had there been a demand for it. The right classification, therefore, would seem, in this particular case, to be that which would place coal first on the list, followed by copper, then by gold. With reference to other minerals, the Bulletin adds that some prospecting for, and development of, bodies of iron had been carried out recently, but no iron ore had been used or shipped. A small quantity of crude placer platinum had been recovered, estimated at less than $1000 in value; this was obtained from prospecting workings now being carried on, and the results were considered encouraging. It is very satisfactory to note that molybdenite has been discovered in British Columbia, in what seem to be commercial quantities, "the deposit appearing to be of considerable size." Seeing the very great eagerness with which this mineral was sought after during the greater part of last year, the province should be able to derive an important revenue from its working and concentration.

## A HUGE BAKING-OVEN FOR RAILWAY CARS

A recent bulletin issued by the Pennsylvania Railroad states that a mammoth oven has been constructed into which the largest car newly painted can be run. The doors are tightly closed and the temperature is raised above the boiling point of water. In three hours the paint is completely dry and hard and the car ready for service. This process has reduced by 95 per cent the time required for drying and by 50 per cent the time a car is held out of service for the entire operation of repainting. The first tests of oven-drying paint were made about two years ago. The present condition of the paint on the cars used in the tests indicates strongly that the artificially dried paint is more durable than that dried in the ordinary manner in the open air.

## BRITISH BOARD OF TRADE

During June and July the Commercial Intelligence Branch of the British Board of Trade received inquiries regarding sources of supply for the following articles. Firms who may be in a position to supply any of the articles asked for should communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73, Basinghall Street, London, E. C.

### Inquiries during June

Acetate of lead
Adhesives, gums, etc.
Aluminum seals
Antimony salt
Annatto
Aniline hydrochloride
Aniline oil
Asbestos cement sheets
Asbestos cloth
Brass sheets and tubes
Bronze figures, small
Bichromate of potash
Clasps for leather purses
Calcined magnesia
Chamois leather
Celloidin
Dyed grasses and raffia
Fabric gloves
Ferrules, brass
Gambier in cakes
Gutta-percha powder
Glass eyes for dolls
Haematite burnishers
Hyposulfite of soda
Kapok
Lacquer for boots
Lead seals
Lysol
Palm kernel oil
Pale gas oil
Phosphate of soda
Pins, white metal
Pyrophosphate of soda
Stearine, m. p. 120
Sunflower oil
Sodium sulfide
Substitute for "amol"
Sulfate of alumina
Wafer paper
Whale oil
Wax matches

Agates for scientific balances
Asbestos powder for filtering wine
Binoxalate of potash celluloid, non-inflammable celluloid tips (round pieces, 9¼" or 9½" diam.) for soldiers' caps
Coconut oil for making margarine
Cork spiral holders for cigar and cigarette tubes
Enamelled hollow-ware
Glass tubing, 0.16–0.18 external diameter
Graphite stalks for pencils
Hard fats such as substituted for cocoa butter
Insulated brass conduit-tube to compete with the Bergmann tube
Machines for glass polishing
Machines for making confetti
Machines for stamping names on combs
Machines for coating ferro-prussiate and ferro-gallic paper
Machinery for corn grinders
Machinery for braid machines (similar to Guido Horn patent)
Metal plates, 18 G. full pickled steel 18" × 24"
Mica discs for talking machines
Mirrors, wood and metal frames, for Kaffir trade
Nails, makers of a special form of nail fastening for galvanized corrugated sheets
Onion skin for paper flower making
Paper making machinery
Pitch paper, or paper that is tarred on both sides with either coal-tar pitch or bitumen
Paints for enamelling iron plates
Quebracho bark and extract
Reconstructed sapphires
Spools for typewriter ribbons
Vulcanite beads flat (for West Africa)
Waxed cloth, double faced for hospital purposes
Zinc dust for sherardizing
Zinc rodding from ⅛" to ⅝" in diameter

### Inquiries during July

Acetone
Acetate of lead
Aluminum plates
Beta naphthol
Bleaching powder
Blow pipes
Borate of manganese
Carbonate of potash
Caustic potash
Casein
Commutators
Core gum
Dynamo armatures
Gelatine sheets—clear
Glass wool
Laundry charcoal
Magnesium chloride
Nitrated castor oil
Nitrocellulose
Potassium bichromate
Picture mouldings
Press buttons
Sodium silicate
Sodium hydrosulfite
Sodium sulfate
Thorium nitrate
Thermometers, clinical
Waste rock crystal
Wire nails
Wire for bookbinders
Washers for insulation

Agricultural implements—special forms of soil drills and seed drills
Aluminium bronze wire of fine sizes
Boot lace tagging machines
Braiding machines for boot laces
Calcined sugar of lead
Corozo nuts for button making
Gas burners, incandescent (cheap)
Gold foil and gold paper
Machinery for making fibro-cement board
Machinery for glass bottles and small chemical bottles
Machines for sugar factory
Machinery for bevelling small mirrors
Machinery for cutting spirals on vulcanite tubes
Machinery for match making
Machinery for preparing the leads for lead pencils
Machinery for polishing terrazzo marble floors
Plant for the manufacture of resin
Perforated nickeline spindles for cop dyeing
"Presspahn" or insulating cardboard
Springs for clockwork motors
Steel strip, cold rolled
Steel for aviation engines
"Trapping" machines for turning ebonite rods
Tinsel cloth for scouring purposes
Venezuelan lingol shells for button making

—D. G. Anderson

## SAWDUST AS A FIRE EXTINGUISHER

As an extinguisher of small fires of oil or grease, sawdust is considered to be much superior to either sand or water [*J. Gas Lighting*, **130** (1915), 449]. Sawdust, wet or dry, thrown on a blazing liquid has a blanketing action, floating on the surface and keeping out the air, so that it actually smothers the flame. Sand is less effective, as it sinks through the liquid. The efficiency of sawdust may be increased by mixing it with sodium

bicarbonate, using 10 lbs. per bushel of sawdust. The bicarbonate liberates carbon dioxide when heated, and this gas smothers the flames. Sawdust is more suitable in cases of fires in electric plants, as it is easier to handle, and spreads more readily than does sand.

### SOFT SODA GLASS SUITABLE FOR X-RAY BULBS

The Glass Research Committee of the Institute of Chemistry find that a glass such as that made from Formula No. 10 (see THIS JOURNAL, **7**, 544) recently published by them and recommended for X-ray bulbs, does not give a green phosphorescent glow if it is made from approximately pure materials. The slight glow given is blue. In view of the fact that a green phosphorescence appears to be preferred by users of X-ray tubes, it seemed desirable to determine the conditions for obtaining this effect. It has been traced to the presence of manganese, and such a glass as Formula 10 will give this green glow if manganese dioxide is added to the batch mixture in the quantities frequently used to correct the color due to iron.—A.

### OIL IN RUSSIA

According to the *Petroleum World*, **176** (1915), the Russian Government is moving to a State control of the oil industry, not by direct nationalization, but by conferring upon Ministers the power to requisition stocks of fuel oil or other products. A decree has been issued giving the Minister of Ways and Communications additional powers for supervising and controlling the supply of fuel to the army and navy, the Ministry of Ways and Communications, and the private undertakings engaged in work required by the interests of the defence of State. The decree authorizes the Minister:

1—To demand information from all State or privately owned undertakings concerning the quantities of fuel stored, expected for delivery, and actually required, also all contracts relating to future deliveries.

2—To inspect all the storages and stocks of fuel in the Empire.

3—To distribute at his discretion the fuel provided for the State requirements, among various State departments or private undertakings as may be deemed necessary.

Prince Shahovskóy, the new Minister of Trade and Commerce, recently presided at a conference between the Government and representatives of the oil industry at which the commandering of oil supplies was discussed.

The Chairman of the oil representatives, Mr. Gukassov, said that the excess of production in Russia in 1915 would be 1,600,000 to 2,000,000 tons over 1914. This would be sufficient to satisfy all the regular consumers of oil and to leave a margin for those that desired to convert their coal-burning furnaces to oil burners. The transport facilities, however, would be equal to only 1,000,000 or 1,100,000 tons.—A.

### WASTE PRODUCTS OF AGRICULTURAL INTEREST

The *J. Soc. Chem. Ind.* **8** (1915) states that middle grade shoddies, containing 5–10 per cent nitrogen, have long been used for fruit and hop farming, especially on the lighter soils. Experiments at Rothamsted in England have also shown that they are also good for ordinary farm crops, and on heavy soils. The main effect is produced in the first year, but the residual value persists for another year or two. Shoddy is one of the cheapest nitrogenous manures on the market; it sells at $1 to $1.24 per unit of nitrogen at the Yorkshire mills; in the South, transport charges increase the price to $1.67 to $1.90.

"Processed" shoddies, which have been treated with sulfuric acid or freed from oil, are of no more value than the untreated material. Untreated leather waste has no manurial value, but experiments with scrap that has been roasted or treated with sulfuric acid have given promising results. Untanned leather and scrap derived from the glove-making industry have been proved to possess marked fertilizing value.—A.

### MAGNESITE DEPOSITS IN BRITISH COLUMBIA

According to the *British Clay Worker*, **1915**, 279, a sample lot of magnesite bricks made from Atlin magnesite has been tested and as a result it is said that the bricks are of high quality and equal to the quality supplied by American manufacturers to the Trail and Granby smelters and to the iron and steel works in Eastern Canada and the United States. The Atlin magnesite deposits are extensive and the material is remarkably pure. The working up of these deposits offers an opportunity for an important industry, as hitherto most supplies of the raw material have been imported from Greece to the United States and manufactured there. The suggestion is made that the raw material could be shipped over the White Pass and Yukon Railway and by steamer from Skagway to Vancouver, where it could be manufactured to supply the requirements of Canadian and United States smelters requiring this highly refractory material. The product, if manufactured there, could be supplied at from a third to half the price now charged by United States manufacturers, so that the industry is not only one of local value but may form the basis of an important export industry.—A.

## OBITUARIES

### THOMAS BLISS STILLMAN

Thomas B. Stillman, late Professor of Engineering Chemistry at the Stevens Institute of Technology, died at his home in Jersey City, N. J., on August 10, 1915, from heart disease, after an illness of about four weeks.

Dr. Stillman was born at Plainfield, N. J., on May 24, 1852, and was a son of the late Dr. Charles H. and Mary Elizabeth Stillman. His early training was obtained in Plainfield, and after attending Alfred University, Alfred, N. Y., for a short time, he entered Rutgers College, New Brunswick, N. J., and was graduated in June, 1873, receiving the degree of Bachelor of Science, and membership in Phi Beta Kappa. His graduating thesis on "The Composition of the Ashes of Plants" was awarded a thesis prize, and was published in the "Report of the State Geologist of New Jersey, 1873." He then entered a post-graduate course in chemistry at the New Jersey State Scientific School, and at the same time was connected with the New Jersey State Geologic Survey, with practical work at the zinc mines of Sussex County.

In 1874, Dr. Stillman was appointed private assistant to the late Professor Albert R. Leeds, of Stevens Institute of Technology, remaining in this position until October, 1876. In the latter year he received the degree of Master in Science from Rutgers College, and in November of the same year he entered the chemical laboratory of Dr. R. Fresenius of Wiesbaden, Germany, as a student of analytical chemical research. While in this laboratory he laid the solid foundations for his future very successful and splendid analytical and engineering chemical work, and as a recognition of some investigations upon the salts of uranium carried out in this laboratory, Dr. Stillman was elected a foreign corresponding member of the Edinburgh Society of Arts and Sciences.

In 1879 he opened an office in New York City for the practice of analytical chemistry. In connection with his professional

work, he was consulting chemist for the Sawyer-Mann Electric Light Co.; associate editor in the science department of the "Scientific American;" and manager of the assay department of the "Mining Record." His experiences at this time gave him a very intimate and practical acquaintance with many of the chemical industries of the country, and since then his services were frequently required as a chemical expert in various engineering and chemical processes and litigations. In 1881, Dr. Stillman again became connected with the Department of Chemistry at Stevens Institute of Technology, and in 1883, Stevens conferred upon him the degree of Doctor of Philosophy. In 1886 he was appointed Professor of Analytical Chemistry, and in 1902, upon the death of Prof. Leeds, he became head of the chemical department and Professor of Engineering Chemistry at Stevens, which position he held until 1909, when he retired as a beneficiary of the Carnegie Pension Fund.

After retiring from his work as a Professor at Stevens, he again entered into practical and consulting chemical work. He became the senior member of the firm Stillman & Van Siclen, chemical experts, of New York City, and in 1911 he was appointed City Chemist of Jersey City and Bayonne, N. J., which position he held at the time of his death.

Dr. Stillman's membership in scientific societies included the Chemical Society of London; the Society of Chemical Industry; the American Institute of Mining Engineers; the American Chemical Society; the International Association for Testing Materials; the American Electrochemical Society; the Deutsche Chemische Gesellschaft; the Société Chimique de Paris; and the Edinburgh Society of Arts and Sciences.

He never aspired to the offices in the various societies of which he was a member, and in recent years he rarely attended the meetings of the chemical societies unless some unusually good program was offered. However, he was a great student of chemical literature, and invariably followed the various journals and was up-to-date in all chemical matters.

Dr. Stillman's important contributions to the science were in the fields of analytical and engineering chemistry. He was a most energetic and untiring worker; fifteen to eighteen hours work per day in his laboratory were not at all uncommon with him, and it was very unusual not to find him hard at work in his "Lab." at any time between 8 A.M. and midnight. A large amount of his research work was of such a nature that it could not be published without breach of faith with his clients, yet the number of his papers published in the various scientific journals of this country and abroad is a large one, and embraces a great variety of chemical engineering subjects.

THOMAS BLISS STILLMAN

He was among the first of those chemists who interested themselves in the problems of municipal water supplies, and for many years he served various New Jersey cities in connection with their problems on this subject. For a number of years he was chemist to the Medical Milk Commission of Newark, N. J.; he was one of the foremost in securing better milk for a number of cities, and was especially active in the development of "certified milk."

Possibly his greatest service to chemistry, and the one which made his name familiar to most American chemists, was his pioneer work on "Engineering Chemistry, a Manual of Quantitative Chemical Analysis for Students, Chemists, and Engineers," the first edition of which was published by the Chemical Publishing Co., in 1897. The publication of this work at that time was a real "life-saver" to many young chemists who were starting out in works laboratories. Many a young man who was greatly puzzled and almost in despair regarding some chemical problem which he was expected to solve and of which he had never heard, or who was required to perform some analysis which had never been mentioned at college, found his salvation in "Stillman." The great practical value of this work is further shown by the subsequent editions which have been called for. At the time of his death, Dr. Stillman was working on a new edition of his "Engineering Chemistry," which he planned to be his life's greatest work. He was also the author of a smaller work on the "Examination of Lubricating Oils," published in 1914.

During the course of his work, Dr. Stillman was granted quite a number of patents, several of which have proved of considerable importance.

Dr. Stillman was an enthusiastic student of genealogical matters, and devoted much attention to genealogical research. He came of one of the oldest and most highly respected families of New Jersey; he was a member of the Sons of the Revolution, the New York Chapter of the Society of Mayflower Descendants, being a direct descendant of Elder William Brewster of the "Mayflower," and a member of the Order of Washington.

Personally, Dr. Stillman was one of the most genial, kind-hearted and unselfish of men. Always cheerful and full of life, he was one of the popular professors at Stevens. Few men are as fortunate in having so many friends as Dr. Stillman, and in his death each one will feel a deep personal loss.

He is survived by his widow, and by a daughter and two sons.

FRANCIS J. POND

# NOTES AND CORRESPONDENCE

## ON MANUFACTURE OF TURKEY-RED OILS FROM FATTY ACIDS

*Editor of Journal of Industrial and Engineering Chemistry:*

In an article in *Chemical Abstracts*, 9 (1915), 1400–1401, entitled "Manufacture of Turkey-red Oils from Fatty Acids," F. Erban mentions the results of three experiments as "low degree," "medium degree," and "high degree" of sulfonation; each of these produced an unsatisfactory product, inasmuch as neither one was wholly soluble and this indeed is the property sought.

The writer has read and heard of a great number of experiments made on the production of a soluble sulfonated oil, some of which were attended by explosions, while others produced dark brown and only partly soluble products. The cause of these failures he attributes to the fact that too much attention is paid to the proportion of oil and acid used and entirely too little attention to the mode and manner of mixing.

1—The temperature of the mixture must not be allowed to rise above 40° C. This is best controlled by surrounding the vessel by water.

2—And one of the most important points of all, the acid should be allowed to run into the oil very, very slowly and the mixture constantly stirred. When manufacturing in fair-sized quantities, this should be a matter of hours. In laboratory experiments the acid should be in a burette and allowed to run in very slowly, drop by drop, while the mixture is stirred constantly. The grade of the product produced depends to a very great extent upon the care exercised in this stage of the process.

3—The product should be washed thoroughly, three or four times, at least, with a saturated solution of common salt. This will wash away the free sulfuric acid.

If the mixture is not constantly and thoroughly stirred the product will be darker and not wholly soluble; practically the same effect is caused by an incomplete washing.

The finished product has an acid reaction. It can be used in this state, made neutral, or slightly alkaline as desired.

The slightly acid product is best when employed for treating animal fibers, as it preserves the luster of the fiber and at the same time produces a silk-like handle.

For vegetable fibers the slightly alkaline product is preferable as it is a very good cleansing agent and also produces a wonderfully soft handle.

In the writer's experiments and manufacture on a small scale of Turkey-red oil, four parts by weight of castor oil were used to one part by weight of sulfuric acid, sp. gr. 1.84.

The writer hopes this information may be a help to other chemists

Wm. J. Schepp
*Chief Chemist and Textile Expert*
National Cloak & Suit Co.
New York City, May 29, 1915

## A NEW NATIVE DYE WOOD

The yellow Locust tree, *Robinia pseudocacia* L., grows abundantly in the Middle States, Virginia and North and South Carolina, and is highly valued as a strong, even-grained, permanent timber. It is also much used for the manufacture of small, hard wood objects.

In a factory working this wood, it appeared desirable to discover some better disposal for the sawdust and chips than of their use as fuel.

Upon extracting the sawdust by prolonged digestion with hot water, a brown liquor is obtained which affords decided colors with the common mordants.

Through the kindness of Messrs. Jno. H. Heald & Company, manufacturers of tanning extracts, Lynchburg, Va., a test of this sawdust has been made. This report states that the "amount of soluble is only about one-third that of black oak bark, so that the yield of dye extract would be low. The dyeing power of this is, however, quite strong, as, using the same amount of the locust sawdust as black oak bark, the locust gives the deeper color."....The colors afforded with mordants are similar to those obtained from black oak, or Quercitron bark. With manganese a strong umber-brown is obtained, and with alum, a bright, strong, yellow, khaki color.

As locust wood is so very hard, it would not prove profitable to chip it for this purpose, but when a supply of sawdust or chips from turning is available, it may prove of advantage to employ it for dyeing in place of Quercitron bark.

F. P Dunnington
University of Virginia
June 14, 1915

## NOTE ON THE DETERMINATION OF ALUMINUM OXIDE AND TOTAL ALUMINUM IN STEEL

It has long been known that aluminum oxide when freshly precipitated is readily soluble in acids and when strongly ignited is very difficultly soluble in acids.

When metallic aluminum is added to steel while casting, its tendency is to unite at once with the oxygen existing in the steel, both as metallic oxides and as CO gas. The products of this reaction are $Al_2O_3$, the metals of the oxides reduced, and carbon. Since in regular practice there is only sufficient aluminum added to "quiet the steel," the aluminum added is nearly all converted to the oxide $Al_2O_3$. This aluminum oxide is, during the operation, heated to the temperature of pouring steel, about 1600 to 1650° C. (2912° to 3000° F.), whereby it is rendered almost entirely insoluble in dilute hydrochloric acid.

In order to test the effect of high temperature on the solubility of $Al_2O_3$ the following experiment was carried out: 10 grams metallic aluminum were dissolved in hydrochloric acid, boiled low and replaced three times with nitric acid. This solution of aluminum nitrate was evaporated to dryness to drive off acid fumes; the residue was transferred to a platinum dish and placed into a muffle furnace where the temperature was gradually raised to a high heat, taking out a portion at intervals, and noting the temperature each time with a Scimatco optical pyrometer. Portions of aluminum oxide were removed at 815, 900, 980, 1065 and 1150° C. Solubility tests were made by taking 1 gram of each portion and digesting for one hour with 100 cc. hydrochloric acid (1 : 1), filtering, and determining $Al_2O_3$ in the filtrate.

| Portion heated to | 815° C. | 900° C | 980° C | 1065° C | 1150° C. |
|---|---|---|---|---|---|
| Gram soluble $Al_2O_3$ | 0.9317 | 0.3962 | 0.2337 | 0.0472 | 0.0390 |

The increase in temperature was at the rate of 8 to 10 minutes between observations. Another portion of the same $Al_2O_3$ prepared above, was placed in a boat in the silica tube of an electric furnace and held for one hour at a temperature of 1000° C.; 1 gram of this was treated as above with 1 : 1 hydrochloric acid and showed 0.0285 gram soluble $Al_2O_3$. One gram alundum, 120 mesh, was treated with hydrochloric acid as above and showed a mere trace of soluble $Al_2O_3$.

The solubility diminishes with increase of temperature and length of time to which the $Al_2O_3$ had been exposed to the heat. If $Al_2O_3$ exposed to 1000° C. will yield 2.85 per cent of its $Al_2O_3$ content, and alundum exposed to a little over 2000° C. yields a trace, it is safe to assume that the $Al_2O_3$ formed in molten steel would yield only 1 or 2 per cent of its content on treatment

with dilute hydrochloric acid, which on such low figures as obtain with percentages of $Al_2O_3$ in steel is certainly negligible.

The above assertion has been borne out in practice, by adding just enough aluminum to deoxidize the steel, avoiding an excess. By employing the method as given below on such steels, all of the aluminum was found to be in the insoluble residue as oxide.

The method is as follows: Dissolve 50 grams drillings in a mixture of 200 cc. strong hydrochloric acid and 300 cc. water at gentle heat, bring to a boil, allow insoluble matter to settle and filter through a double Baker & Adamson grade A paper or Schleicher & Schüll No. 590, and wash with hot dilute (1 : 2) hydrochloric acid and hot water. Ignite the residue in a platinum fusion crucible. Add $^1/_2$ gram pure sodium borate[1] calcined, and heat gently a few minutes till $Al_2O_3$ is in solution. Now add 5 grams pure sodium carbonate and fuse a few minutes longer until all is melted and in a state of quiet fusion. Dissolve fusion in hot water in a platinum or nickel dish, and determine $Al_2O_3$ in the usual manner.

In the filtrate the Al is directly precipitated as phosphate according to Wöhler, as described by Blair. The precipitate is dissolved in $HNO_3$, any chromium oxidized by boiling with $KMnO_4$, and the Al precipitated from the Cr, Cu, etc., with ammonia. This precipitate is dissolved in HCl, evaporated to dryness to separate $SiO_2$, and in the filtrate the Al is again precipitated as phosphate as before.

SAUCON PLANT, BETHLEHEM STEEL COMPANY
SOUTH BETHLEHEM, PA., April 19, 1915 F. O. KICHLINE

## NOTE ON THE DETERMINATION OF SULFATES IN BREAD

In view of the adoption by a certain prominent baking concern of the use of calcium sulfate as an auxiliary to the leavening process, the writer has recently had occasion to estimate the proportion of sulfates existent in a number of samples of bread.

It was soon found that for purposes of accurate comparison between the sulfated and non-sulfated loaves the ordinary procedure, based upon precipitation of the ash solution, was practically worthless. Ignition with calcium acetate, according to the A. O. A. C. official method, afforded results apparently too high, due, it was assumed, to oxidation of organic sulfur. Extraction of the charred ash promised no better, the results thus obtained being exceedingly erratic. The procedure finally followed consisted in direct precipitation of the filtered extract of the bread as obtained with dilute hydrochloric acid.

While the literature was not consulted at the time, the writer has since been interested to note that other workers have encountered similar difficulty in connection with the estimation of sulfates in flour. Thus O'Sullivan (*Analyst*, **1914**, p. 425) refers to the unreliability of $SO_3$ determinations based upon the use of the ash for liquors, his conclusion being that sulfuric anhydride is expelled on ignition in the presence of any appreciable amount of magnesium, unless a carbonate is present. In the same number (p. 429) Cripps and Wright, working upon flour, ascribed low results as obtained by them to the presence of acid phosphates, developed during ashing.

The method followed by the latter chemists consisted in the cold extraction of 100 grams of the flour with 1000 cc. of 1 per cent acetic acid, the decanted extract being acidulated with HCl, boiled, nearly neutralized, and after removal of proteids with Almen's tannin reagent, precipitation with $BaCl_2$ as usual

In a more recent paper upon the same subject Elsdon (*Analyst*, **1915**, p. 142) describes a procedure nearly identical with that as followed by the present writer. Elsdon's process consists in the extraction of 10 grams of flour with 25 cc. concentrated HCl in a beaker on the top of a water bath, the filtered extract being directly precipitated with $BaCl_2$ after dilution with 100 cc. of water. Results thus obtained on normal flours were distinctly higher than by the acetic acid extraction.

[1] It is generally impossible to decompose all the $Al_2O_3$ by a sodium carbonate fusion alone.

While the use of concentrated hydrochloric acid as applied to bread examination had been tried by the writer, some little trouble was experienced due to progressive precipitation of proteids. A seemingly more preferable procedure consisted in the use of dilute HCl, the method finally adopted being as follows: Twenty-five grams of the air-dry ground bread were digested for 2 to 4 hours on the top of the water bath at gentle heat with 200 cc. of 5 per cent HCl, the mixture being well stirred at intervals. After cooling, the clear extract was decanted through a folded filter, the residue washed two or three times with warm water, and the filtrate precipitated as usual with $BaCl_2$. As a rule, the precipitated sulfate was clean. In those cases where it showed contamination with organic matter, the $BaSO_4$, after ignition and weighing, was treated in the Gooch with a few cc. of acidulated hot water, followed by a second ignition and weighing.

While time did not permit any elaborate confirmation of the accuracy of the above procedure, it seems evident at least that the application of the general principle of direct extraction of $SO_3$ in connection with materials of this nature is necessary for truthful results. In view of present commercial practices it would seem that the matter of an accurate method in this connection is worthy of special study.

N. H. LABORATORY OF HYGIENE
STATE BOARD OF HEALTH
CONCORD, N. H., May 15, 1915 CHARLES D. HOWARD

## THE EXACT DILUTION OF LIQUID REAGENTS BY FORMULA

*Editor of the Journal of Industrial and Engineering Chemistry:*

That "there is nothing new under the sun"—at least as regards mathematical formulas—finds still further illustration in a note appearing in the April issue of the Journal, under the caption "To Change the Specific Gravities of Solutions." Here Mr. Bovard suggests a formula for determining the amount of water to be added to a given volume of solution of specific gravity S to bring such to a specific gravity $S_1$.

In an article under the above heading in the *J. Am. Chem. Soc.*, **19** (1897), 587 the writer gave the complement of the above formula, *i. e.*, to what volume ($V_t$) must a given volume ($V_x$) of solution of specific gravity $S_1$ be diluted in order to secure a density of $S_2$, the formula being $V_t = \frac{V_x(S_1 - 1)}{S_2 - 1}$.

And conversely, the formula $V_x = \frac{V_t(S_2 - 1)}{S_1 - 1}$ gives the amount of solution ($V_x$) to be diluted to a required volume $V_t$, where the specific gravities are respectively $S_1$ and $S_2$.

A third formula represented the problem involved where it is desired to dilute to a certain specific gravity with some reagent other than water, it being directed to first consider water as the diluting agent and find $V_i$ as above. Then, if $S_3$ is the specific gravity of the diluting reagent, $\frac{V_i - V_x}{S_3}$ = the volume of the same necessary to be added to $V_x$ to give a liquid of the specific gravity required ($S_2$).

STATE LABORATORY OF HYGIENE
CONCORD, N. H., April 26, 1915 CHARLES D. HOWARD

## REAGENTS FOR USE IN GAS ANALYSIS

### I. ALKALINE PYROGALLOL—A CORRECTION

On page 595 of the article under the above title, THIS JOURNAL, 7 (1915), 587, the statement "by dissolving 87.5 g. of stick sodium hydroxide in 900 cc. of water" should read "by dissolving 87.5 g. of stick sodium hydroxide in 100 cc. of water."

CORNELL UNIVERSITY
ITHACA, N. Y., July 31, 1915 R. P. ANDERSON

# PERSONAL NOTES

The 34th Annual General Meeting of the Society of Chemical Industry was held at the Municipal School of Technology, Manchester, England, July 14–17, 1915, the President, Prof. G. G. Henderson, presiding. The program included the regular Presidential address and papers by the following speakers:

SIR WILLIAM H. LEVER, BART—Co-partnership in Chemical Industries
DR. M. O. FORSTER, F.R.S.—Research and Chemical Industry
CHARLES CARPENTER—Research in Technology
HENRY E. ARMSTRONG—The Development and Control of Industry by Public Influences
G. T. BEILBY, F.R.S.—Chemical Engineering
WALTER F. REID—The Economic Utilization of Coal and the Production of Cheap Power

A visit was made to Trafford Park where the members were shown the Cotton Safes, the plants of the Ford Motor Company and the British Westinghouse Electrical Manufacturing Company and the iron works of Messrs. Redpath, Brown & Company. Excursions were also conducted to the Manchester Sewage Works, the Salford Corporation Sewage Works and the Manchester Corporation Electricity Undertaking.

The 1916 meeting will be held in Edinburgh, Scotland.

John N. Swan announces that he has resigned his position in Monmouth College, Illinois, and has accepted the head professorship in chemistry in the University of Mississippi.

Dr. Otto Kress has been appointed to take charge of the pulp and paper investigations at the Forest Products Laboratory, Madison, Wisconsin, and it is expected that he will take up the work there on September 1st. The position was made vacant by the recent resignation of Mr. O. L. E. Weber.

Elwyn E. Snyder, Jr., has been appointed assistant in industrial chemistry at the Massachusetts Institute of Technology.

Coal operators and miners in western Pennsylvania and West Virginia paid tribute on July 15th to the memory of Dr. Joseph A. Holmes, late chief of the United States Bureau of Mines, whose funeral was held in Washington on that day. Many mines suspended their work for an hour. The Pittsburgh Experiment Station of the Bureau was closed.

Mr. J. C. Wm. Greth, manager of the Water Softening and Purifying Department of Wm. B. Scaife & Sons Company, Pittsburgh, for the past thirteen years, died on August 7th, aged 41 years. The deceased was a member of the American Chemical Society, American Society of Mechanical Engineers, American Society of Civil Engineers, American Institute of Chemical Engineers, Engineers' Society of Western Pennsylvania, Pittsburgh Commandery, No. 1, Knights Templar, Syria Temple A. A. O. M. S., University Club and Duquesne Club, Pittsburgh. His widow and two sons, William and Walter Greth, survive. Mr. Greth was an expert in the water-softening and purification art and contributed very materially to its advancement.

The D. M. Bare Paper Company, Roaring Springs, Pa., have retained Richard K. Meade, of Baltimore, Md., to prepare plans and to superintend the construction of a lime recovery plant. The system employed will contain a number of novel features not heretofore incorporated in such plants. The construction will be of the most substantial type and the buildings of steel. The kiln will be a giant revolving cylinder 6 ft. in diameter and 100 ft. long, and the lime as it falls red hot from this kiln will be automatically cooled and conveyed to the lime house. All of the machinery will be motor-driven.

John Ulric Nef, head of the department of chemistry in the University of Chicago, died on August 13th at the age of fifty-three years.

Edward W. Parker, whose resignation as Chief of the Bureau of Statistics of the United States Geological Survey was announced last May, is now in charge of the Anthracite Bureau of Information, supported by the anthracite mining operators of the United States, with offices at 1032 Miners Building, Wilkes-Barre, Pa. The work of this bureau has been combined with that of the Bureau of Anthracite Coal Statistics, which was formerly under the direction of the late W. W. Ruley, and since his death in charge of A. A. Armstrong. Mr. Armstrong will remain in charge of that portion of the work.

Dr. J. F. Eykman, professor of organic chemistry at Groningen, Holland, has died at the age of sixty-four years.

On July 23rd, Major E. Herrera, Chief of the Spanish Royal Flying Service, and Major Garrido, S. R. A., members of the Army and Navy Commission recently appointed by Spain and now in this country to investigate and purchase supplies, accompanied by Henry S. Moos, purchasing agent for the Spanish Government, visited the Edison Storage Battery Co., Orange, N. J., under the conduction of H. L. Barnitz, an authority on the production of oxygen and hydrogen gases. They were taken through the works by R. A. Bachmann, Vice President, and M. R. Hutchison, the personal representative of Mr. Edison, and were later entertained by Mr. Edison. A luncheon was given the party at the Essex Club.

Mr. C. W. Dyson Perrin, of Malvern, England, a former member of Queen's College, Oxford, has offered the sum of £25,000 for the furtherance of instruction and research in chemistry in the University of Oxford. This is in addition to £5,000 given by him two years ago towards the construction of a new Oxford chemical laboratory which is nearing completion.

Liverpool University has received a sum of £10,000 from Mr. Heath Harrison, the shipowner, for the endowment of the Chair of Organic Chemistry recently established by the Council and filled by the appointment of Prof. R. Robinson, of the University of Sydney.

Dr. Frederick Burr La Forge, of the staff of the Rockefeller Institute for Medical Research, has been appointed expert in organic chemistry in the U. S. Department of Agriculture.

Dr. Robert P. Calvert, former instructor of chemistry in Columbia University, has accepted the position of Director of the Laboratory of General Chemistry at the Experiment Station of the du Pont Powder Company, Wilmington, Delaware.

Dr. M. X. Sullivan has resigned from the Division of Soil Fertility of the U. S. Department of Agriculture, Washington, D. C., and has accepted the position of bio-chemist of the U. S. Public Health Service. Dr. Sullivan will be engaged in the biochemical study of pellagra with headquarters at the pellagra hospital, Spartanburg, S. C.

The U. S. Navy Department has awarded to the International Oxygen Company of New York the contract for the erection of a hydrogen generating plant for ballooning purposes at the Aeronautic Station of the Navy Yard at Pensacola, Florida. The International Oxygen Company has also received the award from the Government for the installation of an I. O. C. System for generating oxygen and hydrogen at the Washington Navy Yard, Washington, D. C.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### BUREAU OF MINES

**Occurrence of Explosive Gases in Coal Mines.** N. H. Darton. Bulletin 72. 248 pp. Paper, 35 cents. "The purpose of the investigation was to obtain information on the origin of the inflammable gases in coal and the conditions under which they occur. It was especially intended to ascertain whether there was any relation between the occurrence of gas and the structural or other geologic features of the coal beds. To this end many months were spent in mines and much time was devoted to the examination of mine maps, bore-hole records, and other data made available by the kindness of various coal companies. Two fields of work were selected—one in the northern anthracite basin of Pennsylvania, where the beds are considerably flexed, and the other in the southern part of the bituminous coal field of Illinois, where the beds lie nearly horizontal.

"In order to take advantage of results of previous investigations of the same general subject, an extended examination was made of reports of various investigators in Europe and America. A digest of the information obtained from these publications is included in the first part of this report, which constitutes an introduction to the discussion of the conditions governing the occurrence of inflammable gas in coal beds."

**The Production of Barytes in 1914.** James M. Hill. Separate from Mineral Resources of the U. S., 1914. Part II, pp. 61–65. In 1914 the production of crude barytes in the United States was 51,500 short tons valued at $150,000. This represented an increase of 6,000 tons but a decrease of $500,000 in value. The sources of the barytes is indicated in the following table:

Production of Crude Barytes in 1914, in Short Tons

| State | Quantity | Value | Av. price per ton |
|---|---|---|---|
| Missouri | 33,317 | $112,231 | $3.37 |
| Tennessee and Kentucky | 8,932 | 14,393 | 1.61 |
| Other States(a) | 9,298 | 27,091 | 2.91 |
| Total | 51,547 | $153,715 | $2.98 |

(a) Includes Alabama, California, Georgia, North Carolina, South Carolina and Virginia.

The value of the imports of barium compounds in 1914 is evident from the following summary:

| | |
|---|---|
| Barium carbonate—natural | $ 8,084 |
| Barium carbonate—manufactured | 36,305 |
| Barium binoxide | 332,709 |
| Barium chloride | 68,866 |
| Blanc-fixe, or artificial barium sulfate | 32,619 |
| Total | $478,583 |

The characteristics of barytes and the uses and occurrences of the ore and trace conditions are discussed.

**The Production of Phosphate Rock in 1914.** W. C. Phalen. Separate from Mineral Resources of U. S., 1914. Part II, pp. 41–56. The marketed production of phosphate rock in the United States in 1914 was 2,700,000 long tons, valued at $9,600,000. This was a decrease of 12 per cent in quantity and about 19 per cent in value as compared with the previous year. The production by principal countries of the world, the domestic phosphate reserve, and methods of mining and preparation of he rock are discussed; and the uses of ground phosphate rock re described. In addition to summaries of imports of potassium nd sodium salts used for fertilizer, the following table is given howing the principal fertilizer material imported for consumption n the United States in 1914, expressed in long tons.

| Fertilizer | Quantity | Value |
|---|---|---|
| Apatite | 20 | $ 300 |
| Bone dust of animal carbon, and bone ash, fit only for fertilizing purposes | 36,000 | 892,529 |
| Calcium cyanamid or lime nitrogen | 21,793 | 1,119,785 |
| Guano | 25,335 | 761,562 |
| Kainit | 313,898 | 1,551,115 |
| Manure salts, including double manure salts | 168,969 | 1,846,475 |
| Phosphates, crude | 15,079 | 136,526 |
| Slag, basic, ground or unground | 9,199 | 105,272 |
| All other substances used only for manure | 171,603 | 507,875 |
| Total | 761,896 | $9,921,439 |

**Strontium.** James M. Hill. Separate from Mineral Resources of the U. S., 1914. Part II, p. 66. During 1914 apparently no strontium was mined in the United States. It is estimated that not more than 2,000 tons of strontium-bearing materials are needed yearly to meet the trade requirements of this country at the present time. Strontium finds practically its only use in this country, except as a drug, in fire works and night signals. "It is understood that at present much of the strontium nitrate used in the manufacture of fireworks and night signals is made from English ores that are delivered in Philadelphia and other eastern ports at so low a cost that domestic ores cannot successfully compete with them."

### SUPERINTENDENT OF DOCUMENTS

**Soils and Fertilizers.** Price List 46, 8th edition. 26 pp. This is a list of the publications sold by the Superintendent of Documents in which soils and fertilizers are described and discussed in their various aspects.

### PUBLIC HEALTH SERVICE

**Pennsylvania Pharmaceutical Association.** Martin I. Wilbert. Public Health Reports, **30** (July 23), 2161–4. In the report of the proceedings of this meeting there is mentioned an interesting resolution adopted by this Association urging the use of the word "mils" as the designation for a one-thousandth part of a liter. This resolution was brought about by the diversity of practice in abbreviating the words "cubic centimeter" and because of the fact that the "cubic centimeter" is not exactly equivalent to the thousandth part of a liter.

**Embalming—A Satisfactory Method of Performing.** Edward Francis. Public Health Reports **30,** 2223–6. This article includes a table of results showing the instability of **formaldehyde** solution in air in the presence of various alkalies, as contrasted with the stability in the presence of borax.

**Sanitary Legislation.** The weekly numbers of the Public Health Reports include summaries of court decisions and new state and municipal regulations pertaining to public health. Very frequently these contain portions of chemical interest. The following paragraphs mention legislation reported in the July numbers of this year. The pages indicated are those of Public Health Reports, Vol. 30.

**Foodstuffs—Guaranty of Manufacturer or Dealer—Food and Drugs Laboratory Established.** California, Act of April 23, 1915. P. 2038. The previous act establishing a state laboratory for analysis of food and drugs is amended.

**Milk and Milk Products—Definitions—Pasteurization.** California, Act of May 4, 1915. P. 2039. This amends the definitions of milk and milk products which have previously been in force in this State. Definitions are given for the following: Milk, skim milk, condensed milk or evaporated milk, condensed skim milk, cream, evaporated or clotted cream, milk

fat or butter fat, butter, cheese (including full-cream, full-milk and half-skim cheese), buttermilk, ice cream, fruit ice cream, nut ice cream, and ice milk. The conditions under which pasteurization must be carried out are also defined.

**Cold Storage—Definition, etc.** California, Act of May 19, 1915. P. 2042. This is a revision of the regulations defining cold storage as applied to foodstuffs.

**Pasteurization of Milk and Cream.** New Jersey, Chapter 285, Act of April 13, 1915. P. 2146. This act gives the Board of Health of the State of New Jersey power to adopt rules regarding the pasteurization of milk and cream.

**Meat and Meat Products—Use of Preservatives from which Sulfur Dioxide Can Be Liberated, Prohibited.** New Jersey, Chapter 74, Act of March 24, 1915. P. 2146. This includes the following paragraph: "No person shall distribute or sell, or have in his possession with intent to distribute or sell, any meat or meat product to which any sodium sulfite, sodium bisulfite, or any drug, chemical, chemical compound, or preservative, from which sulfur dioxide can be liberated, has been added thereto or mixed therewith."

**Nonalcoholic Drinks—Adulteration and Misbranding.** New Jersey, Chapter 357, Act of April 20, 1915. P. 2153. This defines the nonalcoholic drinks and prohibits the sale of any nonalcoholic drink containing any one of a large number of preservatives and other substances listed.

**Vinegar.** Massachusetts, Chapter 239, Act of May 10, 1915. P. 2199. This is a revision of the section defining the legal limits for the properties of vinegar.

**Milk and Cream.** Newport News (Virginia), Regulation of the Board of Health, March 5, 1915. P. 2212. This regulation prohibits the sale of milk which does not score at least 75 per cent according to the methods of State and Federal authorities.

### BUREAU OF STANDARDS

**Investigation of the Durability of Cement Drain Tile in Alkali Soils.** R. J. Wig and Others. Technologic Paper 44. 56 pp. This is the report on the first year's tests which have been carried out by the Bureau of Standards in coöperation with the Chief of Drainage Investigations of the Department of Agriculture, the Engineer of the United States Reclamation Service, and the Association of American Portland Cement Manufacturers. The results of a number of laboratory tests and extended field investigations are given. The importance of care in selection of materials and in the fabrication of the cement tile is emphasized.

### COMMERCE REPORTS—JULY, 1915

Conditions in the Swedish **iron industry** have improved. (P. 10.)

Efforts are being made to establish a **cyanide** factory in Russia, for the benefit of the gold mining industry. (P. 21.)

A new **gas plant** is to be erected in Colon, from which the gas will also be piped to the City of Panama. (P. 46.)

The price of **gas** from the municipal plant of Nottingham, England, ranges from $0.36 to $0.60 per 1000 cubic feet. A marked increase in the consumption of gas for industrial purposes is noted. A chemical works is maintained for the recovery of the by-products. (P. 50.)

Efforts are being made to promote the cultivation in Florida of the **Chinese wood oil** tree (*Aleurites cordata*) from the nuts of which the Chinese wood oil is extracted. The United States imports annually 5,000,000 gallons of this oil valued at $2,000,000; it is used in the **varnish** industry. (P. 76.)

The annual production of **paper** in the United States is over $300,000,000 as given in a report of the Bureau of Foreign and Domestic Commerce upon "The Paper and Stationary Trade of the World." Annual exports were only $21,000,000, but are increasing. (P. 83.)

The **rubber** production of the estates in the Malay States is increasing. The average yield per acre is from 300 to 350 pounds. P. 92.)

The consumption of American **cottonseed oil** in the Netherlands is increasing, due to the shortage of **copra oil, palm kernel oil, neutral lard, oleo oil,** etc. (P. 111.)

Recent rulings of the Steamboat Inspection Service include the following regarding transportation on passenger vessels. **Thermit** may be shipped in tight metal containers. **Fuming sulfuric acid** may be shipped in separately packed containers of not over 5 lbs. each; or in one lb. bottles packed with other chemicals except chlorates, etc. (P. 115.)

Norway's supply of **rutile** is insufficient to meet an increased demand in Europe so that efforts are being made to obtain Amercian rutile. (P. 130.)

Cargoes of **nitrate** are being shipped regularly from Chili to Baltimore *via* the Canal. (P. 132.)

An increased use of **cocoanut oil** in edible fats is noted. The cocoanut cake is useful for cattle food. (P. 136.)

Efforts are being made to develop the **ceramic** resources of Alberta, Canada, especially tile, pottery and fire bricks. (P. 138.)

An **artificial yeast** is being made for use as fodder in Germany, by the action of yeast and a current of air upon a solution containing sugar and ammonium sulfate. (P. 139.)

A plant for the manufacture of **carbolic acid** is being urged in Japan. (P. 139.)

Owing to abnormal conditions, the price of **linseed oil** in Netherlands is very low, while that of linseed cake has advanced. (P. 154.)

The **oil** from the seed of kapok (tree cotton) is used principally in **soap making.** (P. 173.)

The dried juice of the Philippine Papaya (*Carica papaya*) is proposed as a substitute for **pepsin.** (P. 192.)

In a summary of the American **dyestuff** situation it is stated that in many cases the situation is acute in spite of a greatly increased consumption of natural dyes. The American plants are attempting to meet the demands as rapidly as possible, especially of "direct black." Efforts to arrange for the transit of German dyes are still unsuccessful, although the supply of dyes in Germany is apparently ample for our needs. (P. 196.)

The ash of seaweed found in the Philippines yields 15 per cent of **potash.** (P. 199.)

Owing to the falling off of American imports of **barytes,** domestic supplies are being developed for the **paint** industry. (P. 202.)

Although there is a great scarcity of **thymol,** the price having risen from $1.25 to $12 per lb., there is little demand for Indian ajowan seed, formerly exported to Germany for the extraction of thymol. (P. 211.)

Efforts are being made to promote the smelting of **iron** and **tin** ores in San Luis Potosi, Mexico. (P. 216.)

Fuel **molasses** from Hawaii is proposed as a substitute for fuel oil in California. (P. 237.)

In a report by A. V. Bleininger of the Bureau of Standards upon the use of American **clays,** it is stated that heretofore European clays have been found most satisfactory in the manufacture of **glass pots** and **graphite crucibles.** While no single American plastic **fire clay** has been found that is as good as the "Gross Almerode" a good quality of clay has been found in Missouri which, when properly mixed with suitable plastic clays from other states, will probably yield satisfactory products. During the necessary period of experimentation, however, the life of the pots and crucibles will doubtless be shorter than with the European clays. (Pp. 258–60.)

The large plant of the Chili Copper Company near Antofagasta, Chili, was put in operation in May. The completed mill will have a capacity of 20,000 tons of ore per day. The low-grade **copper** ore of Chuquicamata is supposed to contain nearly 300,000,000 tons of ore with 2.1 per cent copper. The power

plant has 40,000 kilowatts capacity, using at present **fuel oil** from California. (P. 277.)

In a report by Thos. H. Norton on "Swiss Dyestuffs for American Use," it is stated that the Swiss dyestuff industry is seriously crippled for lack of crudes and intermediates, formerly obtained from Germany, but now cut off unless Switzerland agrees to stop all sales of dyes to the allies. It is, therefore, suggested that arrangements be made to furnish American raw and intermediate materials to Switzerland in exchange for finished dyestuffs. In addition, it is suggested that the services of a number of experienced Swiss dye chemists be secured to assist in the building up of an American dyestuff industry. Swiss chemists have already similarly assisted the Russian dyestuff industry. A list of over one hundred finished dyes now made by Swiss works is given. (Pp. 278–83.)

It is proposed to erect a **cement plant** near Batna, Brazil, to manufacture cement from shells and coral, and clay.

A marked increase in the price in the United States of **argols, tartaric acid** and **cream of tartar** is noted. An increased production from California is urged. (P. 299.)

A new **sugar factory** is to be erected at Binalbagan, Philippine Islands, at a cost of $1,250,000. (P. 322.)

**Wood pulp** is to be manufactured in Argentina from the tree "*Arancaria imbricata*." A paper factory is also under consideration. (P. 339.)

Further details are given of the new **steel plant** at Newcastle, Australia. (P. 346.)

The International Association for Rubber Cultivation in the Netherlands East Indies, has offered prizes for plans for **rubber** estate factories for producing "crepe" and "smoked sheet." (P. 349.)

A description of the **asphalt** and **petroleum** deposits of the Philippines, especially at Leyte and Tayabas, is given. The exact extent and applications of these materials has not been definitely determined. (Pp. 358–61.)

Steps are being taken to develop the **superphosphate industry** in Southwestern Russia. (P. 382.)

Owing to the scarcity of **dyes,** the British Felt Hat Manufacturers' Association have announced that they will not guarantee shades, penetration, or fastness of colors. (P. 389.)

Deposits of high-grade **asbestos** have been found in Western China. (P. 393.)

Gas tubing made from glue has been proposed as a cheap substitute for **rubber tubing.** (P. 399.)

Efforts are being made to develop **sugar beet** cultivation in New Zealand. (P. 409.)

Production of **matches** in Sweden is hampered by a shortage of **potassium chlorate,** formerly imported from Germany. (P. 410.)

The production of **rubber** in the Dutch East Indies is increasing. (P. 414.)

In a description of the American **wool grease** or **degras** industry it is stated that the price of crude wool grease has advanced from 2 to 8 cents per lb. Most of the American plants use the alkali-sulfuric-acid process, but a few use the solvent naphtha process. (P. 439.)

A marked increase is noted in the output of **copper** and **zinc** from British Columbia. (P. 442.)

Owing to the high prices of English **coal,** Sweden is importing considerable amounts of **coke** from Germany. (P. 446.)

Canada produces 75 per cent of its normal consumption of **clay products,** such as brick, sewer pipe and drain tile, the remainder being imported from the United States. (P. 458.)

The United States Bureau of Mines, in connection with the National Radium Institute, has extracted over 3 grains of **radium** in the form of bromide, at a present cost of $36,050 per gram of radium metal. (P. 465.)

An **oil refinery** is to be established at Sandstone in Calgary, Canada. (P. 482.)

STATISTICS OF EXPORTS TO THE UNITED STATES

GERMANY—186
Potash
Oxalic acid
Fusel oil
Glassware
Wood pulp
Earthenware
Chinaware
Gelatine
Paper stock
Pigments

BRESLAU, GERMANY—Sup. 6*d*
Aluminum
Arsenic
Glassware
Hides
Iron and steel
Paper
Porcelain
Zinc dust
Zinc oxide

STUTTGART, GERMANY Sup. 6*d*
Drugs and chemicals
Gelatine
Tar oil
Paper
Pumice stone
Silver and plated ware

BARCELONA, SPAIN—Sup. 15*c*
Antimony
Beet pulp
Antimony oxide
Argols
Barium chloride
Fusel oil
Glycerine
Lime tartrate
Potash
Saffron
Hides
Olive oil
Oleostearin
Paper stock
Cork
Salt

LEEDS, ETC., ENGLAND—Sup. 19*m*
Brass
Copper
Chemicals
Wool grease
Hides
Iron and steel
China
Earthenware
Glue
Artificial silk

SOUTHAMPTON, ENGLAND—Sup. 19*m*
China
Earthenware
Oilcloth
Pigments
Drugs
Cochineal
Galls
Milk powder
Gums
Hides
Mica
Rubber

ONTARIO—410
Pyrites

KEHL, GERMANY—Sup. 6*d*
Aluminum
Cement
Alizarin
Alum
Coal tar products
Logwood extract
Gums
Earthenware
Kainite
Phosphates
Gelatin
Glassware
Glue
Hides
Iron and steel
Barytes
Chrome (yellow?)
Paper
Artificial silk
Wood pulp

MONTREAL, CANADA Sup. 23*f*
Asbestos
Bones
Citric acid
Wood alcohol
Ammonium sulfate
Arsenic
Bone char
Calcium carbide
Creosote oil
Glycerine
Sodium nitrate
Ammonium nitrate
Apatite
Bone dust
Hides
Iron and steel
Leather
Cod oil
Paper stock
Paper
Tin
Wood pulp
Pulp wood
Zinc ore

DOMINICAN REPUBLIC—Sup. 26*b*
Copra
Hides
Molasses
Resin
Sugar
Wax

HONDURAS—Sup. 31*b*
Cocoanuts
Gold
Hides
Peruvian balsam
Rubber
Sarsaparilla
Silver
Fustic
Logwood

NICARAGUA—Sup. 34*b*
Gold
Silver
Cocoanuts
Hides
Rubber

PERU—Sup. 46*a*
Silver
Lead
Gold
Cochineal
Copper
Hides
Guano
Mercury
Sugar
Benzine
Cocoa leaves
Rubber

VENEZUELA—Sup 48*a*
Hides
Sugar
Balata
Balsam copaiba
Chicle
Gold
Rubber
Tonca beans
Fustic

KIAOCHOW, CHINA—Sup 52*e*
Dried eggs
Hides
Peanuts
Soya bean oil

TIENTSIN, CHINA—Sup 52*e*
Albumen
Beeswax
Vegetable fiber
Hides
Jute
Peanuts
Porcelain

KOBE, JAPAN—Sup. 85*d*
Soya bean oil
Camphor
Isinglass (agar-agar)
Menthol
Matches
Peanuts
Porcelain
Vegetable wax

SINGAPORE—Sup. 55*e*
Benzine
Cutch
Gambier
Gum Benjamin
Gum copal
Gum dammar
Gutta jelutong
Gutta-percha
Hides
Mangrove bark
Cocoanut oil
Resin
Rubber
Tin

AUSTRALIA—Sup. 60*e*
Coal
Hides
Tallow

ADEN—Sup. 49*a*
Gum
Hides

The **nitrate** industry of Chili is improving, the accumulated stocks being largely disposed of together with the current production. (P. 492.)

The Japanese government is planning to extend the Government **steel works** at Edamitsu. (P. 516.)

Deposits of **magnesite** containing 98 per cent $MgCO_3$ have been discovered near Lake Athir, British Columbia. (P. 517.)

A new American **sugar mill,** erected at a cost of $1,000,000 has just been opened at Monte Cristo, Honduras. (P. 524.)

A large **paper mill** has just been opened at Iroquois Falls, Ontario. (P. 527.)

Deposits of **potash salts** have been discovered near Barcelona, Spain. (Supplement 15*c*.)

The following special supplements appeared in July with statistics, etc., regarding commerce and industries.

Germany, Alsace Lorraine and Baden—6*d*.
Spain, Barcelona—15*c*.
United Kingdom, Leeds—19*m*.
Canada, Montreal—23*f*.
Honduras—31*b*.
Dominican Republic—26*b*.
Nicaragua, Bluefields—34*b*.
Peru—46*a*.
Venezuela—48*a*
Aden—49*a*
China, Kiaochow—52*e*.
China, Chungking—52*f*.
Japan, Kobe—55*d*.
Malaysia, Straits Settlements—56*a*
Australia—60*e*
Portuguese East Africa—76*a*
Zanzibar—78*a*

# BOOK REVIEWS

**Transactions of the American Institute of Chemical Engineers.** Volume VI (1913), Office of the Secretary, Cooper Union, New York, N. Y. Published by the Institute through D. Van Nostrand Company, New York, 1914. 8vo., iii + 268 pages.

The sixth volume of these Transactions is slightly smaller than the previous volume of the series. There were two less papers published in it than in the preceding one. Following the commendable system begun in the previous volume the present one starts by giving in full the papers which have been read before the Institute, together with the discussions which followed, throwing to the rear of the volume such matter as the Institute's Code of Ethics, Constitution, Committees and membership list. As in the former volume, the Proceedings of the annual meetings have been omitted entirely from this issue—a commendable procedure for brevity but a doubtful one in view of the importance of some of the Institute's work. The volume is a pleasing one and a number of the articles are illustrated.

The following addresses and papers read before the Institute are contained in the publication:

"Efficiency in Chemical Industries, The Corn Products Industry," T. B. Wagner.
"The Effect of Legislation upon Chemical Industries," T. B. Wagner.
"Distribution of Heat in the Operation of Steam Boilers," Perry Barker.
"General Efficiency in Dyehouses and Bleach Works," L. J. Matos.
"Depreciation and Obsolescence," R. K. Meade.
"Legal Control of Dangers to Health in Factories," C. F. McKenna.
"Low and Mixed Pressure Turbines," J. G. Callan.
"Import Duties on Chemicals and Their Influence on Chemical Industry," F. W. Frerichs.
"The Drying of Linseed Oil with Red Lead and White Lead," J. C. Olsen and A. H. Callaghan.
"A Peculiar Form of Lake Pollution," Wm. P. Mason.
"Relation of the Manufacturer to the Patent System," Wm. M. Grosvenor.
"Effect of Climate on Plant Location," Wm. M. Booth.
"Recent Developments in Commercial Explosives," E. A. LeSueur.
"Electrolysis: Using Supported Mercury Kathode," E. A. LeSueur.
"A Self-Dumping Filter Press," E. J. Sweetland.
"A New Filter Press," A. Burger.
"Ozone: Its Manufacture and Use," A. Vosmaer.
"Apparatus for Determining Non-Condensing Gases in Ammonia," F. W. Frerichs.
"The Present Status of the Wood Turpentine Industry," E. H. French and Jas. R. Withrow.

This volume maintains the Institute's reputation for drawing papers from a wide diversity of angles interesting to the chemical engineer. Special attention should be called to the two addresses by the retiring President of the Institute, Dr. T. B. Wagner. The addresses by retiring presidents of the Institute are notably able papers, but this year's addresses were especially able contributions to chemical engineering literature. The development of the growth of efficiency in the corn products industry by Dr. Wagner is a classic. His optimistic recounting, in the face of his own experiences, of the effect of legislation upon the development of chemical industries stamps him as a broad-minded man no matter where we stand on the "glucose question," and it should win him the thanks of all industrial chemists. A notable and somewhat exhaustive paper was the authoritative one on ozone by Vosmaer.

Although drawn from many fields the papers fall into a very few classes. The note of engineering efficiency runs dominantly through almost all and is evident in the titles of over half of them. The economics of chemical engineering is well developed by authorities, in the papers by Wm. M. Booth, W. M. Grosvenor, R. K. Meade and F. A. Frerichs. It is always refreshing to hear from a real pioneer-like the big-hearted LeSueur. The control of dangers to health receives authoritative attention from McKenna and Mason and the filter presses are discussed by Sweetland and Burger. Burger's ideas appear to be a new departure in the washing of precipitates in filter presses.

The presence of an analytical article, even if by a most genial and earnest member of the Institute, still serves to emphasize the danger to the Institute of opening into its Transactions the flood gates of Engineering Chemistry as was pointed out in the case of Volume V [THIS JOURNAL, **6** (1914), 174].

JAMES R. WITHROW

**Dyestuffs and Coal Tar Products.** By THOMAS BEACALL, F. CHALLENGER, GEOFFREY MARTIN AND HENRY SAND. Published by D. Appleton & Co., New York, 1915. Illustrated. Price, $2.75.

This book is really a monograph consisting of articles on coal tar products, synthetic dyestuffs, dyeing and printing industry, inks, modern synthetic drugs and photographic chemicals selected from the recently published book on "Industrial and Manufacturing Chemistry," edited by Geoffrey Martin. As stated in the preface the *raison d'être* of this volume is the interest aroused in these various coal tar products through the stoppage of their importation from Germany. The appearance of the book is a timely one and consequently it will certainly be of interest to manufacturers and chemists who are considering at all the possibility of manufacturing such products in this country. The volume has been rather hastily gotten together; consequently is very incomplete and sketchy in character.

The presentation of the material is made in a systematic and condensed form and the various articles really contain information of considerable value and interest. The authors, however, have relied more on text-books and the information obtainable from journals, than upon technical experience in the manufacture or handling of the products dealt with. Consequently the book deals more with information about the products than with technical matters relating to their manufacture or use. Some of the sections are rather incomplete. For instance, that on synthetic dyestuffs mentions in a very casual and brief manner the subject of sulfur dyestuffs. The chief sulfur blacks and their method of manufacture from dinitrophenol are not described. The technical details concerning the manufacture of various products are also amateurish and incomplete. Consequently the book would be rather disappointing to a manufacturing chemist who would hope to find definite directions for the preparation of coal tar products. The book in reality is more adapted to the use of students and general readers. It is a departure, however, in the right direction and it is hoped that more scientific monographs on such topics in technical chemistry will be brought out by the necessities forced upon us of looking towards the manufacture of such coal tar products as we cannot now obtain from Germany by reason of the war.

J. M. MATTHEWS

**Handbuch der Lack- und Firnis-Industrie.** By FRANZ SEELIGMANN AND EMIL ZIEKE. xvi + 1074 pp., 249 illustrations. 2nd Ed. Union Deutsche Verlagsgesellschaft, Berlin, 1914. Price, 30 marks.

The first edition published in 1910 contained 953 pages; this later edition contains 1074 pages while the arrangement remains substantially the same and an examination of the book indicates that it has been brought up to date in a satisfactory fashion. The references to the literature are full and so far as the resins and their properties are concerned, the treatment is thorough. The manufacture of varnishes is of course viewed from a European standpoint rather than that of the American manufacturer and user.

PARKER C. MCILHINEY

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Alloys: The Analysis of Non-Ferrous Alloys.** By F. IBBOTSON AND L. AITCHISON. 8vo. 238 pp. Price, $2.00. Longmans, Green & Co., London.

**Alternating Current Work.** By W. P. MAYCOCK. 8vo. 440 pp. Price, $1.50. Whittaker & Co., London

**Boiler Losses: A Study of Boiler Losses.** By A. P. KRATZ. 8vo. Price, $0.35. University of Illinois.

**Coal: Laboratory Work for Coal Mining Students.** By J. SIM AND A. M. WYLIE. 8vo. 144 pp. Price, $0.75. E. Arnold, London.

**Concrete: Engineers' Pocketbook of Reinforced Concrete.** By E. L. HEIDENREICH. 2nd Ed. 12mo. 439 pp. Price, $3.00. M. C. Clark Publishing Co., Chicago.

**Cyanide Handbook.** By J. E. CLENNELL. 2nd Ed. 8vo. 601 pp. Price, $5.00. McGraw-Hill Book Co., New York.

**Dynamos: The Standard Manual of Dynamos and Practical Application of Dynamo-Electric Machinery.** By C. K. MCFADDEN AND W. D. RAY. Revised Ed. 16mo. 168 pp. Price, $1.00. Laird & Lee, Chicago.

**Electricity in Gases.** By J. L. TOWNSEND. 8vo. 496 pp. Price, $4.75. Oxford University Press, New York.

**Engineering Mathematics.** By C. P. STEINMETZ. 2nd Ed. 8vo. 321 pp. Price, $3.00. McGraw-Hill Book Co., New York.

**Heat Engines: Die Verbrennungsmotoren.** By G. D. JERIE. 8vo. 221 pp. Price, $1.50. M. Schaefer, Leipzig.

**Heaters: Handbook of Gas Water Heaters.** By RUUD MANUFACTURING Co. 16mo 236 pp. Price, $1.00. Ruud Manufacturing Co., Pittsburgh.

**Industrial and Manufacturing Chemistry. Vol. I, Organic.** By GEOFFREY MARTIN. 2nd Ed. 8vo. 754 pp. Price, $5.25. C. Lockwood, London.

**Industrial Chemistry: Handbuch der physikalisch-chemischen Technik fuer Forscher und Techniker.** By KURT ARNDT. 8vo. 830 pp. Price, $7.00. F. Enke, Stuttgart.

**Land Drainage.** By J. L. PARSONS 8vo. Price, $1.50. M. C. Clark Publishing Co., Chicago.

**Machine Work: Textbook of Advanced Machine Work.** By R. H. SMITH. 3rd Ed. 8vo. 265 pp. Price, $3.00. Industrial Education Book Co., Boston.

**Machinery Handbook for Machine Shop and Drafting Room.** 4th Ed. 8vo. Price, $5.25. E. and F. N. Spon, London.

**Materials: Strength of Materials.** By E. S. ANDREWS. 8vo. 614 pp. Price, $2.75. Chapman & Hall, London.

**Mechanics' Complete Library of Modern Rules, Facts, Processes, Etc.** Compiled by T. F. EDISON AND C. J. WESTINGHOUSE. 16mo. 592 pp. Price, $1.00. Laird & Lee, Chicago.

**Mineralogy: Determinative Mineralogy with Tables for the Determination of Minerals by Means of Their Chemical and Physical Characters.** By J. V. LEWIS. 2nd Ed. 8vo. 155 pp. Price, $1.50. John Wiley & Sons, New York.

**Mining Costs of the World.** By E. N. SKINNER AND H. R. PLATE. 12mo. 406 pp. Price, $5.00. McGraw-Hill Book Co., New York.

**Silica: Bibliography of Fused Silica.** Compiled by A. E. MARSHALL AND W. W. WINSHIP. 24mo. 15 pp. Price, $0.25. Thermal Syndicate, New York.

**Soil Colloids: Die Bodenkolloide.** By PAUL EHRENBERG. 8vo. 563 pp. Price, $3.75. Theodor Steinkopff, Dresden

**Tables: A Selection of Tables and Diagrams from "Engineering Thermodynamics."** By C. E. LUCKE AND J. J. FLATHER. 8vo. 238 pp. Price, $1.50. McGraw-Hill Book Co., New York.

**Technical Terms Used in Bibliographies. English, Danish, Dutch, French, German, Italian, Latin, Spanish and Swedish Terms. English Terms Have Equivalents in Above Languages.** Compiled by A. F. C. M. MOTH. 8vo. 263 pp. Price, $2.25. Boston Book Co., Boston.

**Tools, Chucks and Fixtures.** By A. A. DOWD. 8vo. 304 pp. Price, $2.50. Industrial Press, Chicago.

**Turbines: Die Wasserturbinen und deren Regulatoren an der schweizerischen Landesausstellung Bern 1914.** By F. PRASIL. 8vo. Price, $1.00. Rascher & Co., Zurich.

**Test Methods for Steam Power Plants.** By E. H. TENNEY. 12mo. 224 pp. Price, $2.50. Longmans, Green & Co., New York.

**Water: Use of Water in Irrigation.** By S. FORTIER. 12mo. 255 pp. Price, $2.00. McGraw-Hill Book Co., New York.

**Water Meters: Eine Studie zur Beurteilung und fuer die Auswahl von Wassermessern.** By R. HACHE. 8vo. 97 pp. Price, $0.25. "Das Wasser," Leipzig.

**Water Purification Plants and Their Operation.** By M. F. STEIN. 8vo 247 pp. Price, $2.50 John Wiley & Sons, New York.

## RECENT JOURNAL ARTICLES

**Air-Compressors: Points about Air-Compressors.** By R. H. ROWLAND. *Power*, Vol. 42 (1915), No. 6, pp. 187–190.

**Agricultural Chemistry: Fortschritte auf dem Gebiete der Agrikulturchemie im Jahre 1914.** By PAUL EHRENBERG. *Chemiker-Zeitung*, Vol. 39 (1915), No. 72, pp. 453–455.

**Ball Bearings: Design and Performance of Ball Bearings.** By B. D. GRAY. *The Iron Age*, Vol. 96 (1915), No. 6, pp. 300–302.

**Blast-Furnace Plant Auxiliaries and General Arrangement.** By J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 8, pp. 495–499.

**Boilers: Study of Draft in Boilers.** By C. F. HIRSHFELD. *Power*, Vol. 42 (1915), No. 6, pp. 196–197.

**Brass: Use of Electricity in Melting Brass.** By H. G. DORSEY. *Iron Trade Review*, Vol. 57 (1915), No. 7, pp. 319–320.

**Cellulose: Ueber die Fortschritte der Zellstoffchemie (1913 und 1914).** By E. HEUSER. *Kunststoffe*, Vol. 5 (1915), No. 12, pp. 138–140.

**Copper: Bolivian Copper Concentration.** By F. A. SUNDT. *Engineering and Mining Journal*, Vol. 100 (1915), No. 3, p. 102.

**Copper Alloys: Fatigue of Copper Alloys.** By ERNST JONSON. *The Foundry*, Vol. 43 (1915), No. 276, pp. 311–312.

**Cupola: Scientific Operation of a Cupola.** By DAVID TOWNSEND. *Iron Trade Review*, Vol. 57 (1915), No. 3, pp. 133–135.

**Distilled Feed Water.** By C. F. HIRSCHFIELD. *Engineering Magazine*, Vol. 49 (1915), No. 5, pp. 724–730.

**Electric Furnace in the Foundry.** By W. L. MORRISON. *Iron Trade Review*, Vol. 57 (1915), No. 4, pp. 177–180.

**Ferrochromium: Zur Analyse des Ferrochroms.** By H. SCHILLING. *Chemiker-Zeitung*, Vol. 39 (1915), No. 73/74, p. 466.

**Ferrocyanides: Volumetric Estimation of Ferrocyanides.** By BERTRAM CAMPBELL. *The Analyst*, Vol. 40 (1915), No. 472, pp. 327–328.

**Flotation in Australia.** By CHARLES GALBRAITH. *Mining and Scientific Press*, Vol. 111 (1915), No. 3, pp. 83–86.

**Gasoline from Natural Gas.** By F. E. MATTHEWS. *Ice and Refrigeration*, Vol. 49 (1915), No. 2, pp. 62–64.

**Glass: Glasschmelzversuche mit Antimonverbindungen.** By L. SPRINGER. *Sprechsaal*, Vol. 48 (1915), No. 24, pp. 211–212.

**Glutinous Substances: Einfacher Apparatur zur Reinigung klebriger Materialien.** By F. F. BLICKE. *Chemiker-Zeitung*, Vol. 39 (1915), No. 67/68, p. 424.

**Heating and Ventilating Large Factories.** By O. H. BATHGATE. *The Electric Journal*, Vol. 13 (1915), No. 8, pp. 378–381.

**Insulation: Maintenance of Insulation for Low Temperatures.** By R. L. SHIPMAN. *Power*, Vol. 42 (1915), No. 4, pp. 118–119.

**Lead: Ueber eine allotrope Modifikation des Bleis.** By HANS HELLER. *Zeitschrift fuer physikalische Chemie*, Vol. 90 (1915), No. 1, pp. 761–762.

**Metal Loss in Copper Slags.** By F. E. LATHE. *Engineering and Mining Journal*, Vol. 100 (1915), No. 6, pp. 215–217.

**Metallurgy: Notes on Homestake Metallurgy.** By A. J. CLARK. *Mining and Scientific Press*, Vol. 111 (1915), No. 3, pp. 87–91.

**Nitrogen: Ueber die elektrische Aktivierung des Stickstoffs.** By A. KOENIG. *Zeitschrift fuer Elektrochemie*, Vol. 21 (1915), No. 11/12, pp. 267–286.

**Non-Combustible Substances: Ueber einige feuerfeste Spezialmassen fuer chemische und metallurgische Zwecke.** By K. ENDELL. *Chemiker-Zeitung*, Vol. 39, No. 67/68, pp. 421–422.

**Oil Hardening: Die Oelhaertung ohne Ueberdruck unter Verwendung von Nickel und seinen Verbindungen als Katalysatoren.** By W. SIEGMUND AND W. SNIDA. *Journal fuer praktische Chemie*, Vol. 91 (1915), No. 9/10/11, pp. 442–468.

**Oxygen: Effect of Oxygen on Steel Quality.** By J. A. PICKARD AND F. M. POTTER. *Iron Trade Review*, Vol. 57 (1915), No. 3, pp. 136–137.

**Paints: How Paints Prevent Electrolysis.** By H. A. GARDNER. *Iron Trade Review*, Vol. 57 (1915), No. 3, pp. 139–140.

**Papermaking: The Chemistry of Papermaking Fibers.** By J. S. BATES. *Paper*, Vol. 16 (1915), No. 18, pp. 11–14.

**Paraffin: Die wirtschaftliche Grundlagen und die Entwicklung der Paraffinindustrie und des Paraffinhandels.** *Petroleum*, Vol. 10 (1915), No. 18, pp. 685–689.

**Potash Situation.** By S. H. DOLBEAR. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 8, pp. 481–482.

**Pulp: Solution of Pulp Problems by Graphic Methods.** By W. J. MCCAULEY. *Engineering and Mining Journal*, Vol. 100 (1915), No. 3, pp. 98–100.

**Radiation: Modified System for Estimating Radiation.** By C. F. TWEED. *Practical Engineer*, Vol. 19 (1915), No. 4, pp. 205–209.

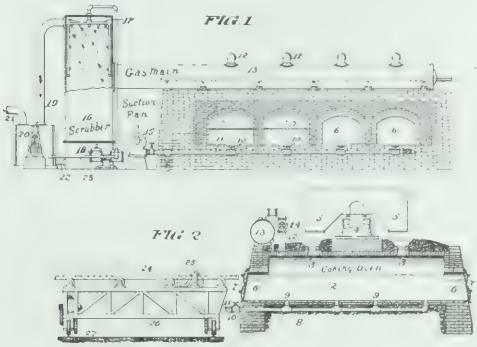
# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. Parker

Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Making Coke and Recovering By-Products. C. A. Weeks, Feb. 9, 1915. U. S. Pat. 1,127,949.** Coal is charged into the oven 2, and combustion started at the bottom assisted by a blast from the tuyères 9. The vents 3 are closed and the valves

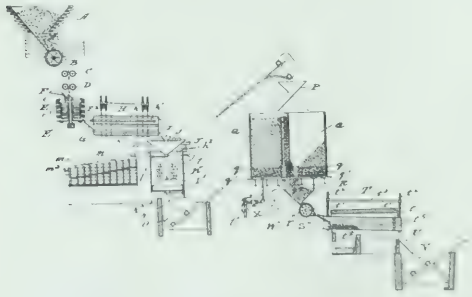



14 are opened. The gases distilled from the coal are drawn off by suction in the main 13 and pass through the scrubber or cooling tower 16 where they are subjected to the action of sprays of sulfate liquor. The gas is then passed into the suction rotary washer 20, where the ammonia not already absorbed in the tower 16 is taken up by sulfate liquor and the purified gas passed to a suitable holder.

In the distillation of the coal the volatile constituents are delivered into a common space within the oven above the coal and the suction, by means of which such constituents are drawn off, is applied to this common space whereby substantial concentration of the blast upon particular portions of the coal is avoided. The suction is continued until the coal becomes fully heated from the bottom to the top. The suction is then shut off until the coking of the coal is completed.

**Acetic Acid from Acetylene. C. Hansen and A. Weindel, Feb. 16, 1915. U. S. Pat. 1,128,780.** Acetylene is treated with a persulfate and a substance containing mercury in the presence of sulfuric acid.

**Treating Natural Phosphate-Rock. F. K. Hoover and A. J. Mason, Feb. 16, 1915. U. S. Pat. 1,128,874.** Disintegrated



mineral deposits, such as phosphate rock, are freed from clay and similar foreign matters by the addition of sufficient water to form a plastic mass, subjecting the mass to a tumbling action in the presence of an added quantity of water to suspend all the material therein and subjecting the material to uprising, classifying and rinsing currents of water.

**Hydrogen. A. Mittasch and C. Schneider, Feb. 16, 1915. U. S. Pat. 1,128,804.** A hydrocarbon and steam is passed over nickel oxid distributed on magnesia maintained at a temperature above 700° C.

**Lead Paste from Red or Orange Lead. W. Eckford, Feb. 16, 1915. U. S. Pat. 1,128,961.** A lead paste which can be stored without hardening is produced from red or orange lead by treating it with lead acetate to remove lead monoxid, washing with water and the resulting wet mass ground with oil to prevent the formation of lead monoxid.

**Peroxid of Hydrogen. F. Fischer, Feb. 16, 1915. U. S. Pat. 1,128,966.** Oxygen or oxygenous gases are forced into an aqueous solution of a suitable electrolyte under high pressure during the simultaneous generation of hydrogen in the electrolyte by electrolysis.

**Solution of Alkaline Silicates. J. G. Vail and J. D. Carter, Feb. 23, 1915. U. S. Pat. 1,129,320.** This is an alkaline solution having the property of forming substantially an insoluble product when dry, prepared by the formation of silicic acid in the presence of an excess of an alkaline silicate, preferably sodium silicate.

**Diastase. S. Fränkel, Feb. 23, 1915. U. S. Pat. 1,129,387.** This is a process for manufacturing pure diastase by removal of the carbohydrates and nitrogen-containing substances by fermentation of malt extract, comprising fermenting the extract with yeast mixed with lactic acid bacteria and neutralizing by means of an alkaline salt the lactic acid formed by the fermentation.

**Methyl Alcohol, Etc., from Wood or Other Cellulose Material. H. O. V. Bergström, Feb. 23, 1915. U. S. Pat. 1,129,542.** Cellulosic material is boiled with water containing an acid at a temperature below that at which the cellulosic material is charred and the resulting vapors led into lye prepared for use in a subsequent boiling operation. The cellulosic material is boiled with the resulting lye and, after the boiling operation, such lye is led through a column apparatus. The vapor escaping from this lye is condensed and the liquid of condensation treated for the recovery of methyl alcohol.

**Paint Composition. J. A. Unglaub, Feb. 23, 1915. U. S. Pat. 1,129,764.** The paint is composed of a pigment, boiled with linseed oil, a solution of sulfate of zinc in water, kerosene oil and water.

**Sulfite Cellulose. E. Oeman, March 2, 1915. U. S. Pat. 1,130,192.** A basic agent, sulfur dioxid and water are added to waste sulfite liquor and the waste liquor thus treated is used for boiling another quantity of wood.

**Asbestos-Containing Composition for Making Shingles. C. B. Ayers, March 2, 1915. U. S. Pat. 1,130,240.** This is an artificial stone adapted for use in sheet form, comprising a product of magnesite, chlorid of aluminum, asbestos and soap stone.

**Making and Waterproofing Paper Tubes. C. F. Lindsay, March 2, 1915. U. S. Pat. 1,130,304.** Paper tubes are treated with a partially ammonia saponified aqueous emulsion of Chinese wood oil and wax. The tubes are later heated whereby the ammonia is driven off and the oils gelatinized therein.

## BRITISH PATENTS

By D. Geddes Anderson
Chemical Engineer and Patent Chemist, Glasgow, Scotland

The following abstracts are taken direct from the patent specifications as sson as these are published by the British Patent Office. The date given at the end of the abstract is the date of acceptance.

**Aluminum Nitride. Société Générale Des Nitrures, Dec. 24, 1914. Brit. Pat. 24,533.** 30 parts of finely pulverized bauxite mixed with 12 parts carbon are added to 100 parts of coal dust, and the mixture burned in any suitable coal dust furnace. The air blown in should be in such quantity that the combustion gives almost exclusively carbon monoxide.—March 4, 1915.

**Evaporating Plant for Distillation of Heavy Liquids. K. I. Crossley and H. W. Brighton, Sept. 3, 1914. Brit. Pat. 19,392.** This invention relates to an improved arrangement of parts in stills for evaporating viscous substances, and has for its object the prevention of boiling over or frothing-up of the material. The improvement includes a restricted passage, controlled by an adjustable valve, between the still and expansion chamber; an indicator and graduated scale for determining the adjusting and setting up of the valve.

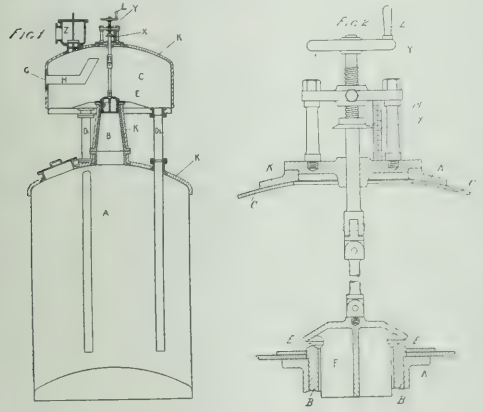


Fig. 1 is a sectional elevation of apparatus, and Fig. 2 shows a larger view of the valve which controls the restricted passage and the means for adjusting and setting the same. E is the restricted passage and F the adjustable valve.—April 22, 1915.

**Manufacture of Drying Oils from Products of Distillation of Mineral Oils. De Bataafsche Petroleum Maatschappij, Dec. 1, 1914. Brit. Pat. 23,376.** A mineral oil fraction of S. G. 0.885 at 15° C. is chlorinated in such a manner that 1,000 liters of it absorb 800 kilos of chlorine. This chlorinated product is then heated with addition of zinc dust to 290–300° C. until the chlorine has been quantitatively expelled as hydrochloric acid. An oil is obtained, the drying properties of which are comparable with those of linseed oil.—April 8, 1915.

**Waterproofing Fabrics. S. Alexander and F. Waterhouse, Dec. 8, 1914. Brit. Pat. 23,709.** The material is dipped in a solution of soap and then in a solution of an iron or copper salt which contains a certain amount of bichromate of potash. A metallic chromate is precipitated in the fabric in addition to the insoluble metallic soap.—April 8, 1915.

**Process of Producing Calcium Cyanamide. Dettifoss Power Co. Ltd., and J. H. Lidholm, Feb. 11, 1914. Brit. Pat. 3,545.** This process is based on the observation that the reaction between the nitrogen and the calcium carbide may be caused to proceed with a great output, if the nitrogen be supplied at a pressure dependent on the dilution of the carbide. By using a higher pressure the percentage of $CaC_2$ of the carbide used may be reduced.—May 11, 1915.

**Treatment of Mineral Oils and Residues for the Production of Lower Boiling Hydrocarbons. C. White, March 3, 1914. Brit. Pat. 5,434.** The oil is distributed in a liquid state over quicklime heated to a temperature of 550° C. in a retort. The vapors are drawn off under reduced pressure. With crude paraffin oil it is possible to obtain a liquid containing from 20 to 25 per cent of hydrocarbon having a boiling point equal to petrol.—May 3, 1915.

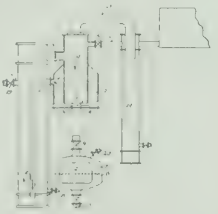
**Purification of Unsaturated Hydrocarbons Containing the Conjugated Double Bond. F. E. Matthews and E. H. Strange, March 18, 1914. Brit. Pat. 6,897.** The hydrocarbon is mixed with liquid sulfur dioxide and iodine, hydrochloric acid, or acid chlorides such as acetyl chloride, sulfuryl chloride.

The product formed is almost entirely the crystalline soluble sulfoxide, which is then decomposed by heat and the initial hydrocarbon obtained in a pure state. An example given is, 174 grams impure isoprene, 16 grams alcoholic solution of hydrochloric acid of 40% per cent strength, 198 grams liquid sulfur dioxide, are heated to 42° C. in a sealed vessel. The yield is 149 grams of pure crystalline sulfoxide.—April 19, 1915.

**Process of Bleaching Sand. J. G. A. Rhodin, April 3, 1914. Brit. Pat. 8,495.** The sand is mixed with 2.5 per cent by weight of common salt, placed in a suitable roasting furnace and heated to 1100–1200° C. for one to two hours.

The sand after this treatment has a lustrous white color and can be used with white cement for concrete work.—May 3, 1915.

**Separation of Sodium Chloride from Nitrate of Soda Solutions. Gibbs and Co., Kestner, Hobsbaum and Grigioni, May 20, 1914. Brit. Pat. 12,474.** It has been found that, by concentrating a liquid containing nitrate of soda and sodium chloride to such a point that the temperature at normal pressure is 123° C. to 124° C., the whole of the sodium chloride is rendered insoluble and precipitates out.



In figure shown, 2 is a separator in connection by pipes 3 and 4 with the calandria 1 of evaporator: 7 is a filter box with wire gauze filtering medium 8.—May 20, 1915.

**Manufacture of Cellulose Compounds. Courtnaulds Ltd., and L. P. Wilson, June 18, 1914. Brit. Pat. 14,675.** The alkali cellulose is treated with an oxidizing agent and a catalyst such as oxide or hydrate of iron, nickel, cobalt, cerium or vanadium, *e. g.*, 5 kilos of cellulose are soaked in a solution of nickel sulfate. Cellulose is then steeped in caustic soda solution in which 1 per cent of sodium peroxide has been dissolved. The alkali cellulose is then pressed to a weight of 16 kilos, milled and immediately treated with carbon bisulfide.—April 29, 1915.

**Soluble Phosphates. W. B. Bottomley, October 9, 1914. Brit. Pat. 20,788.** The mineral phosphate is finely subdivided and mixed with a small proportion of a suitable food for microorganisms, and with aerobic organisms from putrefying organic matter. The mixture is maintained at about 30° C. for a week, at the end of which period the microörganisms will have grown sufficiently to determine the alteration of the phosphate.—April 29, 1915.

# MARKET REPORT—AUGUST, 1915

AVERAGE WHOLESALE PRICES IN THE NEW YORK MARKET FOR LARGE QUANTITIES OF STANDARD CHEMICALS

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lime, gray | 100 Lbs. | 3.75 | @ | 3.80 |
| Alum, lump | 100 Lbs. | 3.50 | @ | 5.00 |
| Aluminum Sulfate, high-grade | 100 Lbs. | 1.75 | | |
| Ammonium Carbonate, domestic | Lb. | 8½ | @ | 9½ |
| Ammonium Chloride, gray | Lb | 6¼ | @ | 6½ |
| Ammonium Phosphate, commercial, 98–100% | Lb | 10 | @ | 10½ |
| Aqua Ammonium, 16°, drums | Lb | 2¼ | @ | 2½ |
| Arsenic, white | Lb. | 3¾ | @ | 4 |
| Barium Chloride | Ton | 100.00 | @ | 110.00 |
| Barium Nitrate | Lb. | 15 | @ | 16 |
| Barytes, prime white, foreign | Ton | 19.00 | @ | 23.00 |
| Bleaching Powder, 35 per cent | 100 Lbs. | 2.00 | @ | 2.25 |
| Blue Vitriol | Lb. | 7¼ | @ | 7½ |
| Borax, crystals, in bags | Lb. | 5 | @ | 5¼ |
| Boric Acid, powdered crystals | Lb. | 9 | @ | 9¼ |
| Brimstone, crude, domestic | Long Ton | 22.00 | @ | 22.50 |
| Bromine, technical, bulk | Lb. | 1.00 | @ | 1.25 |
| Calcium Chloride, lump | Ton | — | @ | 11.78 |
| Calcium Chloride, granulated | Ton | — | @ | 14.78 |
| Caustic Soda, 70 @ 76 per cent | 100 Lbs. | 4.50 | @ | 5.00 |
| Caustic Soda, powdered or granulated, 76 per cent | 100 Lbs. | 5.00 | @ | 5.50 |
| Chalk, light precipitated | Lb. | 4¾ | @ | 5 |
| China Clay, imported | Ton | 20.00 | @ | 30.00 |
| Feldspar | Ton | 8.00 | @ | 12.00 |
| Fuller's Earth, foreign, powdered | 100 Lbs. | 80 | @ | 1.00 |
| Glauber's Salt, in bbls. | 100 Lbs. | 60 | @ | 75 |
| Green Vitriol, bulk | 100 Lbs. | 70 | @ | 80 |
| Hydrochloric Acid, commercial, 18° | 100 Lbs. | 1.50 | @ | 1.75 |
| Hydrochloric Acid, C. P., conc., 22° | 100 Lbs | 2.00 | @ | 2.25 |
| Iodine, resublimed | Lb. | 4.00 | @ | 4.25 |
| Lead Acetate, white crystals | Lb. | 11⅝ | @ | 12⅛ |
| Lead Nitrate | Lb. | 11½ | @ | 12 |
| Litharge, American | Lb. | 6½ | @ | — |
| Lithium Carbonate | Lb. | 90 | @ | 1.00 |
| Magnesium Carbonate | Lb. | 5½ | @ | — |
| Magnesite, "Calcined" | Ton | 30.00 | @ | 32.00 |
| Mercuric Chloride, commercial | Lb. | 1.40 | @ | 1.50 |
| Nitric Acid, 68 per cent, sp. gr. 1.42 | Lb. | 5⅞ | @ | 6¼ |
| Nitric Acid, fuming | Lb. | 7⅞ | @ | 8¼ |
| Phosphoric Acid, sp. gr. 1.750 | Lb. | 28 | @ | 31 |
| Phosphorus | Lb. | 35 | @ | 75 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate, casks | Lb. | 21 | @ | 21½ |
| Potassium Bromide | Lb. | 23 | @ | 23½ |
| Potassium Carbonate, calcined, 80 @ 85% | 100 Lbs. | 22 | @ | 23 |
| Potassium Chlorate, crystals, spot | Lb. | 30 | @ | 31 |
| Potassium Cyanide, bulk, 98–99 per cent | Lb. | 25 | @ | 29 |
| Potassium Hydroxide | Lb. | 23 | @ | 25 |
| Potassium Iodide, bulk | Lb. | 3.70 | @ | 3.75 |
| Potassium Nitrate | Lb. | 18 | @ | 19 |
| Potassium Permanganate, bulk | Lb. | 1.10 | @ | 1.25 |
| Quicksilver, flask, 75 lbs. | | 92.00 | @ | 94.00 |
| Red Lead, American, dry | Lb. | 7 | @ | — |
| Salt Cake, glass makers' | 100 Lbs. | 55 | @ | 65 |
| Silver Nitrate | Oz. | 30⅜ | @ | 30⅝ |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash, 48 per cent | 100 Lbs. | 67½ | @ | 72½ |
| Sodium Acetate | Lb. | 4¼ | @ | 4¾ |
| Sodium Bicarbonate, domestic | 100 Lbs. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate, English | Lb. | 3½ | @ | 3⅝ |
| Sodium Bichromate | Lb. | 11 | @ | 11½ |
| Sodium Carbonate, dry | 100 Lbs. | 1.10 | @ | — |
| Sodium Chlorate | Lb. | 14 | @ | 16 |
| Sodium Fluoride, commercial | Lb. | 12 | @ | — |
| Sodium Hydroxide, 60 per cent | 100 Lbs. | | 2.25 | |
| Sodium Hyposulfite | 100 Lbs. | 1.80 | @ | 2.00 |
| Sodium Nitrate, 95 per cent, spot | 100 Lbs. | 2.35 | @ | 2.40 |
| Sodium Silicate, liquid | 100 Lbs. | 85 | @ | 1.10 |
| Sodium Sulfide, 30%, crystals, in bbls. | Lb. | 1¾ | @ | 2¼ |
| Sodium Sulfite, crystals | Lb. | 2½ | @ | 2⅝ |
| Strontium Nitrate | Lb. | 16 | @ | 18 |
| Sulfur, flowers, sublimed | 100 Lbs. | 2.20 | @ | 2.60 |
| Sulfur, roll | 100 Lbs. | 1.80 | @ | 2.15 |
| Sulfuric Acid, chamber, 60° | 100 Lbs. | 85 | @ | 1.00 |
| Sulfuric Acid, conc., sp. gr. 1.842 | 100 Lbs. | 1.25 | @ | 2.00 |
| Sulfuric Acid, oleum (fuming) | 100 Lbs. | 1.50 | @ | 2.00 |
| Talc, American | Ton | 9.00 | @ | 13.00 |
| Terra Alba, American, No. 1 | 100 Lbs. | 75 | @ | 80 |
| Tin Bichloride, 50° | Lb. | 11¾ | @ | 12 |
| Tin Oxide | Lb. | 43 | @ | 44 |
| White Lead, American, dry | Lb. | 6¼ | @ | — |
| Zinc Carbonate | Lb. | 12 | @ | 13 |
| Zinc Chloride, commercial | Lb. | 10 | @ | — |
| Zinc Oxide, American process | Lb. | 7⅝ | @ | 8⅛ |
| Zinc Sulfate | Lb. | 6½ | @ | 7 |

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid, C. P., in bbls. | Lb. | 1.10 | @ | 1.15 |
| Acetic Acid, 28 per cent, in bbls. | 100 Lbs. | 2.62½ | @ | 2.77½ |
| Acetic Acid, glacial, 99½%, in carboys | Lb. | 15 | @ | — |
| Acetone, drums | Lb. | 26 | @ | 27 |
| Alcohol, denatured, 180 proof | Gal. | 38 | @ | 39 |
| Alcohol, grain, 188 proof | Gal. | 2.60 | @ | — |
| Alcohol, wood, 95 per cent, refined | Gal. | 50 | @ | 51 |
| Amyl Acetate | Gal. | 2.90 | @ | 3.00 |
| Aniline Oil | Lb. | 1.30 | @ | 1.50 |
| Benzoic Acid, ex-toluol | Lb. | 3.00 | @ | — |
| Benzol, 90 per cent | Gal. | 85 | @ | 90 |
| Camphor, refined in bulk, bbls. | Lb. | 43 | @ | — |
| Carbolic Acid, U. S. P., crystals, drums | Lb. | 1.40 | @ | 1.50 |
| Carbon Bisulfide | Lb. | 7½ | @ | 8 |
| Carbon Tetrachloride, drums, 100 gals. | Lb. | 16 | @ | 17 |
| Chloroform | Lb. | 35 | @ | — |
| Citric Acid, domestic, crystals | Lb. | 55 | @ | 55½ |
| Cresol, U. S. P. | Gal | 1.15 | @ | 1.25 |
| Dextrine, corn (carloads, bags) | 100 Lbs. | — | @ | 3.20 |
| Dextrine, imported potato | Lb. | 10 | @ | 12 |
| Ether, U. S. P., 1900 | Lb. | 15 | @ | 20 |
| Formaldehyde, 40 per cent | Lb. | 8½ | @ | 9½ |
| Glycerine, dynamite, drums included | Lb. | 24 | @ | 25 |
| Oxalic Acid, in casks | Lb. | 39 | @ | 40 |
| Pyrogallic Acid, resublimed bulk | Lb. | 1.35 | @ | 1.55 |
| Salicylic Acid | Lb. | 2.75 | @ | 2.90 |
| Starch, cassava | Lb. | 3¼ | @ | 4 |
| Starch, corn (carloads, bags) | 100 Lbs. | 2.45 | @ | — |
| Starch, potato | Lb. | 6½ | @ | 7 |
| Starch, rice | Lb. | 7 | @ | 8 |
| Starch, sago | Lb. | 3¾ | @ | 4 |
| Starch, wheat | Lb. | 6½ | @ | 7 |
| Tannic Acid, commercial | Lb. | 70 | @ | 71 |
| Tartaric Acid, crystals | Lb. | 46½ | @ | 47 |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax, pure, white | Lb. | 42 | @ | 45 |
| Black Mineral Oil, 29 gravity | Gal. | 12½ | @ | 13 |
| Castor Oil, No. 3 | Lb. | 10½ | @ | 11 |
| Ceresin, yellow | Lb. | 10 | @ | 14 |
| Corn Oil | 100 Lbs. | 6.26 | @ | — |
| Cottonseed Oil, crude, f. o. b. mill | Gal. | 33 | @ | 34 |
| Cottonseed Oil, p. s. y. | Lb. | 5½ | @ | 5¾ |
| Creosote, beechwood | Lb. | 3.00 | @ | 4.00 |
| Cylinder Oil, light, filtered | Gal. | 20 | @ | 25 |
| Fusel Oil, crude | Lb. | 2.40 | @ | 2.50 |
| Japan Wax | Lb. | 12½ | @ | 13½ |
| Lard Oil, prime winter | Gal. | 84 | @ | 88 |
| Linseed Oil, raw (car lots) | Gal. | 50 | @ | — |
| Menhaden Oil, crude | Gal. | 35 | @ | 36 |
| Naphtha, 68 @ 72° | Gal. | 12 | @ | 13 |
| Neat's-foot Oil, 20° | Gal. | 93 | @ | 94 |
| Paraffine, crude, 120 & 122 m. p. | Lb. | 2½ | @ | 3 |
| Paraffine Oil, high viscosity | Gal. | 22 | @ | 23 |
| Rosin, "F" Grade, 280 lbs. | Bbl. | | 3.65 | |
| Rosin Oil, first run | Gal. | — | @ | 25 |
| Shellac, T. N. | Lb. | 14 | @ | 14½ |
| Spermaceti, cake | Lb. | | 25 | |
| Sperm Oil, bleached winter, 38° | Gal. | 70 | @ | — |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid, double-pressed | Lb. | 11 | @ | 11½ |
| Tallow, acidless | Gal. | 62 | @ | 63 |
| Tar Oil, distilled | Gal. | 30 | @ | 31 |
| Turpentine, spirits of | Gal. | 41 | @ | 41½ |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum, No. 1, ingots | Lb. | 33 | @ | 35 |
| Antimony, Hallets' | Lb. | 40 | @ | 45 |
| Bismuth, New York | Lb. | 3.00 | | |
| Copper, electrolytic | Lb. | 16½ | @ | 17 |
| Copper, lake | Lb. | 17¼ | @ | 17½ |
| Lead, N. Y. | 100 Lbs. | | 4.40 | |
| Nickel, electrolytic | Lb. | 50 | @ | — |
| Nickel, shot and ingots | Lb. | 45 | @ | — |
| Platinum, refined | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | | 46¾ | |
| Tin | 100 Lbs. | 34.75 | | |
| Zinc, N. Y. | Lb | | 10¾ | |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | 100 Lbs. | | 3.40 | |
| Blood, dried | Unit | | 2.45 | |
| Bone, 4½ and 50, ground, raw | Ton | | 30.00 | |
| Calcium Cyanamid | Unit of Ammonia | | 2.30 | |
| Calcium Nitrate, Norwegian | 100 Lbs. | | — | |
| Castor Meal | Unit | | — | |
| Fish Scrap, domestic, dried, f. o. b. works | Unit | 2.62½ | & | 10 |
| Phosphate, acid, 16 per cent, bulk | Ton | 8.00 | @ | 9.00 |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble, 68 per cent | Ton | | 2.25 | |
| Tennessee, 70–80 per cent | Ton | 5.00 | @ | 5.50 |
| Potassium "muriate," basis 80 per cent | Ton | 220.00 | @ | 250.00 |
| Pyrites, furnace size, imported | Unit | 10½ | @ | 11 |
| Tankage, high-grade | Unit | 2.50 | & | 10 |

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# EDITORIALS

## THE SEATTLE MEETING

The Fifty-first Meeting of the American Chemical Society was held at the University of Washington, in Seattle, August 30 to September 3, 1915.

The meeting was opened by an address of welcome from the University of Washington and the City of Seattle tendered by Dean Priest of the University. A brief response was made by President Herty. The meeting then proceeded according to the program appearing elsewhere in this issue. Dr. Herty's presidential address is given in full in the October issue of the Journal of our Society, and the addresses of Drs. Baekeland and Benson will appear in a later issue of THIS JOURNAL. The Symposium on Wood Distillation proved especially interesting and called forth much valuable discussion.

The complimentary smoker at the Commercial Club on Tuesday evening was attended by some 200 members and guests, the chief feature of the entertainment being a lecture by Prof. Meany, of the University of Washington, on Mt. Rainier, illustrated by colored lantern slides; many members who had not expected to take the Mt. Rainier trip then indicated their intention of doing so. Following this lecture was a Japanese sword contest, and several cartoons were drawn by a Chinese cartoonist.

It was decided to continue the General Meeting during Wednesday morning for the reading of papers of special interest. In the afternoon the Divisions met, and after the reading of papers, elected officers for the coming year. In the afternoon the ladies were entertained at tea by the ladies of the faculty, and some interesting Greek dances were given by some of the young ladies of the University of Washington. At 4.30 P.M. members and guests were taken for an automobile ride around Seattle. On Wednesday evening a complimentary dinner was given to the Council by the Faculty of Science of the University of Washington.

The banquet was held at the Hotel Washington, Thursday evening. The tables were profusely decorated with beautiful flowers and the food was excellent. Dr. E. C. Franklin acted as toast-master and several short speeches were made by visiting members. At 10.45 the special car left for Tacoma, whence the automobile trip to Mt. Rainier and Park started.

Leaving Tacoma at 8 A.M. in three automobiles, a party of 29 passed over seventy-seven miles of excellent road, through some of the most wonderful forests on earth, to Mt. Rainier National Park. The route passes through forests of tall Douglas Firs, extending for miles on either side; many of these trees are eight feet in diameter and over two hundred feet high. To eastern eyes, the extent and magnitude of these forests is indescribable. Reese's Camp, close to the Glaciers, afforded unusually beautiful views. It is doubtful if a more perfect day could have been found in the whole year than the one which the members enjoyed on this occasion.

At Portland, the party was met by Mr. Olmsted, Prof. Stafford and others of the Oregon Section, and conducted to the Imperial Hotel for breakfast. After breakfast the party divided into two portions, one visiting the new Gas Works of Portland where there is an almost perfect installment for converting petroleum into city gas. The remainder of the party proceeded by automobile to Oregon City and inspected the paper mills of the Willamette Paper Co., where both the guiding and sulfite processes for making newspaper are used. All of the members met for a lunch at Portland's Country Club, which equals in beauty any of the Country Clubs of the eastern states. The beautiful Club House was thrown open to the members who met a number of Portland's leading citizens. The afternoon was taken up with an automobile ride around Portland's parks and drives; all met at 4 o'clock to see the lantern slides made by Messrs. Burger and Jones showing views from Portland and from the new Columbia River Highway which is unsurpassed by any highway or drive in America. The lantern slides were truly remarkable, being made by one of the new processes of colored photography and in addition showing the photographer to be a man of unusual artistic sense. The party left at 8.15 for San Francisco; the journey afforded interesting glimpses of southern Oregon and northern California, including a fine view of Mt. Shasta.

The members were met on Monday morning at the San Francisco station by Secretary Drake, Prof. Stillman, Prof. O'Neill, Mr. Chappell, Mr. Hanks, Prof. Bray, Mr. Pilhashy, Mr. Fredenburg and others. In the evening the San Francisco Section gave a complimentary dinner at Techau Tavern to all of the visiting members. It was a grand "get together" time and old friendships were renewed on every hand. Again Dr. E. C. Franklin acted as toast-master.

Several matters of unusual importance were handled by the Council at its various sessions. By invitation of the University of Illinois, the Society will hold its Spring Meeting of 1916 in Urbana, during Easter week. It is also understood that the Annual Meeting of 1916 will be held in New York under affiliation with the American Association for the Advancement of Science.

By vote of the Council, Pres. Herty appointed a committee consisting of B. C. Hesse, *Chairman*, A. D. Little, Wm. Hoskins, B. L. Murray and Russell W. Moore to coöperate with the U. S. Government in obtaining the regular collation and publication of complete and uniform statistics in regard to foreign commerce in chemicals. The Council also requested that this committee call to its aid the editors of *The Journal of Commerce, The Oil, Paint and Drug Reporter, Metallurgical and Chemical Engineering* and THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY, and an appointee from each local section of the Society to assist in obtaining detailed and accurate facts concerning chemical imports.

As the result of the discussion brought out by Dr. Herty's presidential address, it was the unanimous sentiment of the Council that the following letter

should be sent by the President of the Society to President Wilson:

"*The President:*

"SIR:

"The following letter has been written at the request of the Council of the American Chemical Society, and has received the unanimous approval of that Body:

"During the recent meeting of the American Chemical Society at Seattle, the present situation with regard to the manufacture of dyes and other chemicals in the United States, has been under discussion. It is well known that we have been dependent on Germany for many of our most imported dyes, and that some of the textile industries using these have found themselves in a very difficult position since the outbreak of war in Europe.

"We have both the raw materials and the trained chemists essential for the manufacture of these products, but it has been found difficult to secure capital to establish the plants necessary for the supply of our needs. It need hardly be said that it is important to seize the present favorable opportunity to develop this industry in America, if possible.

"A study of the causes which at present interfere with manufactures of this class has led us to the conclusion that one of the most important is the fear that at the close of the war the new industry might be quickly destroyed by the unfair competition which arises from the sale of a foreign product at a price below that at which the same product is sold in its home market. This method of destroying a dangerous competitor has been too common in the past, and is now forbidden by law in the United States. It would seem to be possible to enact laws which will protect our manufacturers from similar practices of foreign corporations.

"It may be that some changes in our tariffs are desirable in the interest of the manufacture of dyes and other chemicals. The Council of the American Chemical Society will not venture an opinion on this point, but would suggest that this is a question which should be carefully considered by disinterested experts who are competent to examine the facts on which an authoritative opinion can be based.

"The industry to which I refer is of such importance to the industrial welfare of our country, that I would most respectfully request that in your next Annual Message you should urge upon Congress the need of legislation designed to eliminate unfair competition from foreign manufacturers. I also earnestly hope that through Congress, or otherwise, information may be secured from disinterested experts as to whether the provisions of our tariff, which relate to the manufacture of dyes, are suitable or not.

"I am sending you herewith copies of a report of a committee of the New York Section of our Society, and of my own recent address as President of the American Chemical Society, in both of which the question of the development of the manufacture of dyes in the United States is considered in more detail.

"I have the honor to be

"Very respectfully yours,

"(Signed) CHARLES H. HERTY, *President.*"

The Council voted unanimously the thanks of the American Chemical Society to H. G. Byers, H. K. Benson, E. J. Bartells, Lee A. White, J. H. Linton, C. A. Newhall, M. K. Falkenburg and Mrs. C. A. Newhall, chairmen of the local committees for the Seattle Meeting and their vote of thanks to the members of their committees for their untiring care of the members at Seattle and for their work toward a successful meeting of the Society at Seattle. Also thanks to Mr. Louis Heinrich of the Seattle Brewing & Malting Company for the courtesies extended to the visiting delegates by him; to the Commercial Club, to the faculty of the College of Science and to the faculty of the Ladies' Club for the entertainment provided by them for the members of the Society.

## ENGLAND'S TARDY RECOGNITION OF APPLIED SCIENCE

Among the duties or privileges of those who maintain a neutral mind in the present crisis of nations, is that of critically examining the behavior of the social and industrial fabrics of the several combatants under the stress of the moment. In what respects do they fail or what are the essential elements of strength of each? The war is indeed a road test of the mechanisms which the several nations have been striving to perfect. The performance of each depends both upon the quality of the materials used and the development of the detail in which they have been combined. It is proposed to consider here, certain flaws which the English seem to be locating in their own organization and the measures being taken for their remedy.

There has been for a long time in certain English circles intense dissatisfaction over the failure, not only of the man in the street, but also of the commercial and technical, and even the governing classes, to recognize the close and unescapable dependence of social and national well-being upon scientific principles, the necessity for the application of scientific discovery to the every-day life of industry, and hence the supreme importance of scientific training, supervision, and research.

The English educational system is founded upon classical ideals and controlled and self-perpetuated by the victims of its method to whom science is an intruder upon the curriculum, a disturber of the decent customs of the past.

In an address in 1861, Huxley said:

"Physical science, its methods, its problems, and its difficulties will meet the poorest boy at every turn and yet we educate him in such a manner that he shall enter the world as ignorant of the existence of the methods and facts of science as the day he was born. The modern world is full of artillery; and we turn our children out to do battle in it equipped with the sword and shield of an ancient gladiator.

"Posterity will cry shame on us if we do not remedy this deplorable state of things. Nay, if we live twenty years longer, our own consciences will cry shame on us."

H. E. Armstrong at Melbourne in August of 1914 (*Nature*, **94**, 213–19) quoting the above continues:

"Now after more than fifty years, not twenty merely, we still go naked and unashamed of our ignorances; seemingly there is no conscience within us to cry shame on us. I have no hesitation in saying that we have done but little through education to remedy the condition of public ignorance which Huxley deplored. In point of fact he altogether underrated the power of the forces of ignorance and indifference; he failed to foresee that these were likely to grow rather than fall into abeyance. In England what I will venture to term the Oxford spirit still reigns supreme—the spirit of the literary class—the medieval spirit of obscurantism, which favors a backward rather than a forward outlook."

Armstrong explains what the "Oxford Spirit" means:

"Englishmen, poor devils, have never been allowed, let alone encouraged, to study in any effective manner, either at our public schools or at the ancient universities and the opportunities have been few elsewhere. During 40 years past Oxford has been without a chemical school—how could chemists be trained there? What is far worse, the business community have received no training at our great schools and universities which has in any way helped them to become acquainted with the idea of science. We are simply victims of the literary party of which the lawyer-politician is the supreme development: he grips us everywhere. * * * * * The Oxford tradition that it is necessary to be well read and play games in the afternoon, has dominated the situation."

This system of education has necessarily imposed its results not only upon the industrial development but also upon the national domestic policies.

As John Perry [*Nature*, **94** (1914), 125–35] has said:

"It is exasperating that all the most important, the most brilliant, the most expensively educated people in England, our poets and novelists, our legislators and lawyers, our soldiers and sailors, our great manufacturers and merchants, our clergymen, and school-masters are quite ignorant of natural science; and it may almost be said that in spite of these clever, ignorant men, and men like them in other countries, through the agency of scientific men, all the conditions of civilization are being transformed.

"It is a curious kind of culture which scorns the lessons of history, the study of man in his relation to nature, the study of the enormous new forces which are now affecting the relations of nations to one another."

"The university man, ignorant of science, becomes a ruler of our great nation, his duty during war and peace being that of a scientific administrator, and without turning a hair he fraudulently accepts this important duty for which he is utterly unfit. The gods must surely laugh, when they see these rulers of ours gibing at scientific things, giving important posts to non-scientific men who scorn and obstruct the scientific men who are under their orders.

"Besides these men we have a larger number of middle class men who will succeed their fathers in the management, not merely of landed estates, but of much more valuable estates in the manufacture and distribution of things. These men become the owners of factories, the spirit of which ought to be scientific research; the competing factories in Germany, France and America are run by men of scientific method, but our owners discourage reform in every possible way. The rule of thumb of their fathers and grandfathers is good enough for them. Their factories are so badly arranged that the works cost of any manufacture is twice what it ought to be and the time taken is twice as great."

W. P. Dreaper [*Nature*, **95** (1915), 428–30] adds his testimony that:

"For reasons which are still somewhat obscure, the British manufacturer has shown in the past a distinct preference towards those industries which develop best on lines of empiricism. Many have held that this is a defect; the present has proved this to the hilt."

Quite the reverse is the situation in Germany [*J. Soc. Chem. Ind.*, **34** (1915), 765]:

"The idea of science is abroad in Germany—the Germans have the sense to employ technically trained, expert foremen, whereas we, as a rule, employ uninstructed men, whose ways are too often intensely conservative and obstructive of progress."

The attitude of the government toward science was well illustrated during the debate of "British Dyes Ltd." when the Parliamentary Secretary of the Board of Trade stated [*Nature*, **95** (1915), 58] that:

"A man conversant with the science and practice of dye manufacture was unfit to go on the directorate because as he would know something of the business, the whole of the other directors, being but business men, would be in his hands."

As Prof. Meldola points out [*Nature*, **95** (1915), 18]:

"The discussions of the government schemes in various parts of the country by dye-consuming organizations, chambers of commerce, and so forth have all centered round political or economic questions; the vital principle, *viz.*, adequate chemical control, has been subordinated or left out of consideration altogether.

"The German colour industry has been built up by the utilization of the results of research carried on in the factories and universities and technical schools for a period of more than forty years. To suppose that we can retrieve our position by starting a company, the directorate of which was to consist solely of business people, is ludicrous.

"One feature of the new scheme which the chemical profession can view with favor is the distinct recognition of research as a necessity for the development of the industry. The Government will, for ten years, grant not more than 100,000 pounds for experimental and laboratory work. That is certainly a concession which marks an advance in official opinion. It will be for the satirist of the future to point out that it required a European war of unparalleled magnitude to bring about this official recognition of the bearing of science upon industry. Who is to direct this research?"

Similar sentiments were expressed at the time by Sir William Ramsay, Sir Henry Roscoe, Mr. W. P. Dreaper, and others [*Nature*, **95** (1915), 41 and 119].

Another manifestation which is at the same time a result of the general diffusion of the "want of the *Idea of Science*" is the absolute failure to realize the service of scientific workers and pioneers with the result that few are employed in the industries of Great Britain.

Mr. Peddie [*Elec.* (L.) **74** (1915), 900] states that:

"While in Germany there was one university-trained chemist for every 15 men engaged in the chemical industry, and in Germany's industry as a whole the ratio was one to every 40 men employed, in Great Britain there was but one university-trained chemist for every 500 men engaged in the various industries."

Such a condition of affairs leads quite naturally to the situation upon which Prof. Percy F. Frankland comments in the course of a statistical review of the chemical industries of Germany [*J. Soc. Chem. Ind.*, **34** (1915), 307–16]:

"The facts which I have brought forward speak for themselves and proclaim in the most convincing manner the stupendous progress which has been made by Germany in the chemical industries during the past 40 years. It is equally certain that England, once pre-eminent for chemical manufactures, has not progressed at the same rate and is at the present moment suffering much inconvenience through being so largely dependent on German chemical products of one kind and another. The country is now reaping the harvest of humiliation which it has sown for itself in spite of the warnings repeated *ad nauseam* by the chemical profession during a whole generation.

"The same carelessness and want of foresight had even allowed us to become dependent on Germany for some of the most important materials used in explosives, *e. g.*, trinitrotoluene, and for many of the most valued drugs required alike for our Army, Navy, and civil population.

"The wretched remuneration of scientific work which has led to a general avoidance by young men of entering upon it as a profession is witnessed by publications appearing in *Science Progress* during 1914. An article in the October number of the same year (p. 197), continuing a discussion begun in April, gives figures showing that the salaries of professors average 628 pounds and of lecturers and demonstrators only 137 pounds."

More recently a protest was elicited from Sir William Tilden [*Nature*, **95** (1915), 119] by an advertisement from the Royal Arsenal, Woolwich, for a chemist with "a thorough training in inorganic and organic chemistry" and "a university graduate or member of the Institute of Chemistry" at 2£ 6d per week.

As Sir William Ramsay [*Nature*, **95** (1915), 309] says:

"The status of chemists in government employment, for example, is not such as to induce any young man who can choose any other profession to devote himself to a career of an official chemist."

Signs are not lacking that the situation and its danger have been of late receiving recognition. According to Sir Ronald Ross [*Nature*, **94** (1914), 366]:

"The war now raging will at least demonstrate one thing to humanity—that in wars at least, the scientific attitude, the careful investigation of details, the preliminary preparation, and the well thought-out procedure bring success, where the absence of these leads only to disaster. So also in everything. After all, the necessity for research is the most evident of all propositions."

As S. Roy Illingworth puts it:

"The inexorable law of the survival of the fittest is as true of nations as of animals and only those nations that are the most efficient in industry can have any chance of maintaining their entity."

Definite action for the promotion of scientific and industrial research by the British government has been begun. J. A. Pease [*Nature*, **95** (1915), 321], President of the Board of Education, following the reception of a deputation from the Royal and Chemical Societies [*J. Chem. Soc.*, **107** (1915), 974], announced in the House of Commons on May 13th, the proposed formation of an Advisory Council for the purpose. During the subsequent debate the unanimity of approval indicated that all parties are ready at last to support such action as soon as a definite policy is formulated.

The plan mentioned by Mr. Pease was that of having a committee of experts who would call into consultation such outside experts as may be desirable and act as an advisory council to consider the solution of technical problems and in this connection advise in selecting scientific workers and in apportioning and expending money for research and education. He further stated that he hoped to have an appropriation of from 25,000 to 30,000£ for the current year and this sum must undoubtedly be increased in future years.

Sir William Ramsay [*Nature*, **95** (1915), 309] has drawn up and published a draft of a scheme setting forth the functions and advantages of such a council and suggesting how its members should be chosen.

However, up to July first, no further action appears to have been taken beyond asking various eminent men to serve on the council whose chief function was apparently to be to encourage education and research.

But the feeling has been rapidly growing, always among scientific men, that the situation calls for immediate and more practical action, especially in the interests of bringing research at once to service in the war. Under the heading "Mobilization of Invention" has appeared much discussion of the matter.

Dr. J. A. Fleming [*Elec.* (L.) **75** (1915), 375] writes:

"A few days ago an eminent electrical engineer was sitting in my room here, and said to me, 'I am too old to enlist or even do manual work in the manufacture of shells, but I have a considerable scientific knowledge which I am just yearning to employ in the service of the country, yet I cannot find any person in authority who will tell me how to do it.'

"This sentence expressed concisely not only my friend's feelings, but my own, and I am confident that of hundreds of other scientific men as well. At the present moment after 10 months of scientific warfare, I myself * * * have not received one word of request to serve on any committee, coöperate in any experimental work, or place expert knowledge, which it has been the work of a lifetime to obtain, at the disposal of the forces of the crown."

Sir William Ramsay [*Nature*, **95** (1915), 519] discussed the matter further in an address at the annual meeting of the British Science Guild on July 1st, when he commented on the continuance of lack of organizations among scientific men and the failure of the government to bring forward any scheme to correct the difficulty. He points out the failure of the government to declare cotton contraband of war early in the year as one of the criminal results of bad organization and lack of scientific advice. He says:

"It is bad policy to regret what might have been; it is much better to try to devise plans to make up for lost time; and the first essential is organization. It is notorious that there is little intercommunication between the various Government Departments; many of them are confronted by the same difficulties; many of these difficulties would be overcome if scientific advice were asked for; and the prime necessity at the present moment is a central body of scientific men to whom the various Government Departments should be compelled to apply for advice and assistance.

"It is clear that we need expect no initiative from members of our Government. But we might, as scientific men, organize ourselves, and then endeavor to induce the Coalition Government to take such steps as were taken by the French Government on August 4th."

He gives as suggestive the outline of a scheme drafted for such organization of the Royal Society for assistance in prosecuting the war and comments upon the importance of extending the activities of such an organization to times of peace.

His idea is reiterated more emphatically by Armstrong [*J. Soc. Chem. Ind.*, **34** (1915), 765] in a speech at the annual meeting of the Society of Chemical Industry:

"In view of the proved inability of our Government Departments to deal with issues which are essentially scientific to appeal

for help, as nominally the Royal and Chemical Societies have done to those whom we have been forced to describe as flouting science, who hold it in disrespect on account of their entire ignorance of scientific method is a confession of failure beyond words to describe."

"Our plain duty in this Society is to organize ourselves and when we are organized to claim the right to guide Government."

In July Mr. Henderson, successor to Mr. Pease as President of the Board of Education, issued a White Paper [*Nature*, **95** (1915), 604] outlining a "scheme designed to establish a permanent organization for the promotion of industrial and scientific research" by the establishment of a single responsible body entrusted with the disbursement of a considerable fund. This consists of a Committee of the Privy Council with

".....a small Advisory Council composed mainly of eminent scientific men and men actually engaged in industries dependent upon scientific research" which shall be responsible to the Committee.

"The primary functions of the Advisory Council will be to advise the Committee of Council on:

"I—Proposals for instituting specific researches.

"II—Proposals for establishing or developing special institutions or departments of existing institutions for the scientific study of problems affecting particular industries and trades.

"III—The establishment and award of research studentships and fellowships.

"The Advisory Council will also be available, if requested, to advise the several Education Departments as to the steps which should be taken for increasing the supply of workers competent to undertake scientific research.

"Arrangements will be made by which the Council will keep in close touch with all Government Departments concerned with or interested in scientific research and by which the Council will have regard to the research work which is being done or may be done by the National Physical Laboratory.

"It is proposed to ask the Royal Society and the principal scientific and professional associations, societies, and institutes to undertake the function of initiating proposals for the consideration of the Advisory Council, and a regular procedure for inviting and collecting proposals will be established.

"All possible means will be used to enlist the interest and secure the coöperation of persons directly engaged in trade and industry.

"It is contemplated that the Advisory Council will work largely through Sub-Committees reinforced by suitable experts in the particular branch of science or industry concerned."

The first members of the Council will be Lord Rayleigh, Messrs. Beilby, Duddell, McCormick, and Threfall, Profs. Hopkinson, M'Clelland, and Meldola, and the Committee of the Privy Council consists of Lord Haldane and Messrs. Ockland and Pease.

In this way does the English Government announce at last a change of policy and propose to retrieve its past inaction. Of this scheme [*Nature*, **95** (1915), 619] remarks:

"By its inception and publication the Government acknowledges and proclaims its appreciation of the work of science, and by this acknowledgment alone gives scientific workers that encouragement and prestige in the eyes of the country which has too long been withheld."

Thus England has awakened after a most costly delay to a situation which she must probably work for years at the best to remedy, a situation which threatens not only her future supremacy but even her present existence.

Is this not a matter for us in America to give very serious and careful consideration? True, it seems to be that we have in certain respects already an advantage over England, as for instance in our Government bureaus and laboratories for research and far more in that natural flexibility of temperament which has already accorded recognition to the intellectual status and practical value of science, and evidenced this recognition by the foundation of technological schools and the introduction of scientific departments and courses in the classical colleges as well as by the endowment of research scholarships and foundations. [The benefactions to institutions of higher education in the United States amount to about $25,000,000 annually; in the United Kingdom the average is less than one-tenth this sum—*Nature*, **95** (1915), 692.]

But one has only to consider the wonderful headway which Germany has been making in the past two decades, largely the result of her carefully organized research, to realize how far we fall behind the pace that she has started and, regardless of the immediate results of the war, is likely to continue. Give to America the same mastery of the raw materials which she commands together with a similar economy and organization in their development and she need maintain no standing army to hold the supremacy of the world. It is toward this ideal that we should strive, neglecting nothing that will bring it nearer.

W. R. Whitney

## COLLECTIVE INDEXES TO CHEMICAL ABSTRACTS

In a few months *Chemical Abstracts* will enter upon its tenth volume. The completion of this volume at the end of 1916 will be the appropriate time, from an editorial point of view, for the publication of a collective index to the ten volumes of the journal. An index covering more than ten volumes would be unwieldy. To insure the prompt appearance of the index, it will be necessary for the work to be organized in the near future, and it is imperative that a decision shall be speedily reached as to whether or not this work shall be undertaken.

That the publication of such an index is desirable, no one will question. It is more than probable that the majority of the individuals who receive *Chemical Abstracts* will feel that a decennial index is a vital necessity for the usefulness of the journal, and certainly the considerable number of libraries preserving bound files will be unanimous in desiring the publication. The labor involved in tracing a topic through the eight volumes now completed is already very considerable, and if one imagines the task presented in searching through twenty or thirty volumes, for example, it is evident that the value of the abstract journal will depend very largely upon the existence of good collective indexes.

The desirability of collective indexes to their abstract journals has been recognized by the foreign chemical societies. The *Journal of the Chemical Society* (London) and the *Journal of the Society of*

*Chemical Industry* (British) publish ten-year and *Chemische Zentralblatt* five-year collective indexes. It is apparent that without collective indexes our abstract journal will not compare favorably with these in a very important feature. The lack of such indexes will discourage the use of *Chemical Abstracts* in favor of these foreign journals, and this tendency will grow indefinitely. Some of the independence which the publication of an abstract journal has given our Society will be lost.

The seriousness of the situation just stated depends on the value placed on *Chemical Abstracts* in comparison with these other abstract journals. It is believed that the general policy followed in the publication of *Chemical Abstracts*, namely the covering of the field completely without sacrifice of quality of abstracts, is representative of American opinion as to the function of an abstract journal. Every effort is made to report *everything* which may be considered as possibly a contribution to the advancement of chemistry, to make our journal a *complete* record of chemical progress. The fact that in 1912, for example, *Chemical Abstracts* published 22,659 abstracts as compared with 5,833 published by the *Journal of the Chemical Society*, 7,200 by the *Journal of the Society of Chemical Industry* and 10,862 by *Chemische Zentralblatt* (1913) is some evidence of the difference in policy of the four journals. The comparison would be still more striking if figures for 1914 were used, but for the foreign journals only the data given above are available. It is considered that anyone undertaking chemical work usually wants all the information available on the subjects in which he is interested and not information that is limited in any way, also that he wants to be his own judge as to the importance and usefulness (to him) of the various contributions to the subjects in question. This greater completeness of *Chemical Abstracts* is considered to be a distinct advantage. The lack of collective indexes would be a disadvantage that would offset any advantages which *Chemical Abstracts* may have. It is hoped that our abstract journal is built along lines which may ultimately mean that it will be *the* chemical abstract journal of the world. This will never be possible without collective indexes.

This index (author and subject) would probably contain between five and six thousand pages. If it consists of 5500 pages and 1000 copies are printed it is estimated that the total cost would be about $16,000. The printing alone would cost close to $14,000. An index of these proportions cannot be prepared out of the funds now available. The annual subscription price for the journals of the Society may seem large to the members, but it must be remembered that a great deal is given in return. The chemist in no other country gets for $10.00 anything like the range of chemical literature given our own members, and it taxes the resources of the Society increasingly to maintain the growing volume of its journals within the subscription price. For comparison, attention is called to the fact that the subscription price ("to members") of the *Journal of the Chemical Society* is £2 ($10), that of the *Journal of the Society of Chemical Industry* 25s. ($6), that of *Chemische Zentralblatt* M. 80 ($19), and that of *Berichte der deutschen chemischen Gesellschaft* M. 25 ($6).

It will be utterly impossible for the index to be prepared and published save as it pays, at least in large part, for itself. It may be that in the future some provision can be made so that later indexes may be published without special subscriptions, at least without advance subscriptions, but this obviously cannot apply in the present case. It will therefore be necessary to appeal to the membership of the Society to rally to the support of this project.

In accordance with recommendations of the Council (made at Seattle) subscription blanks will be distributed to all members. These will be enclosed in the general letter sent out from the Secretary's office about November 1st and will call for an agreement to pay not to exceed $10.00 per copy for the index, the same to be due at the time of delivery. If enough subscriptions are received the price, which will be cost or less, will of course be less than $10.00. It is worth noting that the last decennial collective index to the *Journal of the Chemical Society* was supported by a special subscription price—£2 ($10), "to fellows" and £2 10s. ($12.50), "to public."

The Council will be asked at the Spring Meeting of 1916 to settle definitely whether or not this index shall be published. This decision will undoubtedly be governed by the response to the request for subscriptions. It will be a critical one because it will virtually be a decision for future ten-year periods as well as for the present one. If the index cannot be published now, it is not to be expected that it can be later, when it will be a still greater undertaking. The decision will amount to the settlement of a policy of publication which is second in importance only to the policy of publishing the abstract journal itself.

Now when these subscription blanks reach us what is going to happen? Everyone of us knows that there is a natural tendency for us to put such things aside and then forget them or to assume that there will be enough without our help. Chemists are human. And we all realize also that this sort of characteristic when applied to a group of men amounts to a kind of inertia that is overcome with difficulty. It is a serious matter when an important need is not supplied because of such inertia. Inertia must not prevent us from saving and making our abstract journal.

It will be the duty and privilege of each one of us to decide this matter for the present and for the future. If we value *Chemical Abstracts* we must not withhold our active support at this critical time. It will be to our own interests and a sign of loyalty to our Society for us not only to subscribe for an index but also to help the project along in any other way that we can. We can all help by telling others of the urgent need of subscribing in advance as the whole matter depends on the advance subscriptions. To most of us purchasing an index will be a good investment. Even if it costs $10.00 it will save the equiva-

lent of this amount in time in a short while. Since in a publication as large as the proposed index the cost item for paper, presswork, binding, etc., is quite large it is probable that under the existing circumstances only a few copies over and above the number subscribed for can be published. There will no doubt be a time when these indexes will command a considerable premium. The American Chemical Society is the largest chemical society in the world. It has undertaken much in publishing *Chemical Abstracts*. It is conceded that this undertaking has been worth while and successful thus far. A collective index is necessary to its continued success. We must do at least as well as the smaller foreign societies. America's place in future chemical development is perhaps hard to forecast with precision. It may be expected to be high. We have the resources, and chemical use of them is just beginning. We must properly continue the important work we have undertaken.

E. J. CRANE

# ORIGINAL PAPERS

## AN INVESTIGATION OF FUSIBLE TIN BOILER PLUGS

By C. K. BURGESS AND P. D. MERICA

Received June 14, 1915

The fusible boiler plug in its usual form consists of a brass or bronze casing with external pipe thread, filled from end to end with a fusible metal or metal composition, which has a low melting point. These are fitted at various places into the boiler, in such a position that they are about one inch or more above the dangerous low water level, with one end on the fire and one end on the water side. As long as the water level in the boiler is above these plugs, the temperature of the latter remains below the melting point of the filling (at 150 pounds boiler pressure the temperature is about 180° C. or 324° F.), but if the water falls much below the level of the plug, opportunity is given for a local overheating in the vicinity of the plug. The filling of the plug then melts and is blown out.

The fusible plug has been required to be installed in all steam vessels of the American Merchant Marine since 1852, and is now required in all boilers except pipe. flash, or coil boilers on vessels subject to inspection by the Steamboat-Inspection Service, Department of Commerce. This inspection includes approximately 11,850 boilers requiring installation of boiler plugs.

Fusible plugs are also used in many but not all factory and locomotive boilers in this country and abroad. They are not generally used in marine boilers abroad, nor are they used in the United States Naval service, the practice there not favoring the installation of safety devices of any sort, fusible plugs or otherwise, as it is considered that their presence fosters negligence.

Tin seems to be the metal used at present almost exclusively as the fusible constituent of such plugs, and is required by the above specifications. It would seem to be in this respect a desirable metal, having a low melting point, being only slightly corrodible, and easily obtained pure. Its desirability in this respect is nevertheless to some extent called in question by the results of the investigational survey of fusible tin boiler plugs, which was made at this Bureau, from June, 1914, to March, 1915.

On May 11, 1914, a boiler of the Steamship *Jefferson* exploded, causing the loss of life of several persons. Investigation showed this explosion to have been due to low water and consequent overheating of the boiler plates. This should have been indicated by the fusion of the filling of the Banca tin plug in that region, which plug, however, was found to be unmelted and apparently, or at least superficially sound. This plug was sent to the Bureau of Standards for investigation.

At this Bureau it was sawed open longitudinally and was found to contain traces only of the original tin, embedded in a dirty, greenish matrix. A photograph of this central longitudinal section is shown in Fig. I, in which the light regions represent the remaining tin. The matrix was found to be largely tin oxide, $SnO_2$, which upon test showed a melting point above 1600° C. (about 2900° F.). This oxide was distributed in such a form and quantity that it held the pressure of the boiler, and would not have melted until the bronze of the casing and even the steel of the boiler had melted! When reliance is placed upon such a plug to give warning of dangerous boiler conditions it is to be looked upon as an actual source of *danger* instead of *safety*.

The question arose then: To what is the presence of tin oxide to be ascribed? Was it there originally, has it been formed by corrosion, and if so, is the cause for its comparatively rare occurrence in such plugs to be sought wholly in the different operating conditions of the boilers, or is a fault in the method of manufacture of these plugs at least partially responsible? A search in the literature failed to reveal any reference to failures of fusible tin plugs of this sort, except vague statements that they were not entirely reliable, due to the formation of boiler scale on the inside and soot on the outside and a statement that the filling was likely to change its melting point during service. No data could be found concerning the oxidation of tin at higher temperatures.

A request was then made to the Steamboat-Inspection Service that more plugs be sent in to the Bureau for test, both new ones, and also those which had been removed by the inspectors, in order that by a survey of these plugs information might be obtained bearing on the points raised above. In answer to the request, about 1050 plugs were received of which about 100 had been in service varying from 4 to 12 months. These plugs represented the products of about 105 firms.

### EXAMINATION AND INVESTIGATION OF PLUGS

The plugs were first examined to ascertain whether

their dimensions corresponded to the specifications of the Steamboat-Inspection Service. They were then sawed open axially through the center, and the

FIG. I—OXIDIZED FUSIBLE TIN BOILER PLUG

FIG. II USED PLUG SHOWING "NETWORK OXIDATION"

form and condition of the filling observed, particular attention being paid to the presence of oxide, scoriae, blow-holes, and other faults originating either in the manufacture of the plugs, or during their service.

### TYPES OF DETERIORATION

The condition of the tin in the plugs which had been in service varied greatly. A few of the fillings were piped or showed blow-holes, the surfaces of which were clean and bright.

These plugs were classified according to the types of deterioration which they had undergone in service. In all, five such classes of fillings or groups could readily be distinguished, as follows:

1—Sound fillings.

2—Fillings partially melted away.

3—Fillings expanded in service.

4—Fillings corroded or pressed in at the water side.

5—In 14 plugs from 8 firms non-metallic enclosures or incrustations were found in the filling. Since this mass was found to be in most cases, where not otherwise noted, practically pure tin oxide, $SnO_2$, contaminated at times with traces of ZnO and CuO, it will hereafter be referred to as "oxide." This oxide occurred in several forms.

(*a*)—In 4 plugs from one firm the oxide was practically pure $SnO_2$ with traces of zinc and lead and no traces of sulfates, chlorides or nitrates, and occurred in the form of a network, proceeding from the water end toward the fire end. This type is shown in Figs. II and III, which show successive stages of the progress of the oxidation. The original plug of the Steamship *Jefferson* shows a very much more advanced state of this type of oxidation (see Fig. I).

It is obvious from many considerations that this oxidation occurred in service and that the oxide was not poured in with the tin originally.

For instance it has been attempted and not found possible to pour tin plugs in which oxide veins or granules of such coarse texture are visible. In such attempts to do this the tin was first badly oxidized and then poured at temperatures varying from about 300 to 500° C. (600 to 900° F.).

(*b*)—In 10 plugs from 7 firms the fire end of the plug was filled for a third to one-half of the distance from the end with a solid adherent mass of what was in many cases impure oxide of tin with traces of sulfates, zinc, lead, and copper. The characteristic appearances of these plugs are shown in Figs. IV and V.

In all of these latter cases the incrustation or the network of oxide would probably have held the boiler pressure even after the melting of the tin still remaining in the plug. Obviously these were dangerous plugs.

### PURITY OF TIN AND ITS RELATION TO DETERIORATION

In order to relate if possible the types of failures just enumerated to the purity of the tin in the fillings, the melting points of a number of the old plugs as well as of the new ones were taken. It is well known that the presence of metallic impurities changes the melting point of a pure metal, and indeed the melting point may be used, as it was in this case, as a criterion of the purity of a metal. Impurities in small amounts—such as lead, zinc, bismuth, cadmium, copper—lower the melting point of tin, whereas iron and antimony raise it (see Bornemann, "Die binären Metallegierungen," 1909–1912).

These determinations were made partly with the aid of a modified form of the micropyrometer[1] and partly by taking a cooling curve. This latter method was developed to such a point that a cooling curve could be taken on a 6 to 8 gram sample and the freezing point determined in general to within less than $\pm 0.1°$ C.

Chemical analyses were also made of the fillings showing abnormal melting points.

A consideration of the results of these purity tests shows the following facts:

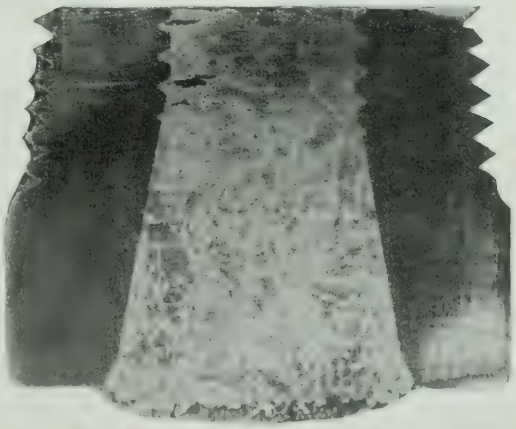

FIG. III × 2- USED PLUG SHOWING NETWORK OXIDATION

I—Banca tin, as required in the specifications of

[1] G. K. Burgess, Scientific Paper No. 198, of the Bureau of Standards.

the Steamboat-Inspection Service, Department of Commerce, was not and is not being used in the filling of a considerable number of the plugs. Analyses of 4 samples of Banca tin by W. A. Cowan[1] showed the tin content to be 99.93, 99.97, 99.96, and 99.96 per cent, respectively, by difference.

Of about 70 melting-point determinations made on used and new plugs only 11 gave values within 0.5° C. of the melting point of pure Kahlbaum, Banca, or Straits tin.

Of 35 plugs analyzed chemically only 6 fillings showed 0.20 per cent or less impurities, or, in other words; only 6 of 35 plug fillings examined chemically were composed of any variety of high-grade tin (see paragraph below).

II—The principal impurities are lead and zinc. It may be noted that it is not possible that the zinc or lead, in amounts greater than the solubility of these metals respectively in tin at high temperatures (180° to 190° C.), could have come from the bronze casing by diffusion in the solid state. By solubility is meant here the amounts of these metals which actually dissolve in the tin to a homogeneous solid solution.

III The results show that Classes 1, 2, 3 and 5*b*

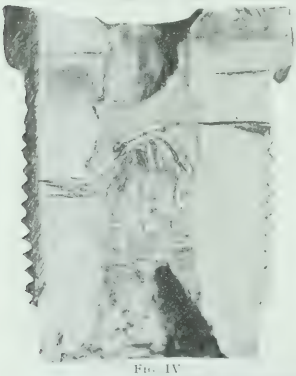

Fig. IV

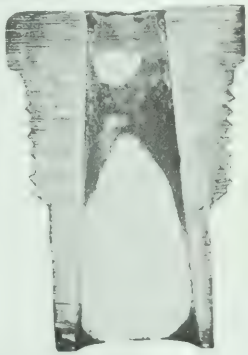

Fig. V

Used Plugs Showing Solid Oxidation

listed above contain plugs having impure tin as well as those containing pure tin (*i. e.*, of melting point of 231.9°). Impure tin is then not always a cause of oxidation or deterioration in these plugs.

IV—All of the 4 plugs, as well as the plug from the boiler of the Steamship *Jefferson* showing the network type of oxide, came from the same manufacturer, were used on 4 different vessels, had low melting points, and contained zinc.

### Theory of "Network" Type of Oxidation

An explanation of this type of failure may be found in the effect of the zinc upon the process of oxidation of the zinc-tin alloy, and a consideration of the constitution of the Sn-Zn alloys will throw some light upon this peculiar phenomenon.

The equilibrium diagram, according to Guertler, shows that the solubility of zinc in tin is very small in the solid state, less probably than 0.2 per cent. By this is meant that although alloys of tin and zinc can be made in all proportions, the zinc is not in the solid state dissolved in the tin, forming a solid solution of homogeneous macro- and micro-structure. A slowly cooled alloy, tin 99 per cent and zinc 1 per cent, has a eutectic structure as shown by photographs by Lorenz and Plumbridge,[1] in which the eutectic crystallites of zinc (dark) can be seen distributed in the tin matrix. Upon long heating just under the eutectic horizontal at about 197° C., the tin and zinc crystals coalesce, the eutectic disappears and the structure attained is that shown in Fig. VI. This will be shown in experiments described below. In this alloy the tin crystals are surrounded by an envelope of zinc.

If now this alloy be brought in contact with a corrosive aqueous solution, the latter will attack the zinc first, eating its way into the plug through the grain or crystal interstices, and the tin filling finally becomes honeycombed in structure. The corrosion of the tin itself may now start from these intercrystalline canals, and the oxidation products remain, forming gradually the oxide network structure already referred to.

There is much analogy of the oxidation of this kind to that produced in Muntz metal sheathing upon exposure on a ship's bottom to salt water. Muntz metal (60 per cent copper and 40 per cent zinc) has a heterogeneous structure, and consists of two structural constituents or phases, the alpha and the beta solid solutions, respectively, the latter containing more zinc than the former. Upon exposure to salt water, material of this sort afterwards becomes so brittle that it can be crumbled up by hand. Examination shows that the salt water has attacked the beta constituent and has removed much of it, eating its way thus into the interior of the metallic mass in such a way that the metal consists of the original structural "framework" of alpha, throughout which the beta filling has been at least partially removed.

Naturally if the water, in this case the boiler water, attacks neither the tin, nor perhaps even the zinc, a plug which contains zinc may remain sound after months of service. It may be mentioned here that alkaline waters, such as would be produced by over-addition of soda boiler-water softener, attack zinc even at ordinary temperatures and probably corrode both zinc and tin at higher temperatures. Furthermore, the temperature of the water and plug will determine to a great extent the velocity of the progress made by the oxidation. At a higher temperature the corrosive action will be in general greater, the velocity of the coalescence of the zinc eutectic will be greater, and what is more important, if the temperature rises above 197° C. (about 205 lbs. per sq. in. pressure), melting will take place at the boundary of the zinc and tin, and the pressure inside will force the melted portions toward the fire end of the plug, thus leaving channels open for the entrance of the water

[1] *Journal of the American Institute of Metals*, **1914**.

[1] *Z. anorg. Chem.*, **1913**.

from the water side. That the fillings of plugs do so travel in their casings from the water to the fire end is shown in the case of plugs under Class 3.

It is thus easily seen why it is that although no plugs have been found showing the network type of oxidation, which do not contain zinc, several have been found which do contain zinc and which have nevertheless remained sound in service during from 3 to 12 months.

In the latter cases, the tin surface on the water side was found to be clean, proving that the boiler water used did not attack it, whereas in other plugs, and particularly in those in which network oxidation had taken place, the water-side surface of the tin was badly corroded. The normal pressure used in the boilers may also have been less in these cases. There is, however, also some significance in the fact that all 5 of the plugs showing this type of failure came from the same manufacturer. The explanation of this fact is to be sought in the simultaneous presence of zinc and absence of lead in the filling of these plugs. This manufacturer happened to be using impure tin which unlike most of the impure tin used by other

FIG. VI × 2—TIN FILLING CONTAINED 0.5 PER CENT ZINC
Heated 500 hours at about 190° C.

manufacturers contained no lead. The action of the lead in this respect is discussed below.

The formation of incrustation in plugs under 5*b* is more puzzling. That this incrustation is not always entirely formed by natural means is shown, however, by the fact that analysis of it showed it to be about 96 per cent $CaSO_4.{}^1/_2H_2O$ in plug No. 122, and $CaSO_4$ was also found in plugs Nos. 1047, 1045, and 9. Since this is at the fire end, with no communication with the boiler water, the inference is that when the plug began to leak plaster of Paris was put in at the fire end to stop the leak. However, in other cases the incrustation is free from calcium and is tin oxide with traces of copper, zinc, and tin oxides containing always sulfates—usually as copper sulfate—and was probably formed by natural processes.

It is to be noticed that the tin in plugs which have oxidized in this manner is either from its melting point or analysis seen to be impure. The presence of sulfate shows that flue gases with sulfur dioxide and oxygen content have been instrumental in oxidizing the tin filling.

The explanation why some plugs containing tin fillings merely melt out at the fire end leaving no oxide, and why in others the tin oxidizes and remains as oxide, is to be sought probably in the variation in operating conditions of the boilers, in variations in the kind of coal used, as for example in the sulfur content of the coal, also very possibly in the devices used by the engineers in charge of boilers to stop up leaky plugs! It is possible that if plugs could be made which would not leak, this kind of deterioration would be largely eliminated.

### TESTING OF THEORY BY SERVICE TESTS AT BUREAU

It was thought advisable to subject a number of the new plugs as well as plugs made up at the Bureau, containing definite amounts of impurities, to the action of water at high temperatures to determine what would be their behavior under these known conditions. For this purpose the plugs were put in a copper autoclave, and heated for various periods at a temperature of from 180 to 195° in either tap or distilled water. In two cases the temperature went too high and some of the plugs of lower melting point fused. Half of each plug was heated and half saved for comparison in each case.

Of 40 new plugs heated for 195 hours, and 20 new plugs for 140 hours in tap water, only three showed any change whatever; these were all from one manufacturer and contained lead in varying amounts. After this treatment all were somewhat distorted, and covered with spongy "eruptions," illustrated in Fig. VII. Whereas no lead could be detected in the micro-structure before heating, owing to the fineness of its distribution, after this heating the lead had coalesced as an enveloping boundary to the tin crystals. The plug filling was apparently only superficially oxidized.

Plugs were then made up at the Bureau of pure Banca tin, Straits tin and Straits tin containing the following amounts of zinc and lead:

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Per cent zinc | 0.5 | .2 | .5 | 1.0 | | | 0.5 | .2 | .5 | 0.5 |
| Per cent lead | | | | | 0.5 | .5 | 1.0 | 1 | 1 | 5.0 |

These were melted in a fire clay crucible in a gas furnace and poured into casings made of 1-in. brass tubing threaded on the inside. They were cast in pairs. Of each composition the first plug was poured, with care taken to avoid oxidation and the consequent contamination of the tin of the plug with oxide. After this was poured, air was forced through the melt for from 3 to 5 minutes, thoroughly oxidizing it, after which it was then poured into the second casing, effort being made in this case to introduce oxide into the filling of the plug. It was desired to determine thus whether the presence of oxide from the pouring aided the process of oxidation in service. It is interesting to notice that even in one of the plugs in which the oxide must have been present to the extent of about 25 per cent, it could be detected only microscopically in the structure of a polished section. No coarse macroscopic oxide structures could be produced resembling those produced in service and described above.

Some of these were then heated in tap and some in

distilled water for about 500 hours at from 180 to 195° C. (350 to 380° F.). There seemed to be no difference in the actions of distilled and the tap water on the plugs.

After heating those containing zinc or lead in amounts equal to or above 0.5 per cent, they were usually found cracked. Indeed in the case of the plug filling with 10 per cent zinc, an almost perfect inverted pyramid had cracked off and had been forced up several millimeters. This was doubtless due to the stresses caused by the expansion between the tin crystals of tin-zinc eutectoid during its melting which begins at about 197° C. (385° F.). In some cases, particularly when lead was present, the filling had become porous, due to the melting out of the low melting eutectoid which in this case melts around 170° C. (330° F.).

No change could be detected in the samples of Banca and Straits tin caused by this treatment other than a slight surface oxidation.

Every plug which contained zinc and no lead showed a network structure after 500 hours in the autoclave. This is shown in Fig. VII. The network structure

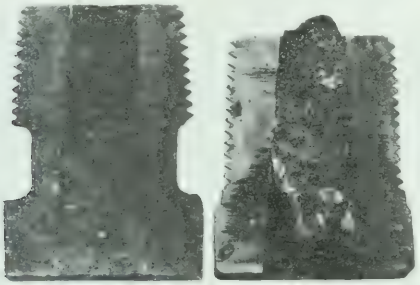

FIG. VII—NEW PLUG: FILLING CONTAINED 8 PER CENT LEAD
Left half, as received; right half, heated in water 140 hours at about 190° C.

was the more pronounced the higher the zinc content and was in many cases better developed near the surface than inside.

It appears then that even with ordinary tap water some oxidation of this type takes place, for if none had taken place the network structure developed by the coalescence of the zinc should have had approximately the same density throughout, which is clearly not the case in this plug.

The structure after heating with distilled water of those plugs which contained zinc and lead showed a much less developed network structure than those containing the same amount of zinc and no lead under the same conditions.

It was shown here and during the examination of plugs which had been in service for periods of from 4 to 12 months and had remained sound, that tin may contain zinc, and be heated to temperatures around 180° C. or 350° F. (corresponding to an average boiler pressure of 150 lbs. per sq. in.) and still not develop the coarse coalesced "network" structure described above. This may have been partly due to the fact that the temperatures to which they were exposed were lower than those to which the plugs of Class 5*a* together with those heated at the Bureau had been exposed. But there is little doubt but that lead, partially at least, prevents the formation of this coarse "network" structure in tin containing zinc. This is shown by the fact that

1—Four plugs (Class 5*a*) contained zinc and no lead, and had developed this structure.

2—Tin samples with zinc and no lead developed upon heating a much more pronounced network structure than those containing the same amount of zinc and 1 per cent lead.

3—Plugs containing zinc and lead, and which had been in service for periods of from 4 to 12 months, did not develop this structure: indeed, in most cases neither the zinc nor the lead could be detected with certainty in their micro-structure. This was true, for example, of one plug containing 1.8 per cent of zinc and 0.1 per cent of lead, which had been in service three months and was still absolutely sound.

It seems then that the progress of the "network" oxidation is dependent upon the previous presence of the coalesced network zinc-tin structure, and if for some reason the zinc is present in another form of distribution the oxidation cannot proceed in this manner.

Upon heating with water in the autoclave no difference could be noticed in the behavior of the sound, *i. e.*, unoxidized, and the plugs oxidized before pouring.

### THE TESTING OF THE PURITY OF TIN

It is suggested that the use of a high-grade tin of the purity of Banca, Straits, Pyrmont, or Williams, Harvey & Co. refined (see analyses by Cowan[1]) would eliminate the danger of deterioration by oxidation of the fillings of tin plugs. Of these varieties, Banca is undoubtedly the most consistently pure, although some samples of other varieties were of almost equal purity, for example, Williams, Harvey & Co., refined. It would seem safest therefore to require tin in such plugs to be 99.9 per cent pure and to contain less than 0.01 per cent each of zinc and lead. This would admit Banca tin and some lots of other varieties. It has, however, been in the past year impossible at times to obtain Banca tin on the market. For such a contingency provision must be made for admitting other and slightly poorer tins. If the specifications called for tin of 99.8 per cent purity, containing less than 0.05 per cent lead and less than 0.01 per cent zinc, most of the high-grade tins would be included, and such tin, with the higher lead content, would probably be as safe for use in plugs as the former, as there is as yet no evidence that a lead content of even 0.1 per cent is harmful in such plugs.

Frequent tests must be made of the purity of the tin bought under such specifications as those recommended above, by chemical analysis. Such analyses may be limited in most cases to a determination of zinc and lead, which seem to be the principal impurities.

A somewhat quicker method of determining whether or not a tin sample is pure is given in the determination of its melting point. In Table I the lowering

[1] *J. Ind. Eng. Chem.*, 7 (1915), 11.

of the melting point of tin for one per cent of various ordinary metallic impurities has been calculated from the results of thermal analysis of these alloys by various investigators (see "Bornemann," 1909–1912). The rough assumption has been made in these calculations that the liquidus curve is linear.

TABLE I—EFFECT OF METALLIC IMPURITIES IN LOWERING THE MELTING POINT OF TIN

| METAL | Per cent present in tin | Melting point ° C. | Lowering of melting point per 1 per cent of metal calculated |
|---|---|---|---|
| Antimony | 7.5 | 240 | +1.0° C. |
| Bismuth | 5.5 | 225 | —1.2° C. |
| Iron | 2.0 | 300 | +30.0° C. |
| Lead | 2.5 | 225 | —2.8° C. |
| Zinc | 3.0 | 225 | —2.3° C |

It is seen that small amounts of impurities may in general be readily detected, although the *simultaneous* presence of metals such as antimony and zinc in proper amounts might give an alloy having a melting point equal to that of pure tin. In the samples analyzed the only impurities found in appreciable amounts were zinc and lead, each of which lowers the melting point; therefore the determination of the melting or freezing point of the tin may be accepted as a useful and rapid test of its purity.

It is not possible to distinguish with certainty between Kahlbaum, Banca, and Straits tin by the ordinary determination of the melting point as made by the cooling curve method.

## CONCLUSIONS

The fact that stands out most strongly throughout this investigation is that zinc should not be present in the tin fillings of fusible plugs. The lowest zinc content actually found in any of the 4 plugs analyzed, which displayed the "network" type of oxidation, was 0.3 per cent, but this cannot be accepted as the *actual* lowest value of the zinc content at which oxidation can take place. Furthermore, although zinc is, because of its greater corrodibility, *most* dangerous when coalesced into a network structure such as is developed upon heating at about 180°, other metals which do not form solid solution with tin may also cause the formation of this structure, as for instance lead. It seems then that in such plugs tin must be used which is as free as possible from zinc and lead. This statement is made notwithstanding the apparent fact that if zinc is present, a small content of lead is actually beneficial; it is better to prevent this oxidation by using *pure* tin than by the addition of lead when the tin already contains zinc.

A consideration of the results of the tin analyses by Cowan[1] shows that it is possible to get Banca and other tin which contains only traces of zinc and at the utmost 0.010 per cent of lead. It is highly probable that the use of tin of such purity would eliminate the danger of oxidation of the "network" type.

With the exception of plug No. 122, which had a melting point of 231.9° and in which the formation of non-metallic enclosures had not proceeded by natural means, as shown above, the plugs of the 5*b* class all contained impurities—probably to the extent of about 1 to 1.5 per cent. The inference is therefore that oxidation of the tin in service would cease with the introduction of the use of a tin of purity equal to that of Banca, probably also of tin of purity equal to that of Straits or Pyrmont. Observations are made above regarding the testing of the purity of tin.

However, one question may be raised. A leaky plug will always be a temptation to careless practice on the part of the engineer in charge in stopping them up. Now the chances that leaks may develop in a plug are fairly large. The coefficient of expansion per degree C. of the material of a casing will be around 0.000020, whereas that of tin is about 0.000023. Tin undergoes an allotropic change at about 160° C. accompanied by a change of volume of about 0.03 per cent. Therefore, opportunity is constantly given for interplay between plug filling and casing during temperature changes. A number of plugs which had been in service, were removed because of leaking.

## RÉSUMÉ

I—An explanation has been sought for the "failure" by oxidation of fusible tin boiler plugs during service. These failures are of two types: (1) those in which the oxide forms as an interlocking "network" throughout the tin of the filling; (2) those in which the oxide forms as a solid hard mass at the fire-end side of the plug.

II—About 950 new and 100 used plugs were examined and classified according to the type of change or deterioration which had taken place in them during service, and a number were tested for purity of the tin, both by determination of the melting point of the latter, and by chemical analysis. Lead and zinc were found to be the principal impurities present.

III—An explanation for the formation of the "network" type of oxidation is found in the presence of zinc in amounts varying from 0.3 to 4.0 per cent.

IV—The conclusion is drawn that, since all plugs examined, which were "dangerous," contained impurities, the use of *pure* tin of the quality of Banca, of Williams, Harvey & Co. refined, or even of Straits or Pyrmont would probably eliminate the danger of oxidation of these plugs in service.

The authors take the opportunity of thanking Messrs. A. B. Lort, and R. W. Woodward for their aid in this work.

BUREAU OF STANDARDS
WASHINGTON, D. C.

[1] *Loc. cit.*

## A NEW METHOD AND FURNACE FOR THE DETERMINATION OF THE SOFTENING TEMPERATURE OF COAL ASH UNDER FUEL-BED CONDITIONS[1]

By A. C. Fieldner and A. L. Feild

In a previous paper[2] on the fusibility of coal ash in various mixtures of hydrogen and water vapor, a standard atmosphere of 50 : 50 per cent hydrogen-water vapor was proposed for softening-temperature tests of coal ash. It was shown that ash fusions made in this atmosphere were similar, as regards the state of oxidation of their iron content, to the well-fused glassy portion of clinkers from boiler furnaces. In both cases approximately 80 per cent of the iron

[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] This Journal, 7 (1915), 742.

was present in the ferrous form. Furthermore, a given ash, especially if it contained more than 10 per cent ferric oxide, softened and formed a slag at a much lower temperature in this atmosphere than in an oxidizing atmosphere of air, water vapor, or carbon dioxide or in a strongly reducing atmosphere of hydrogen or carbon monoxide. In an oxidizing atmosphere the iron component was found in the slag mostly in the ferric form (complex ferric silicates or magnetite); in a strongly reducing atmosphere the iron was reduced to the metallic form and thus prevented from acting as a flux; in neither case was the slag similar to the actual furnace clinker as regards the state of oxidation of the iron content.

Similar results were obtained in determining softening temperatures of the same series of ashes in various mixtures of CO and $CO_2$. The lowest softening temperatures in $CO$-$CO_2$ mixtures were usually slightly higher than those obtained in the corresponding

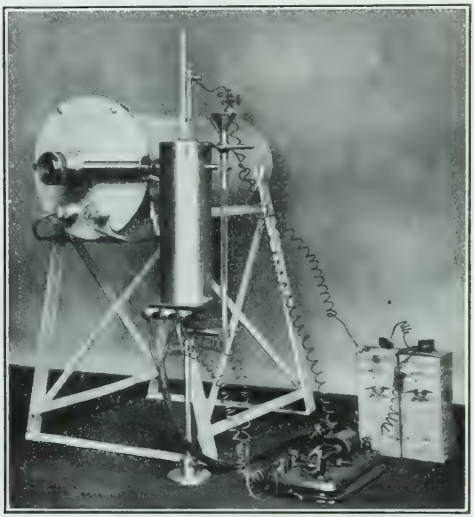

FIG. I FURNACE AND SATURATOR

$H_2$-$H_2O$ mixtures. The difference, however, was not sufficient to militate against the use of the latter mixture as a standard atmosphere in laboratory fusion tests, even though $CO$-$CO_2$ mixtures approach more nearly the actual gases found in a fuel bed. As a laboratory furnace atmosphere hydrogen-water vapor has the following advantages over $CO$-$CO_2$: (1) The desired mixture can be readily obtained by passing hydrogen through water at the proper temperature; (2) hydrogen can be purchased very cheaply in tanks under pressure; (3) molybdenum-wire heating elements may be used in this atmosphere at temperatures up to 1600° C.—these heating elements are exceedingly convenient and with proper care last for long periods of time; (4) the gases are not toxic as is carbon monoxide; (5) the reducing and slagging reactions approach equilibrium more rapidly in hydrogen-water vapor than in $CO$-$CO_2$, therefore, a faster rate of heating may be used.

In the previously described experiments the ash cone was heated in a glazed vitreosil tube, through which a current of hydrogen and water vapor was passed continuously. The tube was heated in a horizontal platinum wire resistance furnace. This apparatus, while satisfactory for the more fusible ashes such as were studied in the former experiments, is not adapted to routine work where samples softening at temperatures above 1400° C. may be encountered. The fused silica tube limits the maximum temperature to about 1400°; at higher temperatures it soon devitrifies and becomes permeable to hydrogen. In fact, there are no satisfactory refractory materials from which tubes can be made that are not permeable to hydrogen at temperatures above 1500° C. It was, therefore, decided to design a molybdenum-wire resistance furnace in which the entire atmosphere inside the gas-tight, sheet-iron shell could be controlled within the required limits of hydrogen and water vapor (30 to 70 per cent $H_2O$ vapor), thus obviating the necessity of a gas-tight refractory tube.

Preliminary tests, in which molybdenum wire was heated to 1400° C. in various mixtures of hydrogen and water vapor, showed no oxidation of molybdenum in mixtures containing 60 per cent water vapor; at 70 per cent water vapor a very slight superficial oxidation was noted, which was very little greater at 90 per cent water vapor. Even heating in 100 per cent water vapor to 1400° caused only a thin surface coating of light-colored oxide. On heating in air the metallic molybdenum was completely oxidized at 1100° C. From these experiments it appeared that no trouble from oxidation of the molybdenum heating element would be experienced in the standard 50 : 50 hydrogen-water vapor atmosphere within the temperature limits required for softening coal ash.

### DESCRIPTION OF FURNACE AND SATURATOR

A photograph of the furnace and saturator is shown in Fig. I. The details of construction are given in Figs. II and III. It consists in part of an outer shell of No. 14 B. & S. gauge sheet iron, 7 in. in diameter and 17 in. long, autogenously welded, gas-tight at the seams, and at the front to a circular 1-in. flange perforated for six equally spaced bolts. Between this flange and the circular end plate, both of which are made of $^1/_4$ in. thick sheet iron, is placed an asbestos gasket, $^1/_{16}$ in. thick, painted with a thick mixture of powdered graphite and glycerin. The end plate and flange are drawn together sufficiently tight, along a ground surface on each, to produce by means of the gasket a gas-tight connection. The mixture of hydrogen and water vapor enters the shell through a $^1/_8$-in. pipe, threaded into a $1^1/_4$ in. iron pipe serving as an observation tube, which in turn is threaded into the center of the front end plate. The free end of the observation tube carries a brass sleeve into which is threaded a brass cap bearing on an asbestos gasket, as shown in Fig. II. This cap is fitted with a glass window, $^3/_4$ in. in diameter, through which the temperature is read optically. The glass is held

between two asbestos gaskets by a threaded brass ring. To insert a cone in the furnace, the entire cap is unscrewed from the brass sleeve. The furnace is supported in an iron frame so that its center is about 17 in. above the table, which is a convenient height for optical measurements of temperature.

The heating element consists of 32 feet of molybdenum wire, No. 16 B. & S. gauge, wound upon the outside of a spirally grooved alundum core, $1^1/_4$ in. internal diameter, 12 in. long, and closed at one end by an alundum disk cemented in with alundum cement. This tube, carrying the coil of molybdenum wire, when placed in position, lies in the axis of the cylindrical shell, 2 in. from the rear end, and 3 in. from the front end, measured to the plane of the flange. In order to support the highly heated alundum core and prevent its deformation, it is placed within another alundum tube, 2 in. internal diameter and 12 in. long. The narrow annular space between the tube carrying the molybdenum coil and the outer alundum tube is filled with dry alundum cement, held in place with wet cement at the ends. The two tubes, thus cemented together, are enclosed by a larger tube of fireclay, running the entire length of the shell, and provided with slots at each end for leading out the terminals of the molybdenum coil. The space between the outer alundum tube and the fireclay tube is filled with powdered magnesite. At the front end, however, the cylindrical heating chamber is continued along the axis by means of two short alundum tubes, of the same diameters as those enclosing the heating coil. The 1-in. annular space between the fireclay tube and the outer iron shell is filled with "kieselguhr." The fireclay tube is supported at the ends and middle by rings of "Transite," 1 in. thick. The terminals of the heating coil, after being led through the slots of the fireclay tube, are joined by means of connectors to heavy copper leads, No. 6 B. & S. gauge, which pass between the fireclay tube and the shell and out of the furnace through two $^3/_4$-in. pipes, 1 in. long, threaded into the front plate. The positions of these can be better seen by reference to Fig. III, which shows a sketch of the front of the furnace. The copper leads are centered in the pipes by an outer and inner disk of "Transite," between which is a layer of litharge cement (see Fig. II). This gives a gas-tight arrangement, which is not affected by the temperature reached by the shell. In order to obtain a background suitable for measuring the temperature of the test-piece with accuracy, three $^1/_4$-in. alundum disks, or stops, are placed at intervals beyond the center of the tube carrying the heating coil. The heating space, which is $1^1/_4$ in. in diameter and 12 in. long, affords a very uniformly heated portion, approximately 4 in. long. The ash cone is placed in a No. 5811 alundum extraction thimble, $1^1/_8$ in. × 3 in., which is pushed back, after being introduced by removing the brass cap on the observation tube, to a distance about 1 in. beyond the center of the heating coil. Under normal conditions the cone was barely visible against the background.

The desired mixture of hydrogen and water vapor is secured by bubbling hydrogen through water held at approximately 81° C. The exact temperature depends upon the prevailing barometric pressure. An apparatus, called a "saturator," which has already been described in a previous paper,[1] provides a continuous current of any desired mixture of hydrogen and water vapor, differing from the theoretical value by less than 4 per cent, as shown by analysis. The apparatus herein described operates on the same principle, but has been greatly modified and improved, with a view to rendering it more reliable and serviceable, and besides possesses many mechanical advantages. A vertical section of this improved saturator is shown in Fig. III, in position as attached to the furnace.

The saturator is constructed entirely of nickel-plated brass, with the exception of the polished wooden base for the binding posts *n*, *o* and *p* and the glass inlet tube *f*, which also serves as a water gauge. The apparatus is mounted on an adjustable support, the base of which is screwed to the table or desk upon

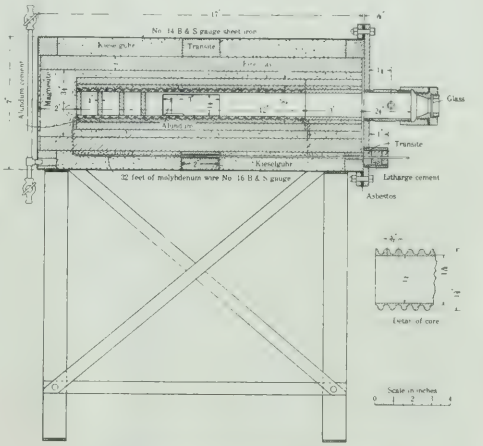


Fig. II Longitudinal Section of Furnace

which the furnace stands. It consists essentially of an air-jacketed cylinder, $^1/_{16}$ in. thick, which is kept about two-thirds full of water, *e*. This water is heated to the desired temperature by a coil of asbestos-covered nichrome resistance wire, No. 30 B. & S. gauge, wound on the outside of the inner cylinder from its base to its center, forming a single layer. The water is held at this temperature within 0.2° by an electrical contact vapor-pressure thermoregulator, which makes and breaks the current in the lower heating coil by the movement of the mercury column at *c*, through a relay in the customary manner. A 250-ohm relay has been found to give satisfactory results when operated by two or more dry cells in series. When direct current is used a condenser of 2 microfarad capacity (not shown in the photograph) is placed parallel with the heating circuit across the relay armature contact to reduce the spark. The

[1] *Loc. cit.*

stationary relay contact must be reversed so as to break the circuit when the relay electromagnet is energized by the dry cells through the thermoregulator. The thermoregulator is essentially that described by Feild,[1] without the refinement of being independent of atmospheric pressure. The inner metal tube carries at the top a sleeve, into which is threaded a cap, *h*. Through this cap passes the thermometer *d* for observing the temperature of the water, and the thermoregulator for controlling its temperature. The former stands in a thin-walled tube of brass, which is filled with oil to provide good thermal connection with the surrounding water. The latter is fixed permanently with litharge cement in the center of a metal stopper threaded into the cap, and dips into the water below. The U-tube of the thermoregulator is made of glass tubing, $^3/_{16}$ in. diameter, and has in its short arm a small quantity of water and a mixture of its saturated

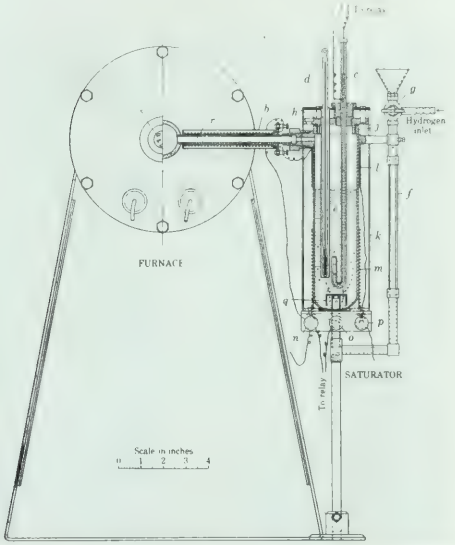


FIG. III—FRONT VIEW OF FURNACE AND VERTICAL SECTION OF SATURATOR

vapor with air. The platinum wire which makes and breaks contact in the upper end of the U-tube is provided with a binding post and screw regulation not shown in Fig. II, but shown in the photograph. The hydrogen enters at the inlet at the upper right-hand corner of Fig. III from a high-pressure tank through a reducing valve, passes through the side-tube at *f*, and enters the center of the cylinder base. Before passing through the column of heated water in the saturator cylinder, the current of hydrogen is broken up into small bubbles by a perforated double bell, *a*. The water vapor absorbed by the hydrogen is prevented from condensing on its passage to the furnace by two heating coils connected in series, both made of asbestos-covered nichrome wire, No. 30 B. & S. gauge. The first of these superheating coils, *l*, is wound on the outside of the upper part of the inner cylinder. The other superheating coil is wound on a brass pipe which slips over the $^1/_8$-in. iron pipe *r*, which connects the saturator with the furnace. The length of both coils is so chosen that the desired degree of superheating is attained without the use of any current regulation. Finally, the inner cylinder holding the water and the side-tube between the furnace and the saturator are both covered with closed metal cylinders, *k* and *b*, which serve as an air bath for the entire apparatus. The air-bath cylinder *k* is split vertically in two halves so as to allow instant removal and access to the heater windings. The saturator is operated directly on a 220 volt, a. c. or d. c. circuit, without any controlling rheostats. Connections are made to the two outer binding posts *n* and *p*. The lengths, resistances, and input for the different coils are as follows:

| Coil | Length | Resistance | Input |
|---|---|---|---|
| Lower heating | 44 ft. | 268 ohms | 171 watts (intermittent) |
| Superheating (on cylinder) | 107 | 640 | 38 watts (continuous) |
| Superheating (on side-tube) | 35 | 209 | 13 watts (continuous) |
| | 186 | 1117 | 222 |

When the water in the saturator is held at 81° C., the metal tube above it soon reaches a stationary temperature of about 96–98°, as recorded by a thermometer placed in the air-bath just outside. The interior of the side-tube reaches about 115° at its center, and about 98° at its coolest part, *i. e.*, at the threaded union connection to the saturator.

After each run is made, the 3-way stopcock is turned to communicate with the funnel above it, the water level on the gauge *f* noted, and water added through the funnel if necessary. The metal tube above the glass, which carries the funnel, stopcock, and inlet tube, is held by a set-screw, so that it may be raised and lowered when inserting a new glass tube or when rewinding the heating coil. The glass tube is held at each extremity against rubber gaskets.

The exact temperature at which the water in the saturator should be maintained to secure a 50 : 50 mixture of hydrogen and water vapor depends upon the barometric pressure. Assuming complete saturation, the temperature which gives the water vapor a partial pressure equal to half of the barometric pressure is easily calculated from the values of the pressure of saturated water vapor at various temperatures. The following values calculated from the table given in the 4th edition of "Landolt-Börnstein," 1912, p. 362, give the temperature yielding a 50 : 50 mixture at various barometric pressures:

| Barometer Mm. | Temp. of water in saturator °C. | Barometer Mm. | Temp. of water in saturator °C. | Barometer Mm. | Temp. of water in saturator °C. |
|---|---|---|---|---|---|
| 682.64 | 79.0 | 710.94 | 80.0 | 740.22 | 81.0 |
| 688.22 | 79.2 | 716.72 | 80.2 | 746.20 | 81.2 |
| 693.84 | 79.4 | 722.54 | 80.4 | 752.20 | 81.4 |
| 699.50 | 79.6 | 728.40 | 80.6 | 758.26 | 81.6 |
| 705.20 | 79.8 | 734.28 | 80.8 | 765.36 | 81.8 |

While it is not considered necessary to make allowance for local changes in barometric pressure in ordinary laboratory tests, the average barometric pressure which prevails under test conditions should be determined or estimated once for all, and the corresponding temperature used consistently. A change of

[1] *J. Am. Chem. Soc.*, **36**, (1914), 72–76.

barometric pressure of 10 mm. affects the percentage of both constituents by approximately 0.7 per cent, while a departure of 1° C. from the correct temperature of the water in the saturator makes a similar change of approximately 2 per cent.

TEMPERATURE MEASUREMENTS AND STANDARDIZATION

Measurements of temperature are made through the glass window by means of an optical pyrometer. A correction must be applied to the apparent reading due to the absorption by the glass. The magnitude of this correction depends upon the temperature, and also upon the thickness and kind of glass used. The corrections are determined by observing the apparent temperature of an alundum disk in a platinum resistance furnace, with and without interposing the glass, the temperature of the disk being kept constant during the two readings, as indicated by a thermo-element embedded in it. The following corrections were observed with a particular window of flint glass, $^5/_{32}$ in. thick. It is advisable to use a thinner and more transparent glass.

APPARENT TEMPERATURE BY WANNER PYROMETER

| Without glass ° C. | With glass ° C. | Correction ° C. | Without glass ° C. | With glass ° C. | Correction ° C. |
|---|---|---|---|---|---|
| 950 | 943 | 7 | 1250 | 1222 | 28 |
| 1000 | 989 | 11 | 1300 | 1268 | 32 |
| 1050 | 1036 | 14 | 1350 | 1315 | 35 |
| 1100 | 1083 | 17 | 1400 | 1362 | 38 |
| 1150 | 1130 | 20 | 1450 | 1411 | 39 |
| 1200 | 1176 | 24 | 1500 | 1460 | 40 |

The corrections for temperatures above 1500° are obtained by extrapolation. It is also possible to determine glass correction directly with the molybdenum furnace by holding the temperature constant and placing a second similar piece of glass in front of the window and again reading the temperature.

The pyrometer, and the black-body condition of the furnace should be checked at frequent intervals by noting the melting points of thin strips of pure electrolytic copper foil and pure nickel wire mounted in a manner similar to the ash cone. The reducing conditions necessary for the melting-point determinations of these metals can be secured by removing the water from the saturator by siphoning through the inlet tube, and passing hydrogen through the furnace without admixture of water vapor. Of course, under these conditions the saturator coils should be cold. The determinations should check within 10° at the copper point (1083°) and within 20° at the nickel point (1450°), after having made the usual glass correction.

METHOD OF MAKING SOFTENING-TEMPERATURE DETERMINATION

Fifty to one hundred grams of 60-mesh coal are spread out on a 6 in. fireclay roasting dish, and completely ashed with occasional stirring in a muffle furnace at a temperature not exceeding 800°. All of the ash is then ground to 100-mesh, and thoroughly mixed.

PREPARATION OF CONES—A sufficient quantity of ash for several cones is transferred to an agate mortar, ground to a fineness of 200-mesh, moistened with a 10 per cent dextrin solution and worked into a plastic mass with a spatula or pestle. The plastic material is then molded into small triangular cones, 1 in. long and $^3/_{16}$ in. at the base. The cones are made by firmly pressing the plastic material into a brass mold[1] of the correct dimensions with a knife spatula. The surface is then struck off smooth, and the cone removed from the mold by applying a small knife blade at the base. By lubricating the mold at the start with a little vaseline, the cone can be removed at once without waiting for it to dry. When nearly dry, the cones are mounted in a refractory base made up of equal parts of kaolin and alumina ($Al_2O_3$). The base mixture is moistened to make it workable, and a portion of it taken and spread upon a sheet-iron plate. The cone is then mounted in a small hole made in the base material, plastered at its base to make it set firmly, and so adjusted that one side of the cone is vertical. It will in most cases bend in the direction of this side. A convenient size for the refractory base is about $^1/_2$ by $^5/_{16} \times {}^1/_8$ in., with the cone placed near one end and arranged to bend diagonally toward a corner on the opposite end. The sheet-iron plate is placed upon a hot-plate and heated until the water is entirely driven off. It is not necessary to burn off the dextrin binder, as experiments have shown no material effect from the dextrin.[2] It is probably removed from the system long before softening takes place.

METHOD OF HEATING—The mounted cone is placed in the capsule near the closed end, and the capsule is then pushed back into the proper position in the cold or nearly cold furnace. Hydrogen gas is passed rapidly through the cold saturator and furnace until it will sustain a flame at the upper exit tube. Subsequent to a previous run this requires only a few minutes; otherwise 20 or 30 minutes may be required. The gas stream is then cut down to two bubbles per second as shown in a wash bottle placed in the hydrogen line. The current is then turned on through the furnace and the temperature gradually raised so that at the end of approximately one hour a temperature of 900° is reached. By this time the temperature of all parts of the shell and observation tube should be hot enough to prevent condensation of water vapor from a 50 : 50 mixture. If this should not be the case, the temperature is held at 900° to 950° until the furnace jacket reaches the proper temperature. Heating is then continued at the rate of 10° to 15° per minute up to a point not less than 200° below the probable softening temperature. The rate thereafter should be adjusted to 5° per minute until deformation begins, and to 2° per minute from the beginning of deformation until the final down point is reached.

The current through the two superheating coils *l* and *b* (Fig. III) is turned on soon after the furnace current is started. The lower coil *m* is not thrown into the circuit until the furnace jacket and observation tube have reached a temperature of approximately 75°, so that no condensation of water vapor may take place from the 50 : 50 mixture.

[1] THIS JOURNAL, 7 (1915), 401.
[2] *Ibid.*, 7 (1915), 477.

In order to prevent any condensation of water vapor within the furnace jacket during a softening-temperature determination the jacket must everywhere be as hot, or hotter, than the water in the saturator, *i. e.*, 81° C. approximately. The diameter of the furnace herein described was purposely made as small as possible without requiring any great increase of power input in reaching the higher temperatures. By adopting a comparatively small diameter, 7 in., the iron jacket rapidly becomes sufficiently hot to prevent the condensation of water vapor from the mixture of hydrogen and water vapor passing through the furnace. When used for a second run during the same day, even after the interior of the furnace has become cool enough to remove the fused cone without danger of an explosion or of oxidation of the molybdenum wire, the outer shell remains sufficiently hot to begin heating the water in the saturator as soon as the air has been displaced and the furnace current turned on.

After completing a softening-temperature determination, the heating current in both furnace and saturator is cut off. The hydrogen current is allowed to pass through the cooling saturator at the rate of 2 bubbles per second until the furnace is cold.

The power required for the operation of the furnace up to the higher temperatures varies from 0.6 kw. at the start to about 1.5 kw. at 1600° C., measured at the furnace terminals. The corresponding voltage across the terminals varies from 15 to 60 volts. The furnace resistance increases with the temperature. A maximum current strength of 45 amperes is required. In this laboratory the furnace has been operated with alternating current from a transformer having a number of leads from the secondary connected to a switchboard, so that by a suitable manipulation of switches the voltage can be varied from 2 to 90 volts in steps of 2 volts. A field rheostat in series with the furnace was used for closer regulation. A wide voltage range is necessary in the operation of any molybdenum furnace because of the large positive temperature coefficient of resistance of the metal.

Where regulating transformers are not available, the furnace may be operated on a 110-volt direct or alternating current circuit, using a water rheostat for regulation. In such cases it would be more economical in both wire and current to use a smaller gauge molybdenum wire. In the design illustrated in this paper, 18-gauge wire would probably require at the highest temperatures a maximum voltage of somewhat less than 110 volts.

PRECAUTIONS IN OPERATING MOLYBDENUM FURNACE

1—The observation tube should never be opened as long as the furnace shows any signs of redness in the heating chamber.

2—A continuous gas stream should flow through the furnace as long as the heating chamber shows a red glow; when necessary, the gas stream may be discontinued through a cooling furnace showing a faint red glow, provided all communications to the exterior are closed.

3—The furnace should be tested for possible leaks.

4—The water in the saturator should not be allowed to reach a higher temperature than 81° C. However, temperatures as high as 90°, when maintained for only a few minutes, seem to have no appreciable effect on the molybdenum wire. In case the saturator water goes above 81° through a failure of thermoregulator or relay, the outer jacket *k* (Fig. III) of the saturator should be removed at once and the heating current in all coils discontinued to permit rapid cooling of the water. In case the temperature of the water exceeds 90°, the hydrogen stream should also be momentarily discontinued, the water in the saturator siphoned off through the inlet tube, and hydrogen quickly sent through the saturator without admixture of water vapor.

5—Care should be taken to prevent an explosion in a cold furnace which may contain hydrogen. An electric flashlight or incandescent bulb should be used exclusively in examining the interior of a cold furnace after completing a run.

RESULTS OBTAINED WITH THE NEW FURNACE

This furnace when operated as described above has given softening temperatures which were easily duplicated within the known errors of observation (about 25°). Furthermore, no sample of coal ash containing less than 50 per cent ferric oxide has as yet produced a fused cone which shows any magnetism in the field of a strong electromagnet, which indicates the efficient reduction of the iron present in the ash to the ferrous state, but not to metallic iron. This condition corresponds to the minimum softening temperature, for the determination of which the present furnace was designed.

In reporting the softening temperature of an ash, the fact that there is no single definite melting point, but rather a softening interval, should be recognized. A convenient method of giving the necessary data in regard to any particular sample is to give both the temperature of initial deformation and the softening point (final down-point): thus, 1250–1282° C. The temperature of initial deformation is that point at which the heated cone first begins visibly to deform. The softening point (final down-point) corresponds to that temperature at which the top of the cone, in case it bends, has touched the base, or, in case it does not bend, the temperature at which it has settled down into a more or less spherical lump, the size of which will vary depending on whether the softening is accompanied by any marked evolution of gases or not. It is necessary for a satisfactory determination that the softening cone at no time touch the sides or end of the alundum capsule in which it is placed.

The furnace described in this paper has been in almost daily use for a period of six months. It has never required any repairs or renewals and has never failed to give a sufficiently high temperature to soften any coal ash that has been submitted for testing.

The average softening point of 50 miscellaneous samples of coal ash determined in the manner herein described was 1291° C., with an average softening interval of 47° C. The softening points varied anywhere from 1060° to 1596° C.

In Table I is given a comparison of the minimum softening points of 19 ashes, obtained in this furnace in 50 : 50 mixtures of hydrogen and water vapor, and those obtained in an oxidizing atmosphere of air in the platinum resistance furnace described in a previous paper.[1]

TABLE I—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN 50 : 50 MIXTURE OF HYDROGEN-WATER VAPOR AND IN AIR

| | Softening Point in ° C. | | | Softening Interval, ° C. | |
|---|---|---|---|---|---|
| Ash No. | 50 : 50 mixture | Air | Difference | 50 : 50 mixture | Air |
| 1 | 1127 | 1365 | 238 | 15 | 65 |
| 2 | 1423 | Above 1500 | .. | 55 | . |
| 3 | 1409 | Above 1500 | . | 59 | . |
| 4 | 1202 | 1400 | 198 | 38 | 30 |
| 5 | 1255 | 1490 | 235 | 82 | 50 |
| 6 | 1322 | 1458 | 136 | 218 | 58 |
| 7 | 1596 | Above 1500 | . | 63 | . |
| 8 | 1153 | 1450 | 297 | 51 | 10 |
| 9 | 1271 | 1425 | 154 | 92 | 55 |
| 10 | 1137 | 1310 | 173 | 10 | 40 |
| 11 | 1132 | 1400 | 268 | 47 | 20 |
| 12 | 1060 | 1335 | 275 | 12 | 80 |
| 13 | 1242 | 1500 | 258 | 52 | 60 |
| 14 | 1351 | Above 1500 | . | 60 | . |
| 15 | 1216 | 1407 | 191 | 31 | 67 |
| 16 | 1251 | 1322 | 71 | 24 | 82 |
| 17 | 1198 | 1343 | 145 | 34 | 63 |
| 18 | 1204 | 1400 | 196 | 45 | 60 |
| 19 | 1555 | ... | . | 80 | . |
| | | Average. | 202 | 56 | 53 |

Acknowledgment is due Mr. W. F. Hausstein, instrument maker of the Bureau of Mines, for his able assistance in designing and in making the improved form of saturator described in this paper.

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## ON THE FUNCTION OF FERRIC OXIDE IN THE FORMATION OF PORTLAND CEMENT CLINKER

By EDWARD D. CAMPBELL

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The part played by ferric oxide in the formation of Portland cement clinker is still considered as being somewhat uncertain. That "celite" is a fusible magma through the agency of which crystallization of "alite" is effected is generally recognized. In an article on the "Constitution of Portland Cement Clinker"[2] the hypothesis was advanced, "that celite consists essentially of a calcium aluminate fusible a little above 1400° and capable of dissolving, when liquid, calcium orthosilicate and calcium oxide, this latter being the more readily soluble and that the solubilities of the ortho silicate and the calcium oxide follow laws parallel to those which govern the solubility of salts in liquid solution." A further statement was also made, "that although the proportion of ferric oxide, $Fe_2O_3$, to the alumina, $Al_2O_3$, is a little higher in the celite than in the alite, the difference is not very marked, and the assumption that ferric oxide is molecularly equivalent to alumina, so far as the formation of celite goes, seems justifiable although the hydraulic properties of the aluminates and ferrites differ in degree."

The probability of the foregoing hypothesis was experimentally tested and the results described in a later article on synthetic celite.[3]

It was there shown that if a celite having the same molecular ratio, $R_2O_3$:$SiO_2$:RO, as that drawn off from Portland cement clinker, but with the $R_2O_3$ substantially all $Al_2O_3$ and the RO all CaO, is melted and slowly cooled from 1590° C. to a little above 1400° C., large crystals of tricalcic silicate separate out from the fusible aluminate. It was further shown that the fusible aluminate constituting the solvent is probably that having the formula $5CaO.3Al_2O_3$.

The object of the experimental work herein described, which was carried out by B. A. Standerline, was to test the validity of the statement, "that ferric oxide is molecularly equivalent to alumina, so far as the formation of celite goes." Two samples of synthetic celite, termed $E_1d$ and $E_2d$, were prepared by melting together accurately weighed portions of Kahlbaum's purest ferric oxide and calcium carbonate with chemically pure silica having a factor of purity of 0.9963. For the purpose of comparison with our former results the percentage compositions and molecular ratios of these celites are given in the accompanying tables.

TABLE I PERCENTAGE COMPOSITION OF CELITES

| | $Al_2O_3$ | $Fe_2O_3$ | $SiO_2$ | CaO | MgO |
|---|---|---|---|---|---|
| $A_3$ | 18.24 | 7.99 | 13.63 | 55.20 | 4.95 |
| $C_1d$ | 23.35 | 0.17 | 13.74 | 62.74 | . |
| $E_1d$ | ... | 32.40 | 12.15 | 55.45 | |
| $E_2d$ | ... | 31.65 | 13.15 | 55.20 | |

TABLE II—MOLECULAR RATIOS OF CELITES

| | 100 $R_2O_3$ | | | | | |
|---|---|---|---|---|---|---|
| | $Al_2O_3$ | $Fe_2O_3$ | $SiO_2$ | CaO | MgO | RO |
| $A_3$ | 78.1 | 21.9 | 99.3 | 433.5 | 53.9 | 487.4 |
| $C_1d$ | 99.54 | 0.46 | 99.3 | 487.4 | .. | 487.4 |
| $E_1d$ | ... | 100.0 | 99.3 | 487.4 | .. | 487.4 |
| $E_2d$ | ... | 100.0 | 110.0 | 496.7 | .. | 496.7 |

The method of preparing the two samples of celite $E_1d$ and $E_2d$ was very similar to that employed for preparing the $C_1d$ celite described in the former paper except that the material was cooled from the maximum temperature a little more slowly than in the previous case. In both cases enough ferric oxide, silica, and calcium carbonate in accurately weighed proportions to yield something over 70 grams of fused product was placed in a covered platinum crucible which was heated over night to a temperature of about 1100° C., and in the morning a blast was put on and the temperature raised to the maximum, 1575° C. for the $E_1d$ and 1600° C. for the $E_2d$. Temperatures were measured as in previous work by means of a platinum rhodium thermocouple, the bead of which was within two or three millimeters of that portion of the crucible containing the fused material. The maximum temperature was held constant from one-half to one hour after which time the temperature was lowered at the rate of 25° per hour, seven hours being required in the case of $E_1d$, and eight hours in the case of $E_2d$, to bring the temperature down to 1400° C., when the gas was turned off and the furnace allowed to cool over night. In both cases the material in the crucible after cooling presented a shiny, dark chocolate-brown surface.

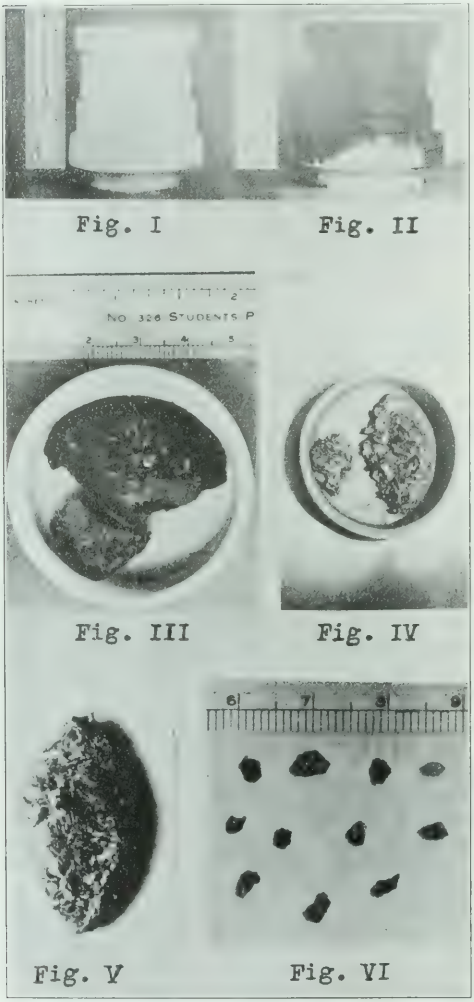
The fracture of the material after removal from the crucible showed distinct separation of crystals much as was formed in the celites formerly prepared, but in which the $R_2O_3$ was $Al_2O_3$. Sufficient of the material was ground fine to enable pats to be made and to test for the presence of free lime. $E_1d$ took an initial set in twenty minutes and a final set in four hours and twenty minutes, although the final set did not become

[1] A. C. Fieldner and A. E. Hall, THIS JOURNAL, **7** (1915), 478. For analyses of these ashes see *Ibid.*, **7** (1915), 401.

[2] THIS JOURNAL, **5**, 627.

[3] *Ibid.*, **6**, 706.

any harder after twenty-four hours. After four hours' immersion in boiling water the pat was completely disintegrated, indicating the presence of free lime. The presence of free calcium oxide was also confirmed by the formation of calcium phenolate when treated with White's reagent.




Figs. I and II—Magnesium Oxide Disks and Dish, before and after Absorption
Figs. III and IV—Dish Containing Pieces, before and after Absorption
Fig. V—Mass of Crystals after Solvent Had Been Drained Away
Fig. VI—Individual Crystals

When a pat was made of $E_2d$ it took an initial set very gradually, in about one hour, but did not reach a final set until between two and three days when, however, it became very hard. On submitting such a pat to a boiling test for ten hours it remained perfectly sound and samples of the freshly ground material, on treating with White's reagent, gave no indication of the presence of free calcium oxide.

It will be noted from the molecular ratios in Table II that $E_1d$ would contain 22.8 molecules excess CaO over what would be required to form a ferrite having an empirical formula, $5CaO.3Fe_2O_3$, with tricalcic silicate, while the $E_2d$ was prepared to correspond exactly with these empirical ratios.

The separation of the fusible constituent from the crystals was effected in substantially the same way as was done in former cases, by placing weighed pieces of the fused material in a dish made of pure magnesium oxide supported upon disks of the same material. The magnesium oxide dish, however, in the present cases was covered during the absorption by a disk of the same material which served to prevent loss of heat by upward radiation and to increase the amount of absorbent material. In both of the present cases two heat treatments were given on different days to insure as complete a removal of the solvent from the crystals as possible. The magnesium oxide disks supporting the dish were heated over night to a temperature of about 1100° when the weighed piece of celite was placed in the dish and after putting on the cover of the dish the temperature was quickly raised until the thermocouple indicated the minimum temperature at which it was thought absorption would begin.

In the case of $E_1d$ the temperature in the morning was first raised to 1425° C., at which it was held constant for three hours and twenty minutes, after which it was raised at the rate of 25° per hour for four hours, and then held at the maximum, 1525° for one hour longer, after which the furnace was allowed to cool. In the second treatment of $E_1d$ the dish to which the first disk was firmly attached was placed on a fresh magnesium oxide disk and the temperature in the morning was quickly raised to 1500° C., being further increased during two hours to 1575° at which it was held for six hours longer before allowing to cool. The crystals recovered weighed 7.5864 grams, which was 31.2 per cent of the material treated.

In the case of $E^2d$, after placing the weighed sample in the heated dish and covering as in the previous case, the temperature was first raised to 1415° and then held between 1415° and 1425° for two hours and forty-five minutes. It was then raised at the rate of 25° per hour during six hours, reaching a maximum of 1575° at which temperature it was held for one hour longer before allowing the furnace to cool. In the second treatment of $E_2d$ the temperature of the furnace in the morning was raised to 1575° at which it was held practically constant for six hours before allowing the furnace to cool. The crystals recovered weighed 7.6976 grams, which constituted 36.9 per cent of the material treated.

The double treatment of crystals from $E_1d$ and $E_2d$ was to insure as complete a removal as possible of solvent from the crystals. Incidentally it showed the stability of the crystals after they had once formed.

That the solvent in which the crystals form is,

when melted, a very mobile liquid capable of being absorbed by capillary action as in our former work is shown in the accompanying illustrations. Figs. I and II show side views of the stack of magnesium oxide disks and dish before and after the absorption, while Figs. III and IV are top views of a dish containing the pieces as they appeared before and after the absorptions. A mass of crystals, as it appeared after the solvent had been drained away, is shown in Fig. V, and a number of individual crystals are shown in Fig. VI.

Duplicate analyses of crystals showing the percentage composition are given in Table III from which the mean molecular ratios given below are calculated.

TABLE III—PERCENTAGE COMPOSITION OF CRYSTALS

| Crystals | $SiO_2$ | $Fe_2O_3$ | CaO |
|---|---|---|---|
| $E_1d$ | 25.33 | 3.75 | 69.94 |
| | 25.42 | 3.76 | 70.05 |
| $E_2d$ | 26.47 | 5.84 | 67.89 |
| | 26.40 | 5.71 | 67.89 |

The mean molecular ratios together with those of $C_1d$ crystals described in our former work are given in Table IV.

TABLE IV—MOLECULAR RATIOS OF CRYSTALS

| Crystals | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO |
|---|---|---|---|---|
| $C_1d$ | 100 | 13.6 | ... | 320.3 |
| $E_1d$ | 100 | .. | 5.6 | 296.6 |
| $E_2d$ | 100 | .. | 8.2 | 276.2 |

A report by Dr. Walter F. Hunt of the Department of Mineralogy on the optical properties of these crystals is as follows:

OPTICAL PROPERTIES OF $E_1d$

"A ground section of this material when viewed under a polarizing microscope showed a pale brown color with segregations of darker material in rods and patches scattered throughout the mass. Intricate lattice twinning was also observed, the lamellae intersecting at about 60°. Small crystals and broken fragments were also examined. The small, flat crystals were roughly hexagonal in outline, the angle varying from 59–61°. The average refractive index was found to be 1.716. The material is biaxial with small optical angle. The birefringence is weak and the optical character is negative."

OPTICAL PROPERTIES OF $E_2d$

"The material examined consisted of broken fragments and small, platy crystals of hexagonal outline. The color under the microscope was brownish and the segregations of dark material were numerous. The material is biaxial with extremely small optical angle. The optical character is negative and the average refractive index was found to be 1.717."

A study of the molecular ratios in Table IV as well as of the optical properties given by Dr. Hunt shows that the crystals are essentially tricalcic silicate. A further study of the molecular ratios given in Tables II and IV would indicate that $Al_2O_3$ acts only as an acid oxide and $Fe_2O_3$, while acting almost wholly as an acidic oxide, shows an apparent tendency to replace part of the CaO in the tricalcic silicate, this tendency increasing when an excess of CaO in the original solution is no longer present. From Table II it will be noted that the molecular ratio of $E_1d$ might be for convenience empirically written,

$33^1/_3\ (5CaO.3Fe_2O_3) + 99.3\ (3CaO.SiO_2) + 22.8\ CaO$,

whereas that of $E^2d$ might be expressed in the same way,

$33^1/_3\ (5CaO.3Fe_2O_3) + 110\ (3CaO.SiO_2)$.

The boiling tests as well as those with White's reagent, which showed the presence of free calcium oxide in the original fused mass of $E_1d$ and its absence from $E_2d$, would lend support to the probable correctness of the above empirical formulae.

Duplicate samples of 4 grams each of the magnesium oxide disks used in the absorptions were dissolved and the weight of silica, ferric oxide, and calcium oxide in each determined by the method of analysis used in our former work for the determination of such constituents in the presence of a large proportion of magnesium oxide. The weights of the constituents recovered and their mean percentage composition are given in Table V.

TABLE V—COMPOSITION OF ABSORBED MATERIAL

| | Constituents recovered Gram | | | Absorbed material Mean per cent | | |
|---|---|---|---|---|---|---|
| | $Fe_2O_3$ | $SiO_2$ | CaO | $Fe_2O_3$ | $SiO_2$ | CaO |
| $E_1d$ | 0.1512 | 0.0265 | 0.1636 | 44.01 | 7.73 | 48.26 |
| | 0.1512 | 0.0266 | 0.1680 | | | |
| $E_2d$ | 0.1725 | 0.0259 | 0.1662 | 47.16 | 7.06 | 45.78 |
| | 0.1719 | 0.0257 | 0.1681 | | | |

The molecular ratios of the absorbed materials calculated from the mean percentage compositions are as follows:

| | $Fe_2O_3$ | $SiO_2$ | CaO |
|---|---|---|---|
| $E_1d$ | 100 | 46.5 | 312.2 |
| $E_2d$ | 100 | 39.6 | 276.4 |

If we assume that the ratio of CaO to $SiO_2$ in the silicate remaining in solution in the absorbed material is the same as that in the crystals which separated out before absorption, then the 46.5 molecules of $SiO_2$ in the absorbed material from $E_1d$ would require 46.5 times 2.966 or 137.9 molecules of CaO, leaving the difference between 312.2 and 137.9 or 174.3 molecules of CaO to combine with 100 molecules $Fe_2O_3$. Calculating $E_2d$ in the same way we would find 276.4—(39.9 × 2.762) = 167.0 molecules of CaO to combine with 100 molecules of $Fe_2O_3$. Since an empirical formula, $5CaO.3R_2O_3$, would call for 166.7 molecules of CaO for 100 molecules of $R_2O_3$ it would seem from the above results that the absorbed material from $E_1d$ still carries some excess CaO in solution while the solvent in $E_2d$ contains no such excess. The fact that the crystals recovered are essentially tricalcic silicate and the solvent in the present case is calcium ferrite of the formula $5CaO.3Fe_2O_3$ would seem to justify the assumption that "Ferric oxide is molecularly equivalent to alumina, so far as formation of celite goes."

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## THE DETERMINATION OF METHYL AND ETHYL ALCOHOL IN SPIRIT VARNISHES[1]

By G. W. KNIGHT AND C. T. LINCOLN

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In the analysis of spirit varnishes for methyl and ethyl alcohol, the analyst is confronted with the problem of determining these constituents in the presence of other organic solvents which are difficult to separate from the alcohols. Chief among these are acetone and other ketones, and pyridine. Although pyridine seldom occurs in large quantity in commercial spirit

[1] Contributed with the permission of the Secretary of the Treasury and the U. S. Appraiser, Port of New York.

varnishes, it is sometimes used in the denaturing of grain alcohol, and consequently enters into the ultimate composition of varnishes which are made from denatured alcohol. Crude acetone, however, is frequently used in considerable amounts both alone and as a constituent of crude wood spirits; so any method to be practicable would have to give accurate results in the presence of these substances.

### DETERMINATION OF ETHYL ALCOHOL

For the determination of ethyl alcohol in varnishes containing volatile organic substances slightly soluble in saturated salt water solution, but soluble in petroleum ether, the method of Thorpe and Holmes[1] gives very satisfactory results. In the presence of acetone and other substances which are miscible in all porportions with water, however, the method is capable of giving very misleading results. As may be seen from theoretical considerations, and as has been actually shown in the practical working of the method in these cases, a number of extractions with the immiscible solvent directly proportional to the percentage of acetone present in the water solution, and inversely proportional to the ratio of the volume of the petroleum ether to that of the water solution, are necessary to reduce the amount of acetone in the final distillate to a negligible quantity. By the time this is accomplished an appreciable quantity of alcohol has been lost.

The most satisfactory method for determining ethyl alcohol, in the absence of methyl alcohol, and in the presence of appreciable quantities of acetone and similar substances, is to treat the alcohol, which is first distilled to separate it from most of the other constituents of the varnish, with phosphorus and iodine, forming ethyl iodide; and the ethyl alcohol present may then be calculated from the amount of ethyl iodide formed as described later on.

### DETERMINATION OF METHYL ALCOHOL

Where "Columbian spirits" have been used in the preparation of the varnish and no appreciable amount of acetone or ethyl alcohol is present, ordinary distillation conducted in such a way as to have not more than 25 per cent of alcohol in the final distillate, and consequent calculation of the percentage by means of the specific gravity tables of Klason and Norlin[2] (combined with the Thorpe and Holmes method, where necessary), gives very satisfactory results.

In the presence of acetone and the absence of ethyl alcohol, the method used for determining ethyl alcohol under similar conditions, as previously described, gives the best results.

### DETERMINATION OF MIXTURES OF ETHYL AND METHYL ALCOHOL—ACETONE ABSENT

The method devised by Leach and Lythgoe[3] is generally recommended in standard works for the determination of methyl and ethyl alcohol in tinctures and essences.

A few years ago one of the writers had occasion to analyze many hair tonics and similar preparations for methyl and ethyl alcohol. After the preparations had been analyzed, the method was tested with solutions containing similar quantities of the alcohols to those found. The results were far from satisfactory. An investigation into the cause of the inaccuracy led to the discovery that the assumption on which part of the method is based, *i. e.*, that the specific gravity of solutions of methyl alcohol in water is the same as that of ethyl alcohol for the same percentages of the alcohol by weight in the solution, is correct only for certain concentrations. The tables of Klason and Norlin for methyl alcohol and those in *Bull.* **107** (Rev.) of the Bureau of Chemistry both calculated for about the same temperatures (60° F./60° F. and 15° C./15° C.) are practically identical for dilutions of from 0 to 7 per cent of the alcohol by weight. From 7 per cent up, however, there is a gradually increasing difference until at 25 per cent by weight there is a difference of over 2 per cent. Consequently the error in the Leach and Lythgoe method increases in proportion as the ratio of methyl alcohol to total alcohol increases, and also in proportion to the percentage of total alcohol in the preparation; the maximum error occurs in the case where the substance analyzed contains nearly 100 per cent of total alcohol and the percentage of ethyl alcohol present is very small. This happened to be the case in the experience mentioned by the writers. The hair tonics contained over 90 per cent of total alcohol and less than 10 per cent of ethyl alcohol, and the error introduced by the Leach and Lythgoe method amounted to about 8 per cent.

To obtain accurate results by this method it is necessary to modify the process of calculating and using the tables. The following example, the same as that given by Leach and Lythgoe[1] to show the method of calculating percentages of the alcohols from the specific gravity and refractometer reading, will illustrate the difference in the results obtained by their process of calculation and the modified one.

Assuming that 25 cc. of the varnish had been diluted to 125 cc. and 100 cc. of distillate collected after purifying by the Thorpe and Holmes process, that the specific gravity of the distillate at 15.6° C./15.6° C. was 0.9735 and the refractometer reading at 20° C. was 35.8, then the Leach and Lythgoe method would give:

38.48 per cent $CH_3OH$ by weight
35.04 per cent $C_2H_5OH$ by weight
---
73.52 per cent total alcohol by weight

Using the same data and the modified method of calculation the following results would be obtained:

32.80 per cent $CH_3OH$ by weight
37.08 per cent $C_2H_5OH$ by weight
---
69.88 per cent total alcohol by weight

or a difference of:

+5.68 per cent $CH_3OH$ by weight
- 2.04 per cent $C_2H_5OH$ by weight
---
+3.64 per cent total alcohol by weight

Thus to obtain results of reasonable accuracy by the use of the Leach and Lythgoe method, the calcula-

[1] *Trans. Chem. Soc.*, **83** (1903), 814.
[2] *Arkiv. Kem. Min. Geol.*, **2** (1907), 27.
[3] *J. Am. Chem. Soc.*, **27** (1905), 964.

[1] *Loc. cit.*

tion of results must be conducted in the following manner in every case where the per cent of total alcohol in the final distillate falls between 8 per cent and 40 per cent of total alcohol by volume and an appreciable amount of methyl alcohol is present. Known mixtures of methyl and ethyl alcohol have been analyzed by the writers, using this modified method of calculation, with satisfactory results. The same example as that given above will serve to show the details of the calculation.

The specific gravity of the distillate 0.97350 corresponds to 18.38 per cent ethyl alcohol by weight and 16.43 per cent methyl alcohol by weight. The refractometer reading, 35.8 at 20° C., corresponds to 52.3 per cent of methyl alcohol on total alcohol, using the figure 18.38 as the per cent of total alcohol tentatively. Multiplying 523 by (18.38 — 16.43) and subtracting the product (1.02) from 18.38 gives 17.36, the approximate per cent of total alcohols by weight. By using this figure now instead of 18.38 to obtain the ratio of methyl alcohol to total alcohol by use of the refractometer reading and tables, 46.1 per cent of methyl alcohol is obtained. Recalculating the percentage of total alcohol now with this new percentage of methyl alcohol, 17.48 per cent is obtained. Repeating the calculation 17.47 is obtained as the true per cent of total alcohols and 46.9 as the true per cent of methyl alcohol of total alcohols, in place of 18.38 and 52.3 per cent, respectively.

The oxidation method of Thorpe and Holmes[1] may also be used in the absence of substances oxidizable to $CO_2$ by potassium bichromate and dilute sulfuric acid (1 : 4). In this method methyl alcohol is wholly oxidized to $CO_2$ and $H_2O$ while ethyl alcohol is converted mostly to acetic acid, 0.5 per cent only being converted to $CO_2$. The $CO_2$ given off is collected in a soda-lime tube and weighed, correction being made for the $CO_2$ formed from any ethyl alcohol that may be present.

### DETERMINATION OF MIXTURES OF ETHYL AND METHYL ALCOHOL—ACETONE PRESENT

Spirit varnishes or other preparations containing appreciable quantities of acetone cannot be analyzed for methyl and ethyl alcohol by either of the above methods with any degree of accuracy. One of the writers has obtained good results by precipitating out the acetone in the cold as iodoform with nascent iodine under conditions similar to those used in the Kebler[2] method for the determination of acetone, shaking out the iodoform with chloroform and the traces of chloroform with petroleum ether, and then redistilling a few times and applying the modification of the Leach and Lythgoe method given above. But, although the method gave good results when tried with known quantities of methyl alcohol, ethyl alcohol, and acetone, the manipulation was difficult and not easily mastered, the volumes of solutions were large and consequent distillations to reduce the volume of the final distillate were tedious, so that a more simple method was sought.

Of the many qualitative methods published, the oxidation method of Denigès[3] recommended by Simmonds[4] for the quantitative determination of methyl alcohol in the presence of ethyl alcohol was thoroughly tried out, but it failed to give satisfactory or concordant results with known mixtures. This method, however, was found to be useful as a qualitative test to detect the possible presence of methyl alcohol in a distillate. Another test of Denigès[1] is useful for the detection of ethyl alcohol in the presence of methyl alcohol. In the former test the alcohols are oxidized to the corresponding aldehydes by $KMnO_4$-$H_2SO_4$ mixture, acetone not interfering with the test; and in the latter test the ethyl alcohol is oxidized to acetaldehyde with bromine water, the methyl alcohol not being appreciably affected. Schiff's reagent is used to detect the aldehyde formed, and in the first test enough $H_2SO_4$ is added to prevent the acetaldehyde formed from affecting the reagent. These tests have the fault inherent to all generic tests, in that they are unreliable in the presence of aldehydes or substances that oxidize to aldehydes when treated with these oxidizing agents.

To obtain accurate results in the presence of acetone it is necessary to resort to a mode of procedure based on the formation of the alkyl iodides, and by analyzing or determining certain physical constants, or further elaboration of these, obtain the amount of the alkyl radicle present. This is a more strictly chemical method than any of those mentioned heretofore, as the reactions are more specific in their nature; but the manipulation is difficult and tedious, and requires considerable skill and time.

Many methods depending on these reactions have been published, of which the prototype is the well-known qualitative method of Riche and Bardy[2] for the detection of methyl alcohol in commercial spirit of wine.

Stritar and Zeidler[3] form the iodides in the usual manner and then determine the quantity by making use of Zeisel's well-known method for the estimation of methoxy groups in which methyl iodide vapor is decomposed by an alcoholic silver nitrate solution and the silver iodide formed determined gravimetrically.

Kramer and Grodyki[4] determined the percentage of methyl alcohol in wood alcohol quantitatively by treating iodine and phosphorus with the wood alcohol and a solution of iodine in hydriodic acid, distilling off the iodide, collecting the distillate in a measuring cylinder under water and calculating the percentage of methyl alcohol from the volume of the iodide formed.

In the Krell method, mentioned by Jones[5] as being used in a modified form in the British Government laboratory for estimating methyl alcohol in wood naphtha, the general outline of the method is very similar, but the addition of the solution of iodine in hydriodic acid is omitted, and the details of analysis are perfected. No other mention of this method was found in the literature.

[1] *J. Chem. Soc.* (trans.), **85** (1904), 1.
[2] *J. Am. Chem. Soc.*, April, **1897**.
[3] *Compt. rend.*, **150** (1910), 832.
[4] *Analyst*, **37** (1912), 16.

[1] *Bull. soc. chim.*, **7** (1910), 951.
[2] *Compt. rend.*, **80** (1875), 1076.
[3] *Z. anal. Chem.*, **43** (1904), 387.
[4] Schmidt, *Lehrbuch der Pharm. Chem.*, **2** (1901), 191.
[5] Allen's *Com. Org. Anal.*, **1** (1909), 91.

Wirthle[1] attempted to quantitatively determine methyl and ethyl alcohol in pure mixtures by the iodide method, but he was unable to obtain satisfactory results. He fractionated and distilled the iodides and calculated the percentage of the alcohols from empirical figures. He also tried weighing the iodides, after purification, and then calculating the percentages of the alcohol from empirical figures. The saponification values of the iodides formed by him were determined and the proper conditions for saponification studied.

Thorpe[2] suggests the use of a method involving the distillation of the iodides, similar to Wirthle's method, and gives a table showing the temperature at which the first drop distils over, and the volume distilling over below 72° C. from 10 cc. of mixed purified iodides, with corresponding percentages of methyl alcohol by volume in the mixture of alcohols for concentrations up to 10 per cent of methyl alcohol. He gives no detailed description of the apparatus used, nor the influence of barometric pressure on the boiling point, but says that ethyl iodide has a constant boiling point of 72° C. Thorpe also recommends the use of a modification of the Riche and Bardy method when the initial boiling point is below 70° C., but merely for the qualitative detection of methyl alcohol. The final result is obtained by dyeing two to three feet of Berlin wool, using a smaller quantity of alcoholic solution of the oxidized aniline mixture than that recommended by Riche and Bardy, absolutely no color being obtained in the absence of methyl alcohol.

Riche and Bardy, Kramer and Grodyki, Krell, Wirthle, and Thorpe, all recommend different proportions of iodide and phosphorus to alcohol. Riche and Bardy used 15 grams of iodine and 2 grams of phosphorus to 10 cc. of alcohol, while Kramer and Grodyki used 15 grams $PI_3$ and 5 cc. of a solution of 1 part $I_2$ in 1 part HI (sp. gr. 1.7) to 5 cc. alcohol. Krell adds his materials in the proportions of 44 grams of iodine and 4 grams of phosphorus to 10 cc. of alcohol. Wirthle, by calculation of the theoretical amount necessary, decides on about 32 grams of iodine for each 10 cc. of methyl alcohol, and 22 grams for each 10 cc. of ethyl alcohol, and in mixtures proportionate amounts. The amount of phosphorus necessary is calculated in the same manner. Thorpe recommends the use of 30 grams of iodine and 2 grams of phosphorus to 10 cc. of strong spirit.

Kramer and Grodyki, by their method of procedure, obtained a yield of about 92.5 per cent of the theoretical. They applied no external heat and used a quantity of iodine largely in excess of the theoretical. Wirthle, using about the theoretical quantity of iodine necessary to carry on the reaction, got yields varying from 88.3 to 93.8 per cent for ethyl iodide, and from 89.2 to 90.5 per cent for methyl iodide. He heated the mixture of iodide, phosphorus and alcohol on a water bath under a reflux condenser and regulated the heating so that the mixture would boil moderately. He was unable to account for the lack of uniformity in yields and consequent inaccuracy of results. The other investigators make no mention of yields.

Applying no external heat and using the quantity of iodine recommended by Thorpe for similar mixtures, we obtained yields of from 92.4 to 92.6 per cent for mixtures of the absolute alcohols containing from 1 up to 10 per cent of methyl alcohol. For pure methyl alcohol using the same procedure we obtained an 85 per cent yield. Working with a large excess of iodine and maintaining an external heat (75° C.), greatly in excess of the boiling point of methyl iodide, as recommended in Krell's method, we obtained yields of 100 per cent with ethyl alcohol and 98 per cent with methyl alcohol. These results would seem to show that it is necessary to use a large excess of iodine and supply a considerable quantity of external heat for a long time to complete the reaction and get a maximum or quantitative yield of the iodides. Either these iodides are endothermic compounds, or, so large an amount of heat is taken out of the reaction mixture in the form of latent heat of vaporization by the volatilization of the easily volatile compounds composing the mixture, that more heat must be supplied to complete the reaction. The slight loss we suffered in the case of methyl alcohol was undoubtedly due to solution of some of the methyl iodide in the 30 cc. of water under which it was collected. Methyl iodide is much more soluble in water than ethyl iodide. Rex[1] gives the solubility in water at 20° C. of ethyl iodide as 0.40 g. per 100 g. of water and of methyl iodide as 1.42 g. per 100 g. water. Although under the conditions of the determination, the water under which the iodides are collected is probably never saturated, their solubility in water is by no means a negligible factor in obtaining quantitative yields. The iodides seem to be as soluble in saturated salt solution as in water. To determine this point, the writers saturated water first with methyl iodide and then with salt. No separation of iodine occurred. Evidently nothing can be gained by collecting the iodides under saturated salt solution, but the ratio of the volume of water coming in contact with the iodides before measuring them to the ultimate volume of the iodides should be as small as possible.

The conditions necessary for a maximum yield of the iodides having been determined, the next step was to ascertain the best mode of procedure for determining the percentages of methyl and ethyl iodide in the mixture and ultimately the percentages of methyl and ethyl alcohol by volume corresponding, preferably eliminating calculation from empirical figures, if possible.

The method of determining the relative proportion of methyl and ethyl iodide in the mixture of iodides, suggested by Wirthle and worked out by Thorpe for mixtures containing 10 per cent and less of methyl iodide, was investigated. Wirthle gives the uncorrected boiling point of ethyl iodide as 70.8° C., while Thorpe says it is always 72° C. Determining the

[1] *Z. Nahr. Genussm.*, **34** (1917), 14

[2] "Dictionary of Applied Chemistry," **1** (1912), 63.

[1] *Z. phys. Chem.*, **55**, 355

boiling point in the manner recommended by Mulliken,[1] the writers obtained in eight entirely different samples on different days uncorrected values of 71.7° C., 71.5° C., 71.6° C., 71.8° C., 71.5° C., 72.0° C., 71.4° C., 71.5° C., and a mean of 71.6°; the thermometer used was carefully standardized at this temperature and found to be accurate. Corrected for stem exposure these values are 72.3° C., 71.2° C., 72.2° C., 72.4° C., 72.1° C., 72.6° C., 72.0° C., and 72.1° C., with an average of 72.1° C. The deviation from the mean in most cases was not more than 0.1° C. and was probably due to differences of barometric pressure, a difference of 10 mm. making a change of the boiling point of about 0.4° C. Mixtures of methyl and ethyl iodide made from corresponding mixtures of ethyl and methyl alcohol containing up to 10 per cent of methyl alcohol were distilled with the same apparatus used above. As had been expected, different results were obtained from those found by Thorpe.

Mixtures of "Columbian spirits" with absolute ethyl alcohol and of wood spirits with absolute ethyl alcohol containing 9 per cent of absolute methyl alcohol of the total alcoholic contents were transformed into the corresponding iodides and 10 cc. of the iodides distilled on the same day. The first drop distilled over at 62° C. in each case and the volume of distillate received below 69° C. was the same in both cases, namely, 4.5 cc. The distillation was repeated in one case and the distillation carried on more rapidly. In this case the first drop was collected at 61° C., showing the need of uniformity of distillation to obtain comparable results.

Similar mixtures of the iodides obtained from mixtures of the alcohols containing 11 per cent of methyl alcohol were distilled on the same day under similar atmospheric conditions and in the same manner as above with concordant results. The first drop was collected at 60.3° C. in each case and the distillate collected below 69° C. measured 5.0 cc. in one case and 5.1 cc. in the other.

Other mixtures made from alcohol containing 10 per cent of methyl alcohol but distilled on different days under different atmospheric conditions gave in one case, 1st drop at 60.0° C. and distillate below 69° C., 4.7 cc.; in the other case, 1st drop at 62.2° C. and distillate below 69° C., 4.3 cc. The method was further tested with other mixtures, but the results were concordant only within varying limits, owing to conditions over which we had no control and to correct for which would entail a considerable amount of tedious calculations. The method appears to have the same faults as the ebullioscope[2] method for the determination of ethyl alcohol, with added difficulties.

In the hope of developing a method that would be simpler and at the same time eliminate variations due to different atmospheric conditions and different types of apparatus, as well as obviate the necessity of working out empirical figures for each percentage content of alcohol, the writers investigated the specific gravity of the iodides and mixtures of the same. The literature was consulted with the following results:

Wirthle gives the sp. gr. of methyl iodide as 2.295 $\frac{(15^\circ\ C.)}{(15^\circ\ C.)}$ and ethyl iodide 1.943 $\frac{(15^\circ\ C.)}{(15^\circ\ C.)}$, but he did not attempt to determine the percentages of the constituents by difference in density.

Other investigators determined the specific gravities as follows: For methyl iodide, Perkins[1] found at 15° C. 2.28517, at 25° 2.25288; Pierre[2] at $\frac{(15^\circ\ C.)}{(15^\circ\ C.)}$ 2.28517; Bardy and Bordet[3] at $\frac{15^\circ\ C.}{15^\circ\ C.}$, 2.2677; for ethyl iodide, Perkins found at 15° C. 1.94332, at 25° C. 1.92431; Mendeléef at 15° C. 1.9309; Linnemann at 14.5° C. 1.9444, corrected to 15° C. 1.9434.

These figures show that both iodides have a relatively high coefficient of expansion; and this fact, together with the volatility of the liquids, undoubtedly explains the lack of uniformity in the results of different investigators. A difference of 10° C. between 15° C. and 25° C. makes a difference in sp. gr. of about 0.02 in the case of ethyl iodide and about 0.03 in the case of methyl iodide, while with water between the same limits, a difference of only 0.002.

The writers obtained the following results:

| | | |
|---|---|---|
| Methyl Iodide, specific gravity..... | (15.6° C./15.6° C.) | 2.2920 |
| | (25° C./25° C.) | 2.2700 |
| Ethyl Iodide, specific gravity..... | (15.6° C./15.6° C.) | 1.9470 |
| | (25° C./25° C.) | 1.9300 |

These results agree fairly well with those reported by Wirthle.

A number of mixtures of the alcohols containing varying percentages of methyl and ethyl alcohol, some without acetone and some containing up to 20 per cent of crude acetone, were analyzed, and formulae were worked out and simplified for the calculation of the percentages by volume of methyl and ethyl alcohol from the specific gravity of the iodides. In no case was there a great variation from the amount of the alcohols known to be present.

The Riche and Bardy method was carefully studied and the conditions and modifications necessary for making it available for a quantitative determination of methyl alcohol for quantities up to 10 per cent worked out.

Spirit varnishes were made up containing Columbian spirits, crude wood alcohol, grain alcohol, oil of turpentine, pyridine, ammonia water, aniline dyes, crude acetone and varnish resin. Varying proportions of the different constituents were put into each varnish. They were then analyzed by the method given below with satisfactory results, none of the above mentioned constituents, all of which may occur in commercial spirit varnishes, interfering with the accuracy of the process to a noticeable extent.

METHOD

[In the absence of acetone and pyridine use the

[1] "Identification of Pure Organic Compounds," **1**, 221.
[2] Leach, "Food Inspection and Analysis," **1904**, p. 545.

[1] *J. Pr.*, [2] **31**, 500.
[2] *Annalen*, **56**, 147.
[3] *Ann. chim. phys.*, [V] **16**, 569

modification of the Leach and Lythgoe method described above.]

Distil a quantity of the varnish, accurately measured at 15.6° C., sufficient to give at least 25 cc. of distillate. Place the varnish in a distilling flask, having the bulb immersed in a steam bath, the side tube connected with a Liebig condenser and the top connected with an aspirator bottle by a tube which has a glass cock attacked and passes through a rubber stopper into the bulb of the flask. Collect the distillate in an accurately graduated measuring cylinder, immersed in ice water and connected with the condenser by an adapter and with a Péligot tube containing water by a piece of bent glass tubing.

When the distillate ceases to come over pass air through the apparatus from the aspirator bottle until no more liquid distils. Allow the distillate to assume a temperature of 15.6° C. and read the volume accurately [if the distillate contains amyl or higher alcohols or esters (detected by the odor) they must be removed by the Thorpe and Holmes method and redistilled over anhydrous potassium carbonate until the final distillate contains less than 50 per cent of water].

Test the distillate for methyl alcohol as follows:

Dilute 1 cc. of the distillate to 10 cc. with water and then to 5 cc. of this solution, contained in a wide test tube, add $2^1/_2$ cc. of a 2 per cent solution of potassium permanganate and then 0.2 cc. of concentrated sulfuric acid. After three minutes add 0.5 cc. of saturated oxalic acid solution and shake. Then add 1 cc. of concentrated sulfuric acid and immediately afterwards 5 cc. of Schiff's reagent.[1] If methyl alcohol is present in the varnish a violet coloration appears in a few minutes. All reagents should be accurately measured in a pipette graduated to hundredths of a cubic centimeter.

Test another portion of the distillate for ethyl alcohol in the following manner:

Heat 0.2 cc. of the distillate and 5 cc. of bromine water (0.3 cc. of bromine in 50 cc. of water) in a boiling water bath for 5 or 6 minutes. Cool the mixture and, if still colored, add 10 per cent sodium bisulfite solution drop by drop until the color just disappears and then 5 cc. of Schiff's reagent. A red or reddish violet coloration indicates the presence of ethyl alcohol.

Place 20 cc. of water and 80 grams of powdered iodine in a 125 cc. distilling flask (in case the first distillate had to be purified to remove amyl compounds or the distillate contains an appreciable amount of water, use in place of 20 cc. of water, such an amount that the final mixture in the flask contains not more than 50 per cent of water). Immerse the flask in ice water. Add 20 cc. of the distillate measured at 15.6° C., connect the side tube of the flask with a long condenser, and the upper end of the condenser with a Péligot tube containing some water. Stopper the flask and allow the mixture to stand 15 minutes with occasional gentle shaking of contents. Then add 8 grams of red phosphorus, stopper the flask, and tip the condenser till it is inclined upward and forms a reflux condenser connected with the flask by the side tube. Keep the temperature of the mixture in the flask sufficiently low by immersion of the flask in ice water to prevent loss by volatilization. When the reaction has ceased, replace the ice water bath by a water bath and gradually heat the water to 75° C., being careful not to heat the flask so rapidly that any of the volatile constituents pass into the Péligot tube. Heat at 75° C. for about 20 minutes. Then allow the contents of the flask to cool to room temperature. Tip the condenser so that it inclines downward instead of upward, and connect the lower end with an adapter through a rubber stopper with a carefully calibrated measuring cylinder which is immersed in ice water and connected with a safety valve in the form of a Péligot tube containing water. Place 30 cc. of water in the measuring cylinder, replace the stopper in the flask with a cork carrying a glass tube fitted with a glass cock (closed) and connected with an aspirator bottle. Heat the flask gently at first, then with increasing heat, until most of the volatile matter has passed over, collecting the distillate under the water in the cylinder. Then raise the adapter till it dips into the water layer, but does not enter the iodide layer, open the stopcock and pass air through the apparatus until no more distils over. Allow the distillate to assume a temperature of 15.6° C. and read the volume carefully.

I—If the preliminary tests of the first alcoholic distillate show the absence of methyl alcohol, the percentage of ethyl alcohol in the varnish may now be calculated by the formula,

$$\text{Per cent ethyl alcohol in varnish} = \frac{3.622\,V_1V_2}{V}$$

where $V$ = volume of varnish used
$V_1$ = volume of alcoholic distillate
and $V_2$ = volume of iodides obtained

II—If the alcoholic distillate contains no ethyl alcohol,

$$\text{Per cent methyl alcohol in varnish} = \frac{3.315\,V_1V_2}{V}$$

III—When both ethyl and methyl alcohol are present together,

$$\text{Per cent total alcohol} = \frac{(0.3315\alpha + 0.3622\beta)V_1V_2}{V}$$

where $\alpha$ = Per cent of methyl alcohol by volume of total alcohol
and $\beta$ = Per cent of ethyl alcohol by volume of total alcohol

The values $\alpha$ and $\beta$ are determined by the following procedure: Transfer the contents of the measuring cylinder into a separatory funnel, add 3 cc. of 10 per cent NaOH solution and shake. Separate the iodides from the aqueous layer and wash in another separatory funnel with small quantities of ice-cold 1 per cent NaOH solution until the iodides are absolutely colorless. Draw off the washed iodides into a 50 cc. Erlenmeyer flask, add a few grams of recently heated potassium carbonate, stopper the flask and let it stand, immersed in ice water, with occasional shaking, for about half an hour. Filter into another 50 cc. Erlenmeyer flask, taking precautions to prevent evaporation by using a funnel that fits the neck of the flask perfectly and covering the funnel with a watch glass. Stopper the flask, immerse in ice water, and use the purified product

[1] Mulliken's "Identification of Organic Compounds," Vol. I, p. 15.

thus obtained for the accurate determination of the specific gravity[1] of the mixed iodides at 15.6° C.

IV—From the specific gravity thus obtained calculate the percentage by volume of methyl alcohol in total alcohol ($\alpha$) by the following formula:

$$\text{Per cent methyl alcohol} = \frac{3905\ (G - G_2)}{39.05\ (G - G_2) + 51.25\ (G_1 - G)}$$

where G = specific gravity $\left(\frac{15.6° \text{ C.}}{15.6° \text{ C.}}\right)$ of mixed iodides

$G_1$ = 2.292; specific gravity (15.6° C./15.6° C.) of methyl iodide

and $G_2$ = 1.947; specific gravity (15.6° C./15.6° C.) of ethyl iodide

Subtracting the percentage of methyl alcohol thus obtained from 100 gives the percentage of ethyl alcohol ($\beta$). From these values, the percentage of total alcohol by volume is readily calculated by Formula III and then the percentage by volume of each in the varnish.

If the percentage of methyl alcohol in total alcohol falls below 10 per cent, the following procedure based on the Riche and Bardy method for the detection of methyl alcohol will be found to give quantitative results of greater accuracy than is possible by the specific gravity method.

Two standard solutions, one of absolute ethyl alcohol and the other containing a mixture of 10 per cent by volume of absolute methyl alcohol and 90 per cent by volume of absolute ethyl alcohol, are treated to form the iodides and distilled and purified as described above, and then subjected to the following treatment together with the unknown:

Place 5 cc. of the iodides with an equal volume of aniline in a 200 cc. narrow neck flask, stopper the flask and allow to stand over night in a dish of water at room temperature. In the morning add 150 cc. of water, heat till the water just begins to boil, add about 30 cc. of 10 per cent caustic soda solution and then water until the light oily layer of dimethyl and diethyl aniline is brought into the neck of the flask. Pipette 1 cc. of the oily layer into a small porcelain dish and mix it well with 10 grams of an intimate mixture of 100 parts of clean sand, 3 parts of finely powdered cupric nitrate,[2] and 2 parts of finely powdered sodium chloride. Heat the dish in an oven at 90° C. for about 8 hours, occasionally stirring the mixture and breaking up the lumps that may form. Then transfer the entire contents of the dish to a 100 cc. graduated flask with hot 95 per cent alcohol, using not more than 80 cc. of alcohol in all, and boil for about 20 minutes. Cool the flask, make up to the mark with 95 per cent alcohol, shake, allow to settle, pipette 1 cc. of the solution into a 500 cc. graduated flask and fill up to the mark with water.

By mixing the standard solutions thus obtained from the absolute ethyl alcohol and the mixture containing 90 per cent of ethyl alcohol and 10 per cent of methyl alcohol in the proper proportions, make up standards ranging from 1 per cent methyl alcohol to 9 per cent methyl alcohol, leaving enough of the initial standards to use for comparison also. Now compare the unknown solution with these standards either in Nessler tubes or a suitable colorimeter. In case the unknown has a tint between any two of the standards, by further dilution of these, the percentage can be determined to tenths of a per cent. If the shade of the unknown is deeper than the 10 per cent standard, it may be matched with the standard by dilution, but the variation from the standard must not be great or the method becomes inaccurate.

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[1] Where time permits, it would be well to run blanks for specific gravity determinations, with absolute methyl and ethyl alcohols, to prevent differences that usually occur with different operators owing to personal equation, etc.

[2] The cupric nitrate must be very finely powdered and the component parts must be intimately mixed in order to make the colorimetric test sufficiently delicate for quantitative work and the mixture used for the standards must be identical with that used for the unknown determination, since different mixtures give different intensities of color with the same quantity of dimethyl aniline.

## NEPHELOMETRY[1] (PHOTOMETRIC ANALYSIS)
## I—HISTORY OF METHOD AND DEVELOPMENT OF INSTRUMENTS

By Philip Adolph Kober and Sara Stowell Graves

Received June 14, 1915

### INTRODUCTION

Quantitative analysis in the past has depended chiefly upon the production of precipitates, more or less insoluble. Until recently these precipitates have been separated from their surrounding media either through filtration or sedimentation, and in most cases washed, dried and weighed. The object of these manipulations, which require considerable practice and skill, is, of course, to determine the mass or weight of the precipitate itself. All chemists know how much time, skill and patience it takes to accomplish the separation, purification and weighing of precipitates. In applied chemistry, where colloids and similar interfering substances are met, the lot of a chemist who endeavors to estimate substances gravimetrically is not a happy one.

Fortunately, the analyst is not entirely dependent on gravimetric analysis, but for many substances, volumetric and colorimetric methods have been developed, which often are equally as accurate and save considerable time. Nevertheless, the great number of estimations depend, as is known, on gravimetric methods. For this reason a photometric method of analysis, called nephelometry, has been developed, which attempts to estimate the mass or weight of precipitate in a solution directly, *i. e.*, without filtering, washing and weighing. The name is derived from the Greek word "nephel," meaning a cloud.

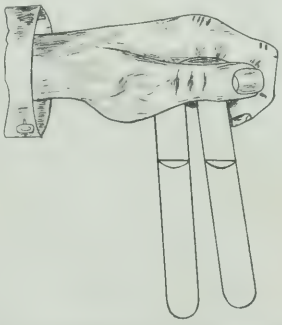

Fig. 1 First Step in the Development of Nephelometry
The amount of precipitate was gauged roughly with the eye. (1859 Mulder.)

[1] Read before the New York Section of American Chemical Society, Chemists' Club, June 11, 1915.

The basis of the method is the measurement of the brightness of the light reflected by a cloud—in other words, by the particles in suspension—very much as in an ultramicroscope. The intensity of light reflected is a function of the quantity of suspended particles, when other conditions are constant.

### HISTORY OF METHOD

The principle of the method may be seen most easily by tracing its development. Fig. 1 shows how,

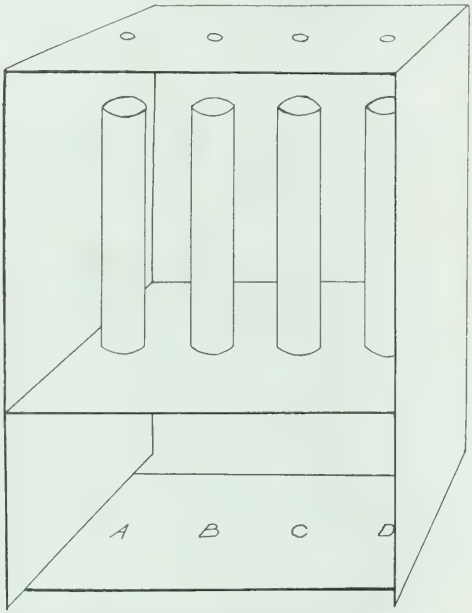


FIG. 2—SECOND STEP IN THE DEVELOPMENT OF NEPHELOMETRY

The amount of absorbed light was compared to that of a standard. Used by Stas in 1874. Light was reflected from illuminated scale through tubes, containing precipitate, to the eye.

when two test tubes were held side by side and the amounts of turbidity were roughly compared, the first step in the development of nephelometry was taken. Thus, Mulder, in 1859, roughly compared opalescent silver chloride suspensions obtained in his filtrates from atomic weight determinations. Fig. 2 shows the use, by Stas in 1874, of a series of tubes, about 4 cm. in diameter, with perfectly plain bottoms. Four tubes were supported adjacent to each other upon a shelf over holes of nearly the same diameter. Beneath the shelf was placed an illuminated scale and everything above the shelf was kept in darkness. When the marks on the scale viewed through two heights of opalescent solution appeared equally illuminated, Stas assumed that there was an equal weight of precipitate in the two tubes. It will be observed that Stas measured the absorbed light, which for fine, white clouds is not nearly as sensitive as the reflected light. This will be shown and discussed in detail later.

Fig. 3 shows the first real nephelometer, made by Professor Richards of Harvard; in 1894, in connection with his atomic weight work on strontium. Two test tubes were slightly inclined so that one could

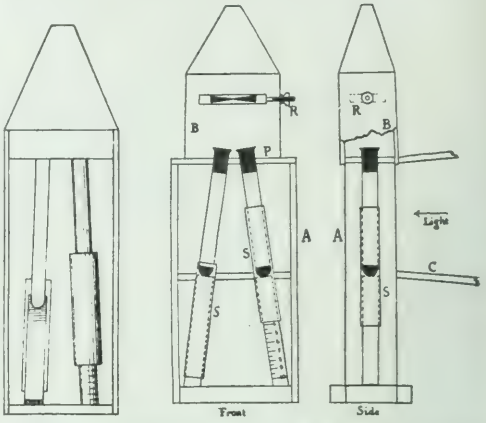


FIG. 3 FIG. 4

FIG. 3—FIRST NEPHELOMETER Made by Richards in 1894. Substance contained in two test-tubes; observed from above. Sliding jackets (graduated) were used to match the light reflected.

FIG. 4—SECOND NEPHELOMETER. Made by Richards and Wells in 1904. The sensitiveness of the instrument was increased by painting the ends of the tubes and inserting two prisms.

look into both with one eye, without moving. Around the test tubes were two opaque sliding jackets. When the slides were adjusted so as to give equal opalescence in the two tubes, the precipitates were assumed to be

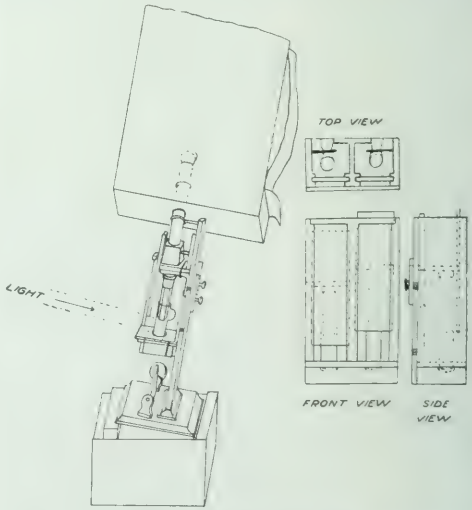


FIG. 5 THIRD NEPHELOMETER

Made by Kober in 1912, from a Duboscq colorimeter with wooden attachments. This instrument eliminated errors due to the meniscus and produced a much better optical equipment.

present in amounts inversely proportional to the length exposed to the light.

Ten years later, in 1004, Richards and Wells.

made a number of improvements in the apparatus, and Fig. 4 shows the improved instrument. The tubes destined to hold the solutions under examination were test tubes free from striations, holding about 32 cc. and painted black around the top and bottom with asphaltum paint. These opaque bands formed the most convenient method, according to the authors, of obliterating reflections from the meniscus and from the curved bottom of the test tube.

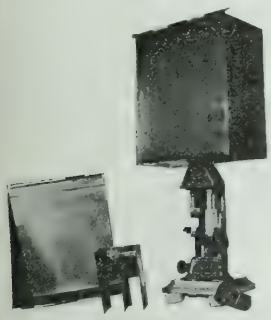

FIG. 6—FOURTH NEPHELOMETER
Similar to the third but with metallic attachments substituted in the place of the wooden. Made by Kober in 1913.

The nephelometer designed by Richards, in order to obtain a correction for his atomic weight work, was used to estimate small quantities of substances which he found in his filtrates. Richards expressly stated that the instrument was not intended for determining large amounts of substances.

Since the nephelometer described by Richards and Wells yields its best results only on taking a large number of readings, and since for practical work so much time for readings is objectionable, an improvement was highly desirable. It was thought that a similar instrument of greater accuracy which would yield reliable results with a few readings, comparable to those obtained with a Duboscq colorimeter, would greatly enhance the value of the nephelometer for the chemical analyst.

No doubt the Richards instrument sufficed for the purpose for which it was designed, and therefore efforts to improve the instrument were heretofore superfluous. However, since an instrument was desired, not simply to yield a slight correction to some other analytic process itself, but to yield all the figures of the determination, greater accuracy was now required.

## DEVELOPMENT OF INSTRUMENTS

Without going into the various considerations connected with the construction of the nephelometer, developed in the Harriman laboratory, it is sufficient to say that the optical workmanship of the Duboscq colorimeter proved to be an excellent basis on which to build a nephelometer and Fig. 5 shows our first nephelometer.

It was made by one of us, without any special tools, from small packing box boards. The parts, however, owing to moisture, soon warped and metal parts had to be substituted as may be seen in Fig. 6. The only changes necessary were a coat of black asphaltum paint on the plungers, a special nephelometric tube and a metallic receptacle for the same. The great advantage besides increased accuracy, in this instrument, is that it is still usable as a colorimeter, as the change from colorimeter to nephelometer and *vice versa* can be made in a few minutes.

This instrument gives very good results, but has a number of disadvantages:

(1) Only about 40 mm. height of liquid can be used.

(2) Repeated painting of the plunger is necessary because of the solvent action of some liquids, and the chipping off of paint through use.

(3) The cost, as it now stands, paying duty on the Duboscq colorimeter, is close to $100.00.

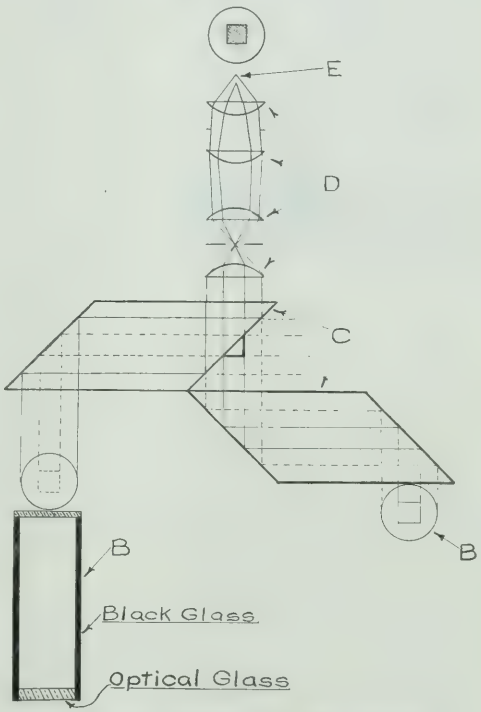


FIG. 7—OPTICAL EQUIPMENT OF THE NEW INSTRUMENT
Designed by Kober and shown for the first time. B—New plungers which change the height of liquid under observation. C—New arrangement of prisms, which gives a Lummer-Brodhun effect. D—Lenses of terrestrial eye-piece. E—Appearance of field; right-hand plunger changes light in the square, left-hand plunger changes light in circular space.

As it was impossible to get these French instruments at any price, owing to the war, we have had built, through the firm of Lenz & Naumann,[1] a new instrument, along the lines of a Duboscq colorimeter, but embodying all the latest results of our own experience.

Fig. 7 shows an almost ideal plunger, obtained after much experimentation. The end of the plunger of optically perfect glass was fused or melted to the black glass sides, thus making it impervious to all kinds of solvents, and eliminating cement troubles once for all. Fig. 7 also shows the optical arrangements, and the construction of the prism and eyepiece. This gives a Lummer-Brodhun field, which

[1] Pullman Building, 17 Madison Ave., New York City.

increases the sensitiveness of the readings. Fig. 8 shows the latest form of the instrument and also the operation of a dark curtain which cuts down stray reflections and always insures a black background.

FIG. 8.—NEW INSTRUMENT
Designed by Kober, made by Lenz & Naumann, New York. As may be observed black curtains operate with the cups, always insuring a black background

Furthermore, the instrument can be inclined at an angle and securely fastened there. The holes in the base permit one to screw the instrument tight to a table or other supports and thus prevent the apparatus from being jarred or accidentally moved out of the correct range of the light. The graduations for reading the heights of liquids are so constructed that they are adjustable and can be set exactly on zero, when there is zero light or color in the instrument. At least 100 mm. of liquid may be used, thus enabling us to estimate finer clouds and smaller amounts of substances.

This instrument, "made in America," in fact in this city, can be obtained for $36.00, thus reducing the cost some 300 per cent besides giving all the improvements just mentioned.

LIGHT—Accuracy in nephelometry is dependent on the uniformity and constancy of the light thrown upon the tubes. Although errors due to uneven distribution of light may in most cases be eliminated by careful standardization of the light, the errors due to changes or inconsistency in distribution are beyond control. Attempts to develop an ideal nephelometric light, *i. e.*, one in which the rays are both parallel and uniform, have thus far not been very successful, but the lamps shown here (Fig. 9) are the best that we have been able to obtain, after two years of experimentation. The object in trying to get parallel rays is to eliminate as much as possible the zero light of the instrument.

The theoretical qualifications for such a light are: (1) a point source of light, that can be conveniently attached to ordinary lighting circuits; (2) an optical system, the simplest being the Ramsden ocular, for making the rays parallel (Fig. 10).

Arc lights being excluded, the simplest form would be a filament lamp, where the filament was very compact. The compactness of the filament obviously depends on the length and thickness of the filament, but as most filaments are very fine, the main difficulty was encountered in the length. If low voltage had been available, say six volts (that of 2 to 3 storage cells), correspondingly shorter filaments could have been used, making the task much easier. Although storage cells are in universal use, for pleasure and business in automobiles, yet the introduction of them for nephelometric lights would almost make the price prohibitive.

In these new lights parallel rays are practically obtained, but for many purposes an ordinary powerful filament lamp well screened held about three feet from the instrument will give good results. These lights, as well as other attachments, can be obtained from the firm of Lenz & Naumann.

GENERAL CONSIDERATION

As to the accuracy obtainable with this type of nephelometer, the following figures will suffice: Two solutions of casein were made, unknown to the analyst. One was to serve as a standard, the other as an "unknown." The following readings were obtained:

| | Readings in Mm | | | | | | Average |
|---|---|---|---|---|---|---|---|
| Standard | 14.0 | 13.8 | 14.1 | 14.1 | 14.1 | 14.1 | 14.03 |
| Unknown | 14.9 | 15.1 | 15.1 | 15.1 | 15.1 | 15.1 | 15.06 |

Ratio of Unknown to Standard. . . . . 0.921

The standard was made by taking 25 cc. of stock solution, and the "unknown" by taking 23 cc. and diluting to 250 cc. The ratio, therefore, is 23 ÷ 25, or 0.920, which makes the error in this case about 0.1 per cent.

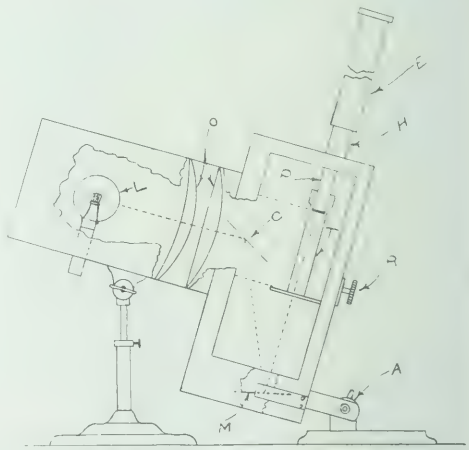


FIG. 9a.—NEW INSTRUMENT WITH LAMP HOUSE

A—Screw for changing slope of instrument to suit the convenience of observer. L—Light. O—Ocular, which produces almost parallel rays of light. C—A mirror (removable) inserted when the instrument is used as a colorimeter, which throws the light on M, the regular colorimeter mirror or reflector. T—Cups for holding liquid, either colored or containing a suspension. P. Plungers. H. Prism house. E. Terrestrial eye-piece. R. Rack and pinion which moves cups up or down. When mirror (C) is not used light falls on tube (T) at right angles; ready for nephelometric work. When used for colorimetry, cups (T) which have clear, transparent bottoms, are used. When used for nephelometry, cups (suggested by M. S. Fine), of the same shape but having perfectly black, opaque bottoms, are used.

As has been stated, the nephelometer can be used only when the substance to be determined is in the form of a suspension, which is stable long enough to allow readings in the nephelometer before floccula-

tion occurs. At the first thought one would expect that the instrument is applicable to only one class of substances, namely, colloids, but this is far from the truth. Professor Harry Jones, in his book "New Era of Chemistry," published before the development of nephelometric methods, states that "precipitation," meaning settling out of the substance, "is not the natural condition in chemistry" and, he adds, "is one of the most important phenomena in all chemistry and we are so familiar with precipitation from our analytical days that we are accustomed to look upon it as the natural condition when a solid is formed as the result of a reaction between two solutions. We see from the above (meaning some previous discussion) that such is not at all the case. A moment's thought will show why this is true. When substances react they react, we believe, molecule for molecule. The solid when first formed either has molecular dimensions or there are only a few molecules of the solid aggregated." He then concludes that "the colloidal solution or at most the colloidal suspension is the natural condition of solid matter when first formed as the result of a reaction."

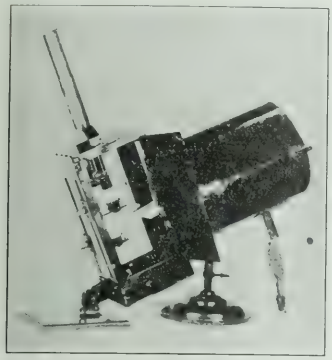

FIG. 9b—EXTERIOR OF NEW INSTRUMENT AND LAMP HOUSE

Shows the scales with verniers; also doors which when closed permit no light to be seen except in the eye-piece

Our experience has shown that the chief requisite for making these suspensions and for keeping them as such for a definite time, is that the substance be in a dilute solution, usually not stronger than 100 milligrams per liter. Therefore to apply the method to large amounts of substance it is only necessary to dilute suitably. Clouds, produced by one part in 500,000 of liquid, can also be determined quantitatively.

Since, therefore, the amount of substance seems immaterial, it is important to know whether the nature of the precipitate imposes any limitations on the method. It is necessary to consider:

I. COLOR—If the precipitate is highly colored and remains in suspension, it is best determined colorimetrically; if slightly colored, it is best determined nephelometrically.

II. FORM OF PRECIPITATE—It must be colloidal, in the form of a suspension. A large number of precipitates found in practical work are colloids; a number are partly so, while some are so entirely crystalloidal, such as barium sulfate, that they settle immediately. In work published by us certain solutions of protective colloids have been used; such as egg albumin and soluble starch, which causes crystalloids like barium sulfate and other partly colloidal precipitates to remain in suspension long enough for the application of this method.

*The nephelometric method must be used for colorless colloidal suspensions and for the accurate determination of amounts of material which give no delicate color reaction and are too minute to filter, but which are daily demanding our interest and attention.*

The use of the method has been extended to all classes of substances and since by careful work considerable accuracy can be obtained, the application promises to be general in the different branches of chemistry.

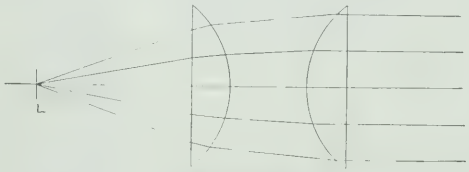


FIG. 10—RAMSDEN OCULAR

Two plano-convex lenses, the convex sides facing each other. (L) Position of point source of light.

At a later meeting we hope to have the privilege of discussing our theory and of describing the applications of nephelometry, to the estimation of proteins, fats, uric acid and other purines, ammonia, phosphorus, silver, chlorides, acetone, and nucleic acids.

HARRIMAN RESEARCH LABORATORY
ROOSEVELT HOSPITAL, NEW YORK CITY

## THE EFFECT OF AMMONIUM CHLORIDE UPON FERRIC AND ALUMINUM HYDROXIDES DURING IGNITION

By H. W. DAUDT

Received May 17, 1915

Complete removal of ammonium chloride from precipitates of ferric and aluminum hydroxides is commonly prescribed on account of the danger of formation and volatilization of the metallic chlorides. A statement by Hillebrand[1] to the effect that complete removal of ammonium chloride from aluminum hydroxide before ignition is unnecessary led to the carrying out of experiments which completely confirm this statement.

Approximately 0.2 g. of pure iron wire was weighed out after thorough cleansing by scouring with clean, wet sea sand and drying. Each weighed portion was dissolved in hydrochloric acid, the solution was oxidized with nitric acid, and ferric hydroxide was precipitated by adding the solution to an excess of redistilled ammonia[2] in a platinum dish. After coagulation at boiling temperature, the precipitate was washed by decantation with the number of 50 cc. portions of hot water indicated in the following table. After being collected upon a filter paper, it was ignited to constant weight in a weighed platinum crucible, finally with a blast lamp.

[1] "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, *Bull.* **422**, Note C, p. 99 (1910).

[2] Baxter and Hubbard have shown ferric hydroxide to be essentially insoluble in an excess of ammonia, *J. Am. Chem. Soc.*, **28** (1906), 1508.

| No. of washings | 10 | 6 | 1 | 1 | 0 |
|---|---|---|---|---|---|
| Per cent iron | 99.79 | 99.79 | 99.74 | 99.79 | 99.8 |

Since there are no appreciable variations in the results,[1] it is evident that ammonium chloride in such small quantities produces no loss of iron during ignition of the hydroxide.

In the case of aluminum, approximately 0.2 g. of pure foil[2] was thoroughly cleansed and weighed, and, after solution in hydrochloric acid, aluminum hydroxide was precipitated in a platinum dish. Only a very small excess of ammonia was employed, on account of the slight solubility of aluminum hydroxide in ammonia. The precipitate was filtered, washed and ignited in the same manner as the ferric hydroxide.

| No. of washings | 7 | 5 | 0 | 0 | 0 | 0 |
|---|---|---|---|---|---|---|
| Per cent aluminum | 99.74 | 99.72 | 99.88 | 100.00 | 100.00 | 99.97 |

In these experiments the omission of the washing of the precipitate has not the effect of lowering the result, and we may conclude that here, as with ferric hydroxide, washing the precipitate free from ammonium chloride is unnecessary. The first two results are probably low because of excessive washing with pure water.

### THE EFFECTS OF CONSIDERABLE QUANTITIES OF AMMONIUM CHLORIDE[3]

Precipitates of ferric and aluminum hydroxides were saturated with ammonium chloride solutions of various concentrations, then dried, ignited and weighed.

Several grams of pure iron wire were dissolved in an excess of hydrochloric acid. The solution, after oxidation with nitric acid, was made up to a definite volume and weighed. After complete mixing, portions of it containing approximately 0.2 g. of iron were drawn off and weighed in small glass-stoppered flasks. The weighed portion in each case was then transferred to a Jena glass beaker, where the precipitation of the ferric hydroxide was made with freshly distilled ammonia. Only a slight excess of the precipitating agent was used, and the precipitate, after coagulation by boiling, was immediately transferred to the filter paper in order to avoid, as far as possible, the solvent action of ammonia on the glass vessel. Hot water was used in the transfer of the precipitate, which was then thoroughly washed with an ammonium chloride solution of definite concentration. The precipitate was then carefully dried and ignited to constant weight in a platinum crucible. The results given below express the per cent of iron in the iron wire:

| Per cent $NH_4Cl$ in wash solution | 0 | 0 | 1 | 1 | 5 | 10 | 10 |
|---|---|---|---|---|---|---|---|
| Per cent Fe found | 99.80 | 99.87 | 99.87 | 99.80 | 99.55 | 97.20 | 94.04 |

Apparently washing with ammonium chloride of 1 per cent strength causes no appreciable effect on the per cent of iron found, whereas, when solutions containing as high as 5 and 10 per cent are employed, a loss does occur. Furthermore, it was observed that a film of brown sublimate had formed on the inner edge of the crucible and on the bottom of the crucible lid when the two more concentrated solutions were employed.

In the case of aluminum, chemically pure aluminum nitrate was dissolved in water and hydrochloric acid, the solution made up to a definite volume and weighed. Portions of this solution were drawn off, weighed, and subjected to analysis.

Filtration and washing of aluminum hydroxide has always been a difficult and tedious task. It therefore seems appropriate to give a full description of certain details of manipulation which, when closely followed, made possible the carrying out of the above operations very easily and quickly. The solution of the aluminum salt, containing only a small excess of acid, was heated until steam was given off copiously, while stirring constantly. Freshly distilled ammonia was carefully added, until its odor could be detected in the steam. The solution with suspended precipitate was boiled for approximately three-quarters of a minute—not more than a minute. The solution was immediately transferred to a prepared filter paper, no attempt being made to decant the supernatant liquid. A very rapid filtration was obtained in this way. The precipitate remaining on the sides of the beaker was transferred as rapidly as possible by means of boiling hot water, and then washed with hot water or with an ammonium chloride solution of definite concentration. The results below express the per cent of the aluminum in the aluminum nitrate:

| Per cent $NH_4Cl$ in wash solution | 0 | 1 | 1 | 5 |
|---|---|---|---|---|
| Per cent aluminum found | 7.260 | 7.252 | 7.244 | 7.261 |

Evidently the aluminum hydroxide ignition is not affected by washing with a solution containing as high as 5 per cent ammonium chloride.

### CONCLUSIONS

I—Washing precipitates of ferric and aluminum hydroxides free from ammonium chloride is unnecessary, as in ordinary analytical practice the concentration of ammonium chloride is never as high as one per cent. When the precipitate of the above hydroxides is dissolved in acid, and another precipitation is made, it is not necessary to wash free from chlorides even when other metallic salts are present in the original solution; for, in that case, the second and final precipitation is made in a solution containing a small quantity of ammonium chloride, and only minute quantities of other salts.

II—It is of advantage to have small quantities of ammonium chloride present in the wash waters, on account of the fact that these precipitates tend to become colloidal when electrolytes are altogether absent in the wash solution.

III—Aluminum hydroxide can be filtered and washed very easily and quickly if certain details of manipulation are observed and carried out.

The author wishes to acknowledge his indebtedness to Dr. G. P. Baxter for valuable suggestions.

WASHINGTON, D. C.

[1] These experiments were carried out in collaboration with Dr. G. P. Baxter of Harvard University.

[2] The aluminum was apparently very pure. The solution in acid was clear and colorless and without weighable residue. The hydroxide as well as the oxide was white in color.

[3] This work was carried out at the University of North Dakota.

## ESTIMATION OF SELENIUM IN SULFUR

By W. Smith

Received May 21, 1915

The separation used depends upon the facts that the bromides of sulfur and selenium when shaken with excess of cold water decompose according to the following equations,

$$2S_2Br_2 + 3H_2O = H_2SO_3 + 3S + 4HBr,$$
$$SeBr_4 + 3H_2O = H_2SeO_3 + 4HBr,$$

and that the decomposition of the selenium compound proceeds very rapidly compared with that of the sulfur compound.

When the acids of selenium (small amounts of selenic acid being present, due to oxidation of selenous acid by bromide water) are heated with excess of hydriodic acid they are reduced to selenium[1] as follows:

$$H_2SeO_4 + 6HI = 4H_2O + 3I_2 + Se$$
$$H_2SeO_3 + 4HI = 3H_2O + 2I_2 + Se$$

In order to test the completeness of the above reaction a standard solution of selenic acid was prepared from selenium purified from four precipitations, and the selenium contained was estimated as described below, with the following results:

| Selenium | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Added, gram | 0.0160 | 0.0586 | 0.0586 | 0.0586 |
| Found, gram | 0.0158 | 0.0590 | 0.0590 | 0.0590 |

The details of the method, based upon the above reactions, are as follows: Weigh a quantity of finely ground sulfur (preferably about 50 grams) into an Erlenmeyer flask, then add a few cc. more bromine than grams of sulfur used; allow to stand for fifteen minutes (it is advisable to conduct this work in a fume cupboard in which a little ammonia has been sprinkled).

Transfer to a 100 cc. separating funnel and shake vigorously with 40 cc. of bromine water for 1 minute; separate the sulfur bromide from the aqueous solution, and pour the latter through a wetted filter paper. Add about 2 cc. of bromine and 40 cc. bromine water to the sulfur bromide, and repeat the extraction four times, the last extract being kept separate. If insufficient bromine be added sulfur separates during extraction; this can be avoided by the addition of more bromine to the sulfur bromide. If the quantity of sulfur in the aqueous solution be small it can be removed by boiling the bromine water.

The last extract is treated in the same way as the combined first extractions (proportionate amounts of potassium iodide, and hydrochloric acid being used). If the presence of selenium be proved in this last portion, extraction is repeated as often as necessary.

The solutions, which must contain an excess of bromine, are boiled till clear; any remaining free bromine is removed by careful additions of powdered potassium metabisulfite, or sulfite, until the solution just becomes colorless. The selenium in the red form may commence to precipitate at this stage.

Dilute to about 250 cc., add 15 cc. of hydrochloric acid and about 5 grams of potassium iodide and boil; this completes the precipitation of the selenium, and gradually converts the red into the black allotrope.

[1] A. W. Pearce, *Research Papers of Kent Chemical Laboratory*, **1** 1901), 338.

The free iodine is removed by the addition of a few cc. of the solution of potassium metabisulfite or sulfite. Boil for 20 minutes, filter through a tared Gooch crucible, wash the selenium with hot water, and dry at 100° C. until a constant weight is obtained.

The method has been found to work successfully on standard sulfur samples which were prepared as follows:

No. 1—By mixing red selenium with sulfur.

No. 2—By mixing black selenium with sulfur.

No. 3—By melting black selenium with sulfur.

No. 4—By melting black selenium with arsenic and sulfur in the molecular proportions of $AS_2SSe_2$.

The following results were obtained by the above method with from 10 to 30 grams of the standard sulfur samples.

No. 1
Red Selenium Mixed with Sulfur

| Amount added Gram | Amount found Gram | Error |
|---|---|---|
| 0.0454 | 0.0465 | +0.0011 |
| 0.0405 | 0.0410 | +0.0005 |
| 0.0454 | 0.0460 | +0.0006 |
| .. | .. | .. |
| . | .. | .. |
| . | . | .. |

No. 2
Black Selenium Mixed with Sulfur

| Amount added Gram | Amount found Gram | Error |
|---|---|---|
| 0.0390 | 0.0390 | 0.0000 |
| 0.0488 | 0.0493 | +0.0005 |
| 0.0341 | 0.0338 | —0.0003 |
| 0.0488 | 0.0497 | +0.0009 |
| 0.0488 | 0.0488 | 0.0000 |
| 0.0219 | 0.0212 | —0.0007 |

No. 3
Black Selenium Melted with Sulfur

| Amount added Gram | Amount found Gram | Error |
|---|---|---|
| 0.0227 | 0.0220 | —0.0007 |
| 0.0488 | 0.0478 | —0.0010 |
| 0.0488 | 0.0492 | +0.0004 |
| 0.0171 | 0.0171 | 0.0000 |
| 0.0488 | 0.0490 | +0.0002 |
| 0.0244 | 0.0250 | +0.0006 |

No. 4
Black Selenium Melted with Arsenic and Sulfur in Molecular Proportions of $AS_2SSe_2$ and Then Mixed with Excess of Sulfur

| Amount added Gram | Amount found Gram | Error |
|---|---|---|
| 0.0244 | 0.0252 | +0.0008 |
| 0.0488 | 0.0496 | +0.0008 |
| 0.0488 | 0.0495 | +0.0007 |
| 0.0283 | 0.0280 | —0.0003 |
| 0.0464 | 0.0470 | +0.0006 |
| .. | .. | .. |

A number of samples of commercial sulfur were analyzed and the following are some of the results obtained from Japanese samples:

| | | | | |
|---|---|---|---|---|
| Per cent arsenic | 0.80 | 0.70 | 0.50 | 0.30 |
| Per cent selenium | 0.152 | 0.085 | 0.055 | 0.045 |

It will be noted that there would appear to be a certain parallelism between the amounts of arsenic and selenium present in the above samples.

Tellurium, if present, will be estimated as selenium by this method, but examination of several samples of crude selenium obtained from sulfuric acid chambers proved that it was present in very small quantity, if at all, the maximum being 0.1 per cent of the selenium present.

The method used for the determination of tellurium was that of Browning and Flint[1] which is given below. If a sample of sulfur containing both selenium and tellurium be encountered, they could be estimated by the method described for the estimation of selenium, and tellurium could be determined as follows:

Dissolve the mixed selenium and tellurium which is contained in the Gooch crucible in a small quantity of hot, strong nitric acid; gently evaporate the solution just to dryness; dissolve the mixed oxides of tellurium and selenium in a small quantity of 1:2 hydrochloric acid, and warm for a few minutes. Dilute this solution with 200 cc. of boiling water and add ammonium

[1] Browning and Flint, *Am. J. Sci.*, **28** (4th Series) (1909), 112.

hydroxide in very slight excess; then make very slightly acid with a drop or two of acetic acid, allow to stand for 30 minutes and cool.

Now decant the liquid through a tared Gooch crucible, and wash the tellurium dioxide with cold water and dry at about 110° C. until constant weight is obtained.

LABORATORY CUMING SMITH & CO. PTY., LTD.
YARRAVILLE, MELBOURNE, AUSTRALIA

## EFFECT OF FREE FATTY ACIDS UPON THE FLASH AND FIRE POINTS OF ANIMAL FATS AND OILS

By ARTHUR LOWENSTEIN AND J. J. VOLLERTSEN

Received July 2, 1915

The authors having frequently noticed that the presence of an appreciable amount of free fatty acids in fats and oils depressed the flash and fire points of the fats or oils, an investigation was made to determine the relation between samples containing varying amounts of free fatty acids, the neutral glycerides, from which the free fatty acids were derived, and the total fatty acids of the fats and oils themselves.

It will be noted from Table I that in every case the presence of free fatty acids depresses the flash and fire point. The flash and fire determinations of the total fatty acids readily explains why this is true. A study of the data reveals interesting relations between flash and fire tests of the total fatty acids of different fats and oils as well as the tests of their neutral glycerides. A study of the flash and fire tests of the oils themselves reveals the fact that with an increase in the free fatty acid content there is a corresponding decrease in the flash and fire tests.

TABLE I—EFFECT OF FREE FATTY ACIDS UPON THE FLASH AND FIRE POINTS OF ANIMAL FATS AND OILS

Temperatures given in degrees Fahrenheit

| ORIGINAL SAMPLE | FREE FATTY ACIDS % | ORIGINAL SAMPLE Flash test | ORIGINAL SAMPLE Fire test | NEUTRAL GLYCERIDES Flash test | NEUTRAL GLYCERIDES Fire test | TOTAL FATTY ACIDS Flash test | TOTAL FATTY ACIDS Fire test |
|---|---|---|---|---|---|---|---|
| Acidless tallow oil | 0.20 | 620 | 670 | 624 | 668 | 368 | 438 |
| | 0.50 | 616 | 674 | 624 | 682 | 370 | 432 |
| Extra lard oil | 2.30 | 540 | 665 | 598 | 677 | 368 | 428 |
| "Off Prime" lard oil | 3.65 | 504 | 622 | 604 | 676 | 376 | 436 |
| No. 2 lard oil | 33.15 | 418 | 472 | 620 | 672 | 370 | 436 |
| "AA" white grease | 2.00 | 518 | 648 | 554 | 656 | 372 | 430 |
| "A" white grease | 4.05 | 488 | 628 | 548 | 646 | 350 | 412 |
| Prime tallow | 2.5 | 506 | 630 | 550 | 652 | 342 | 406 |
| Packers' No. 1 tallow | 8.90 | 490 | 526 | 536 | 666 | 374 | 424 |
| Packers' No. 2 tallow | 37.5 | 364 | 394 | 510 | 595 | 342 | 416 |

A similar investigation is under way relative to the influence of the presence of free fatty acids on the flash and fire tests of vegetable and fish oils.

The method of preparing the neutral glycerides and the total fatty acids was as follows: the neutral glycerides were prepared by shaking out the sample with alcoholic solution of caustic potash. The required amount which was necessary for exact neutralization was figured out from the percentage of free fatty acids present and a slight excess over this amount added. After shaking, the solution was allowed to settle out in the cold and the fat carefully drawn off, washed once with 50 per cent alcohol and four or five times with distilled water. The fat was then filtered and dried before the flash and fire determinations were made.

The total fatty acids were prepared by saponifying the fat entirely with alcoholic soda, driving off the excess of alcohol, dissolving in hot water, and precipitating by means of 1:1 sulfuric acid. The fat was thoroughly washed with water, filtered and dried.

The Cleveland open fire tester was used for determining the flash and fire tests.

The authors desire to express their thanks to Mr. P. Malekow who assisted in the analytical work.

MORRIS AND COMPANY
CHEMICAL LABORATORY
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## THE LYE HULLING OF CORN FOR HOMINY

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The method of hulling "home-made" hominy is a simple process. Enough lye is added to water in a large iron kettle to make the solution feel slippery to the fingers and field corn is boiled therein until the tips of the corn slip off easily. The tips and the hulls are often rubbed off by hand, after which the corn is carefully washed. The washing is usually done by simply hanging the basket containing the corn in a stream of flowing water and leaving it there, sometimes for two days. Such a method leaves much to the discretion of the operator.

In the factory this method is employed with modifications. The corn used is carefully selected of the best white variety. The hulling is done in large wooden tanks which have drains at the bottom and inlets for cold and hot water at the top. These tanks are fitted with large iron stirrers for the vigorous agitation of the lye liquor and have a capacity of about ten to twenty bushels of corn.

The corn to be hulled is dumped into the vat, the vat filled with hot water, which is kept hot with live steam, or cold water heated with live steam, and the stirrer started. The lye is poured in when the liquid is well heated and the hot mixture stirred until the black tips of the corn are loosened; then the lye liquor is drained off. The corn is washed in the hulling tanks first with hot and then with cold water until the lye is removed and at the same time the friction of the stirrers removes the loose tips, which are floated off with the wash water. This process of hulling and washing usually takes about three hours or more. This is the older process of hulling. In many factories now the corn is kept in the lye liquor but a short time and then put through a hulling machine which removes the hulls and tips by friction. (In the experiments described in this paper the corn was kept in the lye liquor until the tips and hulls were all loosened as is still the practice in many factories.) Without further treatment the corn is scalded in especially constructed wire baskets and mechanically put into cans. These are moved on a belt through hot water, usually containing a little salt, and this liquid fills them. The corn is cooked for several hours under pressure after it is sealed in the cans.

It was found, upon examining six well known brands of lye hominy, that two showed a large number of black grains, about one grain in twenty being black, while the remainder of corn in these cans was of per-

fect appearance. The grains of hominy in cans bearing two other brands showed some signs of turning black. The contents of a can of another brand was very white, whiter than could be obtained by straight lye hulling.

The present work was undertaken in connection with the problem presented by the blackening of the corn. The hulling of corn now sold on the market in many cases is imperfect and it is hoped that the results given below may prove of value to some who are interested in the subject. The experiments were all done on a laboratory scale but the stirrer and other apparatus were made as nearly like those employed in the factory as possible. The friction of the stirrers in individual hulling vats in factories may be somewhat different from that used in the following experiments. The results on hulling must be considered only roughly quantitative, since the operator's judgment is necessarily the only criterion of good hulling. In this paper, when corn is said to be well hulled, it is meant that not simply the tip is removed but also that as much of the hull of the corn has been removed as is practical in the factory process.

Preliminary to the study of the lye hulling of corn, a number of substances were tried qualitatively to see what their effect would be in place of lye. Solutions of salt, acetic acid, hydrochloric acid and calcium chloride gave no result. Sodium bicarbonate partially hulled the corn after several hours' heating, while soda-lime and lime gave fairly good results when heated for a long time. Lye was the only substance which gave satisfactory results for hulling in the ordinary way.

For the first hulling trials, chemically pure sodium hydroxide was used, after which Lewis' lye was most frequently employed. The kind of lye used is stated in each case. Table I shows the strengths of several

TABLE I—STRENGTHS OF COMMERCIAL LYES

| NAME | MANUFACTURER | Per cent lye as NaOH: Found by titration | Claimed on label |
|---|---|---|---|
| Lewis(*a*) | Penn Salt Mfg Co., Philadelphia, Pa. | 97 | 98 |
| Lewis(*b*) | | 95 | 98 |
| Eagle high test(*a*) | Eagle Lye Works, Milwaukee, Wis. | 91.4 | 100 |
| Eagle high test(*b*) | | 91.1 | 100 |
| Merry War | E. Meyers, St. Louis, Mo. | 82.0 | |
| Greenwich conc.(*a*) | Penn. Salt Mfg. Co. | 78.2 | |
| Greenwich conc.(*b*) | | 78.0 | |
| E. L. W. Am. test | Eagle Lye Works | 77.4 | |

brands of commercial lye. The values given in the table are calculated as NaOH, and were obtained by direct titration with carefully standardized HCl, using methyl orange as the indicator.

According to this table, Lewis' lye was the strongest lye of those tested. Eagle High Test is a very good lye. The others, however, contained considerable amounts of sodium sulfate and other impurities.

Hulling tests were made using chemically pure NaOH solutions of various strengths at 70° C., keeping the volume of the liquid and the weight of the corn constant. Table II shows the variation of the time of hulling with the concentration of the lye.

Using the Greenwich lye at 70° C. instead of chemically pure NaOH, by experiment, it takes about

TABLE II

| No. | Per cent NaOH present | Cc. liquid | Grams corn | Time of hulling |
|---|---|---|---|---|
| 1 | 0.6 | 500 | 50 | 2 5 hrs. |
| 2 | 1.2 | 500 | 50 | 2 hrs. |
| 3 | 2.4 | 500 | 50 | 1.5 hrs. |
| 4(*a*) | 6.0 | 500 | 50 | 1 hr. |

(*a*) Lye too strong for good hulling.

4 per cent of it to do the work of 2.4 per cent C. P. material.

In the previous trials, the volume of the liquid and the weight of the corn were kept constant. In Table III the concentration of the lye is kept constant and the other two factors varied. This determination was made at 70° C.

TABLE III

| No. | Lewis' lye Per cent | Cc. liquid | Grams corn | Time of hulling |
|---|---|---|---|---|
| 1 | 2 | 500 | 17 | 2 hrs. |
| 2 | 2 | 200 | 17 | 1.75 hrs. |
| 3 | 2 | 200 | 35 | 1.5 hrs. |
| 4 | 2 | 200 | 52 | 1.25 hrs. |
| 5 | 2 | 200 | 70 | 1 hr |

With 2 per cent Lewis' lye larger amounts of corn than those used in (5) of Table III cannot be run well because the liquid becomes too thick and syrupy. It appears strange at first that there should be such a large decrease in the time of hulling when the weight of corn is increased. As will be shown later, however, friction is a necessary factor in removing the hulls of the corn. One per cent Lewis' lye was also tried at 70° C. with the following results:

TABLE IV

| No. | Concentration of NaOH Per cent | Cc liquid | Grams corn | Time of hulling |
|---|---|---|---|---|
| 1 | 1 | 200 | 17 | 2 hrs. |
| 2 | 1 | 200 | 35 | 2 hrs. |
| 3 | 1 | 200 | 70 | 2.25 hrs. |

Here the increase of the weight of the corn in the solution seems to have little effect. The liquid in (3) becomes too thick for good stirring, and, as will be pointed out later, the grains of corn soak up considerable amounts of lye, so that the alkalinity of the liquid is much decreased.

Table V shows the effect of temperature on the time of hulling.

TABLE V

| No. | Temp. ° C | Per cent lye | Cc. liquid | Grams corn | Time of hulling |
|---|---|---|---|---|---|
| 1 | 25 | 10 | 200 | 35 | Practically no result in 2 hrs. |
| 2 | 50 | 3 | 200 | 70 | Over 2 hrs. |
| 3 | 70 | 1 | 200 | 35 | 2 hrs. |
| 4 | 90 | 1 | 200 | 35 | 1.75 hrs. |
| 5 | 90 | 1 | 200 | 70 | 1.67 hrs. |

The solution in number 5 shown in Table V became too thick for good work. Also, experiments showed that solutions heated to such a high temperature as 90° C. evaporate rapidly and these solutions gummed up very soon. Further trials showed that above 90° C. the time of hulling is about $^3/_4$ to $^2/_3$ of the time necessary at 70° C.; the grains of hominy seemed more firm when hulled at a temperature that is not too high. In our opinion, it is more preferable to do hulling at 70° C. to 80° C. and more practical than to attempt it at a higher temperature because the saving in alkali would hardly compensate for the trouble that it takes to watch the mixture at a higher temperature. From the above tables, it is to be seen that the concentration of the lye should not be less than 1 per cent and need not be greater

than 2 per cent at 70° C. for hulling in about 1 and 1/2 hours' time, which is a reasonable time limit. In the same way, the weight of corn per 100 cc. of lye solution should not be more than about 35 grams, and not less than about 17 grams, for economy's sake. To obtain the best results in hulling, it is better not to have too much corn in the lye liquor.

A study was undertaken to determine the amount of washing which is necessary to remove the lye from the corn after hulling. Since the lye penetrates into the grains of corn, a large number of washings would be expected, and in order to obtain the best results it is necessary that the lye be completely removed.

It might be pointed out before describing these experiments that just as it is better to wash precipitates many times with small portions of wash water, draining completely each time, than a few times with large amounts of wash water, it is better also to wash corn many times with small portions of wash water, with the provision that the corn be allowed to soak for a few minutes in each portion of wash liquid. In practice, the fresh water is run in and the waste allowed to flow out at the same time, keeping the volume of the liquid the same. The manufacturer would obtain the same results with less wash water if he used the water in small portions, draining after each washing. It may be, however, that this method would be impractical in the large factory on account of the time consumed.

For these experiments the corn was first hulled, using in each case 200 cc. of a 2 per cent solution of Lewis' lye and 35 grams of corn at 70° for 1 1/2 hours. The table below shows the alkalinity of the ash of the corn before and after washing, using 200 cc. of wash water at laboratory temperatures and allowing five minutes' stirring for each washing. The wash liquor in each case was drained off on a 1/4 inch mesh screen. The alkalinity as stated here is in terms of the cubic centimeters of 0.1 *N* HCl necessary to neutralize the water solution of the ash from 100 grams of the corn, using methyl orange as the indicator. The last three columns of the table are given so that the number of washings necessary to remove 99 per cent of the lye, for example, could be roughly calculated. Column No. 5 is stated in terms of the per cent of alkalinity remaining in the corn (which was not in the original corn) after 1, 2, 3, etc., drainings, assuming for the sake of calculation that this alkalinity after the first draining is 100 per cent. Column No. 6 gives the fraction of the partial alkalinity remaining after each washing.

TABLE VI

| No. | No. of drainings | Alkalinity | Alkalinity not in original corn | Alkalinity Per cent | Fraction of alkalinity remaining |
|---|---|---|---|---|---|
| 1 | Original corn | 43 | ... | ... | ... |
| 2 | 1 | 803 | 460 | 100 | ... |
| 3 | 2 | 299 | 256 | 55.7 | 0.55 |
| 4 | 3 | 246 | 203 | 44.1 | 0.79 |
| 5 | 4 | 185 | 142 | 30.8 | 0.69 |
| 6 | 5 | 152 | 109 | 23.7 | 0.77 |

Average, $0.70 = \frac{1}{1.43}$

This means that the fraction 1/1.43 of the lye remains with the corn after each washing. To remove all but 1 per cent of the lye, it would take, therefore, $(1/1.43)^{12}$, which equals 1/107, or twelve washings. In the same way it would take about eighteen washings to get all but 1/10 of 1 per cent of the alkali clinging to the corn as it came from the lye liquor.

Hot water, as would be expected, hastens the process of washing. Table VII is similar to the preceding table except that water at 70° C. was used for washing instead of water at laboratory temperature.

TABLE VII

| No. | No. of drainings | Alkalinity | Alkalinity not in original corn | Alkalinity Per cent | Fraction of alkalinity remaining |
|---|---|---|---|---|---|
| 1 | Original corn | 43 | ... | ... | ... |
| 2 | 1 | 533 | 490 | 100 | ... |
| 3 | 2 | 236 | 193 | 39.4 | 0.394 |
| 4 | 3 | 125 | 82 | 16.7 | 0.423 |
| 5 | 4 | 83 | 40 | 8.16 | 0.489 |
| 6 | 5 | 61 | 18 | 3.65 | 0.447 |

Average, $0.438 = \frac{1}{2.28}$

From this average value, it takes about six washings to remove 99 per cent of the lye and nine washings to remove 99.9 per cent of the lye clinging to the corn after the first draining. At about 25° C., it takes, then, just twice as much washing as it does at 70° C. to remove the same amount of lye from the corn.

It might be observed here also that nearly 2 grams of alkali are held by 100 grams of corn under the above conditions before washing. This may, in part, explain why the 1 per cent solution of lye is not strong enough for good, rapid hulling no matter how much the friction is increased during the process.

Since factory lyeing vats are somewhat different and methods of washing vary, further washing experiments were not tried. Suffice it to say that the washing of hominy after it has been hulled is one of the important steps in the process and great care should be exercised. If a large vat completely changes the water in five minutes, the washing should be continued for an hour with hot water, or a much longer time with cold water in order to make sure that all the lye is removed.

The process of hulling as shown by the above experiments is due partly to chemical action of the lye and partly to friction. The central parts of the grains of corn consist of starch which constitutes over 50 per cent of the whole corn. The hulls and exterior portions of the corn consist largely of gluten and albuminous matter. During the heating of the corn with the lye solution, the hot water tends to swell the gluten and albuminous material and the lye attacks them so that the outside matter becomes very soft. The hull is then mostly rubbed off by friction of the stirrers, the grains rubbing together, the friction of the liquid, etc., and much of the hull and exterior part of the corn which are removed in this process remain suspended in the lye liquor. A microscopical examination of the corn showed the above conclusions to be true. It would appear then that the more friction a manufacturer can introduce into his vat by way of rapid stirring toward the end of the hulling process, the less time it would take.

CONCLUSIONS

1—No common substance was found which could be used as a good substitute for lye in hulling corn.

2—The analyses of several common brands of commercial lye are given.

3—In practical terms it was found that not more than 2 lbs. of lye to 12 gal. of water were necessary to good hulling and not less than 1 lb. of lye to 12 gal. of water could be used with good results.

4—There need not be less than about 1 bu. of corn to 40 gal. of lye liquid and should not be more than 1 bu. of corn to 20 gal. of lye liquid.

5—70° C. (156° F.) has been found a convenient temperature for hulling in about $1^1/_2$ hours at the concentration just given, but above 90° C. (194° F.) hulling can be accomplished in about $^3/_4$ to $^2/_3$ of the time specified for 70° C.

6—Care must be observed in washing if all of the lye is to be removed from the corn. The amount of washing necessary has been roughly indicated.

7—It has been pointed out that the process of hulling is partly chemical and partly mechanical and that for the best results in hulling, very efficient stirring is necessary.

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## THE CARBOHYDRATES AND THE ENZYMES OF THE SOY BEAN

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In recent years various soy bean preparations have come into quite extensive use as special foods for the diabetic. The soy bean is especially suited for such a dietary as it is very rich in protein and fat, and furthermore contains only traces of starch. Notwithstanding this almost complete absence of starch, analyses of commercial flour made from the soy bean invariably show from 20 to 25 per cent of nitrogen-free extract. A number of investigators have studied this nitrogen-free extract from various points of view, but as far as the writers are aware no complete separation of the different carbohydrates existing in the soy bean has been published. The form of these carbohydrates is vital to the claims of the soy bean as a valuable food for the diabetic, for starch is by no means the only carbohydrate objectionable to those afflicted with diabetes. The purpose of the present study, therefore, was to attempt a rather complete quantitative separation of these carbohydrates in the material in question.

The literature of the soy bean is very voluminous and no attempt will be made to review it here. The published analytical data are indeed conflicting. One author found 9.3 per cent sucrose, others only 3 or 4 per cent, or less. Likewise certain European investigators report from 3 to 5 per cent starch, while Japanese chemists have not identified starch in the native soy bean. Many analyses of our own confirm the Japanese standpoint. These discrepancies as to starch content are probably due to the ripeness of the beans, or rather to the method in which they are allowed to ripen. Harz[1] found that when the beans do not ripen thoroughly or when they are allowed to ripen after the vines are cut, starch may be present, certain varieties being more likely to contain it than others, whereas if the beans are thoroughly ripened they are practically free from starch. Numerous authorities, including Schulze, Maxwell and Levallois, have identified galactan in the soy bean, Levallois[2] finding 9 to 11 per cent. Likewise, Borghesani[3] found from 2.86 to 3.86 per cent pentosan in five varieties.

For the past two years various varieties of soy bean have been grown on the Experiment Station Farm. Calculated to a uniform moisture content of 10 per cent these showed compositions given in Table I.

Typical analyses of commercial soy bean flours made in this laboratory also appear in Table I.

TABLE I

| VARIETY | Water | Ash | Protein N×6.25 | Fiber | N-free extract | Fat |
|---|---|---|---|---|---|---|
| SOY BEANS GROWN ON EXPERIMENT STATION FARM: | | | | | | |
| Ito San | 10.00 | 4.90 | 39.29 | 3.91 | 26.64 | 15.26 |
| Ito San | 10.00 | 4.76 | 39.96 | 3.85 | 25.67 | 15.76 |
| Quebec | 10.00 | 5.26 | 38.24 | 3.57 | 25.86 | 17.07 |
| Quebec | 10.00 | 5.64 | 40.46 | 3.68 | 24.88 | 15.34 |
| Kentucky | 10.00 | 5.54 | 36.55 | 4.37 | 26.82 | 16.72 |
| Medium yellow | 10.00 | 4.68 | 40.99 | 3.79 | 25.27 | 15.27 |
| Manhattan | 10.00 | 7.77 | 40.66 | 3.67 | 23.58 | 14.32 |
| Ebony | 10.00 | 5.16 | 40.59 | 5.21 | 24.97 | 14.07 |
| Peking | 10.00 | 6.29 | 37.70 | 5.87 | 27.11 | 13.03 |
| Medium green | 10.00 | 4.85 | 40.66 | 4.10 | 24.55 | 15.84 |
| Okute | 10.00 | 5.83 | 38.56 | 4.73 | 25.02 | 15.86 |
| Wilson | 10.00 | 5.09 | 37.38 | 5.78 | 27.56 | 14.19 |
| Arlington | 10.00 | 5.19 | 35.07 | 5.81 | 29.55 | 14.38 |
| Swan | 10.00 | 6.88 | 39.15 | 4.64 | 26.30 | 13.03 |
| Morse | 10.00 | 4.67 | 37.75 | 4.98 | 28.42 | 14.18 |
| Cloud | 10.00 | 5.64 | 37.23 | 5.43 | 28.98 | 12.72 |
| Mikado | 10.00 | 5.33 | 33.15 | 5.03 | 29.59 | 16.90 |
| Wing's mongol | 10.00 | 5.98 | 35.59 | 5.46 | 26.97 | 16.00 |
| Hollybrook | 10.00 | 5.73 | 38.49 | 4.28 | 28.44 | 13.06 |
| AVERAGE | 10.00 | 5.54 | 38.29 | 4.64 | 26.64 | 14.89 |
| COMMERCIAL SOY BEAN FLOURS: | | | | | | |
| | 4.9 | 4.4 | 45.7 | 1.9 | 22.6 | 20.5 |
| | 4.2 | 4.2 | 43.1 | 2.2 | 24.9 | 21.4 |
| | 3.0 | 5.0 | 42.3 | 5.4 | 24.5 | 19.8 |
| | 4.4 | 4.6 | 42.3 | 4.7 | 25.8 | 18.2 |
| | 7.8 | 4.4 | 39.9 | 3.9 | 24.9 | 19.1 |
| | 6.5 | 4.1 | 41.0 | 3.4 | 25.0 | 20.0 |
| | 4.6 | 5.1 | 42.9 | 4.2 | 22.4 | 20.8 |
| AVERAGE | 5.1 | 4.5 | 42.5 | 3.7 | 24.3 | 19.9 |

A comparison of the analyses of the soy beans and the commercial soy bean flour shows that the latter contains much more protein and fat and considerably less of all the other ingredients, doubtless due to bolting and other purifying manufacturing processes.

The beans selected for the present investigation were of the Hollybrook variety and grown on our own farm. The following is a summary of their analysis expressed in percentages:

TABLE II

| Water | Ash | Protein (N × 6.25) | Ether extract | N-free extract and fiber | Total |
|---|---|---|---|---|---|
| 12.67 | 4.64 | 36.69 | 14.92 | 31.08 | 100.00 |

| CONSTITUENTS INCLUDED IN NITROGEN-FREE EXTRACT | | | |
|---|---|---|---|
| Galactan(*a*) | 4.86 | Undetermined hemicelluloses | 0.04 |
| Pentosan | 4.94 | Dextrin | 3.14 |
| Organic acids (as citric) | 1.44 | Waxes, color principles, tannins, etc. (by diff.) | 8.60 |
| Invert sugar | 0.07 | | |
| Sucrose | 3.31 | | |
| Raffinose | 1.13 | TOTAL | 31.32 |
| Starch | 0.50 | Galactan from raffinose | 0.24 |
| Cellulose | 3.29 | | |
| | | Per cent N-free Extract and Fiber | 31.08 |

(*a*) Including 0.24 per cent galactan from raffinose.

The scheme of analysis in brief was to treat the finely ground meal successively with boiling 95 per cent alcohol, cold water, malt extract, 1 per cent hydrochloric acid, and 1.25 per cent sodium hydroxide, and

[1] Credit for the chemical work reported in this paper is entirely due to Dr. Bailey.

[1] *Zeit. Allg. Oesterr. Apoth. Ver.*, **23** (1885), 40.

[2] *Compt. rend.*, **98** (1881), 281.

[3] *Staz. sper. agrar.*, **40** (1907), 118 120

to determine the kind and amount of carbohydrate removed by each of these solvents.

ALCOHOL EXTRACT

The bean meal was freed from fat with petroleum ether, and the dried residue then boiled under a reflux condenser with neutral 95 per cent alcohol for 8 hours. By this treatment reducing sugars, dextrose, levulose, invert sugar and maltose, as well as sucrose and raffinose, are extracted. Raffinose is less soluble in alcohol than the other sugars named, according to Beilstein one gram being soluble in 1000 cc. of cold 90 per cent alcohol, freely soluble in 80 per cent alcohol at 60° C., and slightly soluble in boiling absolute alcohol. The same authority states that 0.9 part of sucrose is soluble in 100 parts of 90 per cent alcohol at 14° C., and one part in 250 parts of cold 97 per cent alcohol. From this it is seen that while raffinose is much less soluble in alcohol than sucrose, it is somewhat soluble in boiling absolute alcohol and, therefore, would be more so in boiling 95 per cent alcohol. It is estimated that in the portions digested with the boiling 95 per cent alcohol not over one gram of raffinose was present in a volume of from 400 to 450 cc. of alcohol. It seems reasonable, therefore, to assume that practically all of this sugar was removed at this stage, especially as it is known that sucrose and raffinose are in most cases removed together, and that, in spite of their difference in solubility, it is extremely difficult to separate them.

The alcohol extract was evaporated nearly to dryness and then taken up with water, the solution thus obtained not being clear. One cc. of basic lead acetate was added, causing a considerable precipitate, and the excess of lead removed with anhydrous sodium sulfate. A clear straw-colored solution resulted, in aliquots of which polarizations and reductions of Fehling's solution were made before and after inversion.

The direct reducing power of the solution was very slight, an aliquot corresponding to 20 grams of the original material yielding only 0.0319 gram of $Cu_2O$, equal to 0.07 per cent of invert sugar. After inverting 50 cc. of the solution in the usual way, an aliquot corresponding to 5 grams of the original substance yielded 0.4367 gram of $Cu_2O$, equal to 4.27 per cent of sugar, calculated as invert sugar and sucrose.

The direct polarization of the solution, calculated to the basis of normal weight of original material in 100 cc. and read in a 200 mm. tube, was +5.4° V. at 14–15° C. The invert readings for the same amount of material were practically zero, the average of ten readings being +0.02° V. Polarizations of a duplicate alcohol extract prepared as above gave a direct reading of +5.3° V., and an invert reading of +0.06° V.

The fact that the invert readings were not decidedly minus indicates the presence of some sugar other than sucrose. A sucrose solution reading +5.4° V. direct, on hydrolysis should read —2.3°. There is present, therefore, some simple sugar, or a complex one which hydrolyzes into dextro-rotatory sugars, which counterbalance the levulose rotation. This sugar cannot be dextrose or maltose because of the slight direct reducing power of the solution. Three qualitative tests were made which bear on the identity of the sugar or sugars in the alcoholic extract.

OSAZONE FORMATION—The simple hexose sugars in a state of purity form osazones in less than 20 minutes. Sucrose forms glucosazones in about 30 minutes, but, as Browne and others have noted, the presence of organic matter, such as other sugars, greatly affects the rate of the osazone formation. After heating the direct solution about one and three-quarters hours a considerable amount of glucosazone was formed, m. p. 201–203° C., rapid heating (this should be 204–205°). According to Tollens, raffinose yields an osazone after about two hours, its m. p. being 187–189°. The osazone observed by us is apparently due to sucrose, its formation being retarded for the reason noted above.

INVERTIN TEST—The enzyme invertin hydrolyzes sucrose into reducing sugars; it also acts upon raffinose and its failure to produce reducing sugars at all in the direct solution would indicate the absence of either of these sugars. It was found, however, that 0.1 gram of invertin acting upon 2 cc. of the direct solution for 15 minutes at 60–65° C. caused a heavy precipitate of $Cu_2O$ with Fehling's solution.

EMULSIN TEST—Emulsin hydrolyzes raffinose but is without action on sucrose:[1] 0.1 gram of emulsin + 10 cc. of direct solution + 10 cc. of water, incubated at 38–40° C. for about two hours, gave a very decided increase in reduction over a blank in which the action of the enzyme was inhibited by boiling.

From the above data, therefore, it is concluded that raffinose is present, and that we are justified in using Creydt's formula for sucrose in the presence of raffinose, in estimating these sugars from the polarimetric readings:

$$\text{Sucrose} = 0.5188\,a - \frac{b}{0.8452} = 3.31 \text{ per cent},$$

$$\text{Raffinose} = a - \frac{\text{sucrose}}{1.852} = 1.13 \text{ per cent},$$

or, a total of 4.44 per cent as against 4.27 per cent obtained by copper reduction as noted above.

COLD WATER EXTRACT

The alcohol-extracted material was dried and weighed: 13.024 grams of this residue were digested with 200 cc. of cold water for 24 hours, filtered and the water-insoluble material washed with about 200 cc. of cold water. The water extract was partially evaporated at 60–70° C., a little sodium carbonate being added to neutralize the faint acidity, and made up to a volume of 200 cc. The solution was opalescent and required the usual treatment with basic lead acetate before polarization.

The direct reducing power of the solution was very slight, an aliquot representing 1.628 grams giving no visible copper reduction. After hydrolysis for two and one-half hours with the usual amount of hydrochloric acid (sp. gr. 1.125), an aliquot representing 0.814 gram gave 0.1710 gram of $Cu_2O$, the precipitate being of a yellowish red color. This is equivalent to 5.73 per cent calculated as dextrin in the original

[1] Neuberg, *Biochem. Zeit.*, **3**, 519.

material. It will be shown later that much of this reduction was due to pentosan and galactan.

Direct polarization on the basis of normal weight in 100 cc., in a 200 mm. tube showed +11.5° V. at 10° C.; after the usual inversion for 10 minutes the reading was +5.7° V., and after hydrolysis for two and one-half hours it was +4.4°, both readings at 10° C.

The solution though opalescent gave a negative test for soluble starch. After adding strong alcohol to an aliquot of the water extract and allowing to stand for several days, the white gelatinous precipitate was filtered off, the filtrate evaporated, and the latter after making up with water to the same basis as above polarized +1.4° V., showing that the strong rotatory power was due to substances precipitable by alcohol, such as dextrin, vegetable gums and mucilages.

A test for mucic acid in the direct solution gave at first negative results, but after standing considerably longer than the prescribed time a white crystalline residue was obtained of the general appearance of mucic acid (m. p. 214° C., r. h.). This indicates the presence in the water extract of a galactose-yielding sugar, or complex, besides dextrin, and might be due to a small amount of raffinose not entirely removed by the boiling alcohol, but more probably to water-soluble galactan in the form of, or derived from, the vegetable gums and mucilages referred to above. (The very close agreement in the polariscopic readings of the two extracts prepared with 95 per cent alcohol, the second one being digested twice as long as the first, however, makes it improbable that any raffinose could have been left in the residue from the alcohol extraction.)

### MALT EXTRACT DIGESTION

Four grams of the material extracted with ether and boiling alcohol were washed with cold water first by decantation and then on the filter until the washings amounted to about 300 cc. and failed to reduce Fehling's solution on treatment with hydrochloric acid. This residue was digested with freshly prepared malt extract in the usual manner for two ninety-minute periods. The solution was then hydrolyzed and its reducing power determined, showing the equivalent of 0.50 per cent of starch in the original material.

### CELL WALL CONSTITUENTS

ONE PER CENT HYDROCHLORIC ACID EXTRACT—The residues from the starch determinations were thoroughly washed with water, alcohol and ether, and dried. At this stage all the more readily soluble sugars and the starch have been removed, and there remain the cell wall constituents, *viz.*, true cellulose and those complex substances closely related to cellulose and collectively termed "hemicelluloses." The hemicelluloses are less resistant to dilute acids than true cellulose, and they yield copper-reducing bodies of the hexose and pentose types. It is here that the true pentosan and galactan are found. In the soy bean Schulze[1] has shown that the hemicelluloses give rise to the pentose sugar arabinose and the hexose galactose.

[1] *Jour. Phys. Chem.*, **14** (1890), 253

The above residue from the malt digestion was accordingly boiled with 1 per cent hydrochloric acid for one hour under a reflux condenser—this acid having been found to be very effective in hydrolyzing pentosans.[1] The solution was then filtered, the residue washed with hot water, the filtrate neutralized, cooled and made up to a definite volume. An aliquot equivalent to 0.4 gram of the fat-free and alcohol-extracted substance reduced 0.0801 gram of $Cu_2O$, equivalent to 0.0345 gram of dextrose, or 5.93 per cent in the original material. As stated above, this reduction is not due to dextrose, but to the combined action of arabinose and galactose. With the data obtained up to this point, we cannot say in what proportion these sugars are present. Their reducing powers, according to Browne's experiments,[2] are

$$\frac{\text{glucose}}{\text{arabinose}} = 1.032, \text{ and } \frac{\text{glucose}}{\text{galactose}} = 0.898.$$

Calculating the reducing power obtained above as due entirely to arabinose we obtain 5.75 per cent, or as due entirely to galactose, 6.60 per cent. It is seen that expressing the results as "sugars due to hydrolysis of hemicelluloses, as dextrose" gives a figure close to the mean.

In order to gain data for the more definite expression of the copper-reducing substances obtained at this stage of the analysis, determinations of galactan and pentosan were made.

GALACTAN—Another residue from malt digestion was oxidized with nitric acid as in the official method for total galactan. A yield of 0.1480 gram of mucic acid (m. p. 212–214° C., r. h.) was obtained, equivalent to 3.38 per cent of galactose, or 3.05 per cent of galactan on the original basis.

PENTOSAN—A third residue from the malt digestion was treated in the usual way for furfurol-yielding substances, the equivalent of 3.09 per cent of pentosan, or 3.37 per cent araban being found.

Thus it appears that galactan and pentosan are present in practically equal amounts and, therefore, the reduced copper can best be expressed on the basis of the mean specific reducing powers of galactose and arabinose. Calculating in this way we obtain 6.18 per cent of carbohydrate which is due to a galactoaraban complex. This percentage agrees closely with the sum of the percentages of galactan and araban as determined.

1.25 PER CENT SODIUM HYDROXIDE EXTRACT—The residue from the hydrochloric acid treatment was then boiled for 30 minutes with 1.25 per cent sodium hydroxide solution, the filtrate being neutralized and hydrolyzed for two and one-half hours with hydrochloric acid. This filtrate was shown to have no copper reducing power.

CRUDE CELLULOSE—The residue from the previous treatment was thoroughly washed with water, alcohol and ether, and dried. It weighed 0.2065 gram, equivalent to 3.55 per cent on the original basis (not corrected for ash).

TRUE CELLULOSE—This residue was then moistened

[1] Councler, *Chem. Ztg.*, **18** (1894), 1617.
[2] *J. Am. Chem. Soc.*, **28** (1906), 439.

with water and exposed to chlorine gas for one hour, then washed with water, boiled in a solution of 2 per cent sodium sulfite and 0.2 per cent sodium hydroxide, filtered, washed and dried. The residue from this treatment weighed 0.1945 gram, equivalent to 3.34 per cent on the original basis (not corrected for ash). The ash of this residue weighed 0.0027 gram, or 0.05 per cent on the original basis, making the true cellulose 3.29 per cent.

### DISTRIBUTION OF PENTOSANS AND GALACTANS

Distinct from the insoluble hemicelluloses of the cell wall constituents are the soluble pentose- and hexose-yielding substances. In this group, broadly termed saccharo-colloids by Tollens, belong the vegetable gums and mucilages, which, from the nature of their transformation products, must be regarded as pentosans and galactans. They are soluble in water and generally insoluble in strong alcohol, though some appear to be dissolved to a slight degree in the latter solvent, especially if somewhat dilute. It should not be forgotten, of course, that certain true sugars yield mucic acid and furfurol due to some particular complex in the sugar molecule. Thus raffinose yields mucic acid and sucrose yields furfurol, due to the galactose and levulose complexes respectively.

According to Schulze, water-soluble pentosans are present in small amount in the soy bean. We have endeavored to gain some idea of the distribution of pentosan and galactan by determining the mucic acid and furfurol yields in the hot-alcohol-extracted and in the water-extracted and malt-digested residues.

In respect to mucic-acid-yielding substances the total galactan found was 4.86 per cent. In the alcohol-extracted material 4.62 per cent was present and in the water-extracted and malt-digested residue 3.05 per cent. It appears, therefore, that a small amount of the mucic-acid-yielding substance was removed by hot 95 per cent alcohol. This is attributable to the galactose complex in the raffinose molecule. Extraction with water and digestion with malt removes 1.57 per cent, showing that galactose arising from water-soluble galactan was in part responsible for the copper-reducing power of the hydrolyzed water extract already noted. There remains 3.05 per cent, or 62.7 per cent of the total galactans, in the cell wall constituents.

With regard to pentosans there were found in the original soy bean meal furfurol-yielding substances equivalent to 4.94 per cent pentosan. Hot alcoholic extraction removed 0.83 per cent, and 1.02 per cent was removed by treatment with water and by malt digestion. Thus 3.09 per cent, or 62.5 per cent of the total pentosan, remains in the cell wall constituents. The small amount removed by alcohol is largely due to substances insoluble in water, precipitated or occluded in the lead precipitate, when the alcoholic extract is taken up with water and treated with basic lead acetate. This lead precipitate was found to yield copper-reducing matter equivalent to 0.5 per cent pentose. The nature of the saccharo-colloids is rather obscure but they are quite probably the vegetable gums and mucilaginous materials present in seeds and plant tissues, which are dissolved in a slight degree by alcohol, and which are removed more completely by water in the next stage of our analysis. The removal of fructose as such, or in complex, may also offer a partial explanation. The 1.02 per cent of pentosan removed by water contributed to the copper-reducing power of the hydrolyzed water extract.

### ORGANIC ACIDS

Organic acids are largely precipitated by lead acetate, and the attempt was made to determine these by the scheme outlined by Schulze, *viz.*, precipitating the aqueous solution of the alcohol extract with lead, removing the excess of lead, decomposing the lead precipitate with hydrogen sulfide, removing the excess of the latter, and then precipitating the acids with calcium or strontium. An attempt to precipitate these acids with calcium acetate, as is done in the case of malic acid, failed for some unknown reason. Strontium hydroxide, however, gave uniform results, but somewhat lower than expected although there are no recorded analyses for comparison. The lead precipitate from 50 grams of material was decomposed with hydrogen sulfide, and the excess of the latter removed from the filtrate by evaporation. The clear, white solution was made up to 500 cc. and aliquots of 50 cc. taken for analysis. The aliquots were evaporated to 20 cc., 2 to 3 cc. of a saturated solution of strontium hydroxide and 180 cc. of 95 per cent alcohol were added, and the mixture was heated on the steam bath for one hour, then filtered while still hot. The precipitate obtained was yellowish in color, the filtrate being clear and giving no further precipitation with additional strontium hydroxide. On igniting the precipitate and titrating the strontium oxide 1.44 and 1.29 per cent of organic acids, calculated as citric, were obtained.

### UNDETERMINED SUBSTANCES

The amount of nitrogen-free extract which remains unaccounted for is 8.60 per cent. This is attributed largely to those undetermined substances removed by alcohol, since there was obtained about 16 per cent of alcohol extractives of which a little more than one-third have been determined. The exact nature of the undetermined extractives cannot be stated with much certainty, but they undoubtedly include chromogenic substances, vegetable waxes and possibly tannin complexes. It has already been noted that basic lead acetate produced a voluminous precipitation of these alcohol-soluble materials, but the purpose of this investigation has been served in demonstrating to what extent they were copper-reducing or yielded copper-reducing bodies on hydrolysis. It has been shown that the amount of such substances was small. We shall include these undetermined extractives in the alcohol fraction through lack of data for their distribution.

### SUMMARY

A consideration of the above data shows that the meal examined contained 4.51 per cent total sugars, 0.50 starch, 3.14 dextrin, 4.94 pentosan, 4.86 galactan (less 0.24 due to raffinose), 3.29 cellulose, 1.44 organic

acids and 8.60 per cent waxes, color principles, etc. Of these constituents only the first three, *viz.*, the sugars, starch and dextrin, amounting to 8.15 per cent, may be considered objectionable in a strict diabetic diet. The remaining nitrogen-free extract, 22.93 per cent, about three-fourths of the whole, consists of pentosans, galactans, organic acids, waxes, etc., forms which are not generally considered a source of danger in a diabetic diet.

TABLE III—SUMMARY OF ANALYSIS OF NITROGEN-FREE EXTRACT AND FIBER

| | |
|---|---|
| HOT 95 PER CENT ALCOHOL EXTRACT: | |
| Insoluble in water or precipitated by lead acetate: | |
| Saccharo-colloids as pentosan | 0.83 |
| Organic acids, as citric | 1.44 |
| Waxes, color principles, etc., by difference | 8.60 |
| Soluble in water and not precipitated by lead acetate: | |
| Invert sugar | 0.07 |
| Sucrose (Creydt) | 3.31 |
| Raffinose (Creydt) (0.24 galactan derived from galactose complex in raffinose) | 1.13 |
| COLD WATER EXTRACT: | |
| Soluble starch | 0.00 |
| Reducing matter after hydrolysis, calculated as dextrin (including 1.57 galactan and 1.02 pentosan) | 5.73 |
| MALT EXTRACT: | |
| Starch | 0.50 |
| 1 PER CENT HYDROCHLORIC ACID EXTRACT: | |
| Hemicelluloses, reducing matter calculated as galacto-arabinose. (Determined directly in the malt residue, galactan 3.05, pentosan as araban 3.37) | 6.18 |
| 1.25 PER CENT SODIUM HYDROXIDE EXTRACT: | |
| Reducing sugars | 0.00 |
| CHLORINATED RESIDUE, TRUE CELLULOSE | 3.29 |
| TOTAL | 31.08 |

## THE ENZYMES OF THE SOY BEAN

A number of investigators have reported the presence in the soy bean of various enzymes. The most conspicuous and important is the urease of Takeuchi,[1] which acts specifically upon urea, liberating ammonia. He has called attention to the economic possibilities of this enzyme from an agricultural standpoint, and Van Slyke and others[2] have made practical analytical use of it in the form of standardized urease preparations for determining nitrogen in urea-containing substances, such as blood, urine and other animal secretions and juices. Stingl and Morowski[3] have reported the presence of a powerful amylase. Bertrand and Riokind[4] discovered a glucoside, vicianin, and an enzyme capable of effecting its hydrolysis.

In this examination of soy bean meal a number of additional enzymes have been found. They will be mentioned only very briefly since the wide distribution of enzymes in seeds and other vegetable tissues and the readiness with which they can, in most cases, be detected, make a survey of such materials for the detection of enzymes of decreasing interest. The meal was ground with sand and distilled water, the suspension filtered through cheesecloth and the turbid filtrate used in most of the trials recorded.

AMYLASE—An aliquot representing one gram of material completely transformed 0.1 gram of soluble starch in 3 hours at 55°, while with 0.1 gram of material acting on an equal weight of substance the transformation reached the erythrodextrin stage, as indicated by iodine tests.

SUCROSE—Polariscopic readings indicated no hydrolyzing action upon cane sugar. Turbid filtrates and direct suspensions of the meal in water were allowed to act upon a $N/2$ solution of sucrose for periods of time up to 18 hours at temperatures ranging from 20° to 55°.

PROTEASE—No gelatin-liquefying action was detected but in trials with Witte peptone at 40° and with HCN as the antiseptic positive tryptophane tests were obtained after 48 hours, the same being very marked after 72 hours. Trials in which the peptone was omitted gave negative tryptophane tests, indicating no action upon the native proteins of the soy bean itself.

OXIDASES—Water suspensions of the meal decomposed hydrogen peroxide slowly at room temperature. They were without effect upon tincture of guaiacum except in the presence of hydrogen peroxide, when a blue coloration was rapidly produced.

LIPASE—There is a distinction between those enzymes capable of decomposing various esters (butyrases) and the true lipases which act upon the natural fats. The soy bean was found to effect both of these reactions. True lipases have been found in the seeds of Ricinus, rape, opium poppy, hemp, flax and maize, and are presumably present in all oily seeds.

The first trials made were with the turbid filtrate prepared as described above. The substrate used was butyrin (Merck's) and the antiseptic, toluol. Portions equivalent to one gram of material were allowed to act on 0.25 cc. of butyrin at 40°, all trials being neutralized to phenolphthalein at the beginning, and the acidity subsequently developed determined by titration with $N/10$ sodium hydroxide at 24-hour intervals. The duration of the experiment was 96 hours. The results can best be expressed by a tabulation of some typical trials and their controls (Table IV).

TABLE IV—THE ACTION OF SOY BEAN PREPARATION WITH BUTYRIN

| No. | Solutions Tested: Butyrin | Water | Addition (Toluol added to all) | Cc $N/10$ NaOH required after: 24 Hrs. | 48 Hrs. | 72 Hrs. | 96 Hrs. | Total |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.25 cc. | 20 cc. | | 0.1 | 0.1 | 0.1 | 0.1 | 0.4 |
| 2 | None | None | 20 cc. extract | 0.3 | 1.1 | 0.8 | 0.7 | 2.9 |
| 3 | 0.25 cc. | None | 20 cc. extract | 2.5 | 1.5 | 1.2 | 1.2 | 6.4 |
| 4 | 0.25 cc. | None | 20 cc. *boiled* extract | 1.1 | 1.0 | 1.0 | 1.0 | 4.1 |
| 5 | 0.25 cc. | 20 cc. | 1 gram meal | 5.5 | 2.5 | ... | 3.0 | 11.0 |
| 5a | None | 20 cc. | 1 gram meal | 1.5 | 1.0 | ... | 4.4 | 6.9 |
| 6 | None | 20 cc. | 0.5 gram glycinine | 0.3 | 0.3 | 0.3 | ... | 0.9 |

It is apparent that following the course of lipolysis by means of periodic titrations with alkali is complicated by the acid production of the soy bean, in substance, and its extracts both boiled and unboiled. While the acidity developed in Trials 3 and 5 was greater than in the various controls, the very considerable and irregular acid development in the latter is a disturbing feature. The development of acidity by cereal grains is generally recognized and one of us (J. P. S.) has given some attention to this point in a study of the determination of acidity in cattle feeds,[1] but the satisfactory explanation of the phenomenon is not yet presented. That the protein of the soy bean is not the disturbing factor is shown by Trial 6. The most pronounced ester decomposition is exhibited during the first 24-hour interval, some retarding influence being exerted thereafter.

[1] *Jour. Coll. Agr., Univ. Tokyo*, **1** (1909), 1.
[2] *Jour. Biol. Chem.*, **19** (1914), 2.
[3] *Monatsch. f. Chem.*, April, 1886.
[4] *Bull. Soc. Pharm.*, **14** (1907), 161.

[1] U. S. Dept. Agr., Bur. of Chem., *Bull.* **122** (1909), 160.

Another experiment was tried following the suggestion of Reynolds Green ("Soluble Ferments," p. 227). Five grams of fat-free material were extracted with 100 cc. of 5 per cent NaCl containing 0.2 per cent KCN for 2 hours at 35–40°. The preparation was filtered and trials made (1) directly with the filtrate and (2) with the filtrate after "activating" by making slightly acid with dilute acetic acid and allowing to stand 2 hours longer at 35–40°. The unactivated filtrate (1) showed no power to hydrolyze butyrin; the activated filtrate (2) was decidedly active. Twenty cc., equivalent to one gram of soy bean meal, acting upon 0.25 cc. butyrin required at 24-, 48- and 72-hour periods 2.0, 1.7 and 2.0 cc., total 5.7 cc., $N/10$ NaOH to neutralize the acidity developed. The control in which the extract had been boiled required at corresponding intervals 0.6, 0.7 and 1.0 cc., or a total of 2.3 cc. This activated extract also showed lipolysis of an emulsion prepared with soy bean oil. It appears that the spontaneous acid production of the soy bean itself has been largely eliminated by the above process. The amounts of acid developed by the control are uniform and much less than in previous controls, and the decomposition of butyrin is uniform and progressive, not diminishing as in previous trials.

There is present then a true lipase, which is dissolved by 5 per cent NaCl and which is either activated by acetic acid or generated by that acid from its zymogen.

### CONCLUSION

In addition to the urease, amylase and glucoside-splitting enzyme reported by other workers, the soy bean contains also a protease of the peptoclastic type, a peroxidase and a lipase. Negative results have been obtained for sucrase and protease of the peptonizing type. It was thought unnecessary to examine the material for urease and no attempt was made to corroborate the presence of the glucoside-splitting enzyme. The presence of an active amylase has been corroborated.

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## ACID RATIO: A NEW METHOD FOR DETERMINING THE PROTEOLYTIC STRENGTH OF GERMINATED GRAIN IN TECHNICAL ANALYSIS

By CARL A. NOWAK

Received May 10, 1915

The proteolytic activity of malts has been studied extensively by R. Wahl, the results of whose experiments were published in the *Proceedings of the 8th International Congress of Applied Chemistry*, **14**, 215–229. In this paper Dr. Wahl gives the details of a method devized by him, based upon the principle first made use of by Schidrowitz; namely, that the proteolytic enzymes exert a liquefying action upon semi-solid gelatine and that the relative proteolytic strength can be measured by the extent of this liquefying action. By using this method Wahl has arrived at a series of very valuable results regarding the peptic powers of various malts prepared from different types of barleys. While I have made use of Wahl's method on a number of occasions, I have found that the method is altogether too exacting in order to be serviceable in technical work. Unless the determination is carried out with the utmost care the results fail to be reliable.

Owing to the varying composition of the gelatine employed and the exacting conditions for performing the experiment, such as a fixed incubation temperature at which the solution is to be kept for a number of hours, the necessity of ice for chilling the water, the special preparation of a bacterial acid solution, etc., I have found that, when employing this method in practice, considerable difficulties are encountered. As a matter of fact it seems almost impossible for two chemists working independently and each employing reagents of his own preparation, to arrive at similar results.

Although I have had occasion to experiment with almost every one of the known methods for determining the extent, or progress, or products of proteolysis in malt solutions, such as the Fuld-Levison-Edestin method, the electrical conductivity method, etc., I have found that, aside from the gelatine method above mentioned, there is only one other method which is applicable to malt solutions.

This method is the one I have employed and has for its basis the Soerensen formaldehyde titration as originally published in *Biochem. Ztschr.*, **7** (1908), 45. It has been so modified by me as to greatly simplify manipulation in order to put the method within the reach of every one accustomed to relatively simple laboratory work. By thus simplifying the method with only a comparatively slight sacrifice as to accuracy, I have been able to reduce experimental error to a minimum so that the results obtained will be of such degree of correctness as to be equal in every respect to the usual standard of accuracy maintained in technical analysis. Furthermore, the preparation of the different reagents has been greatly simplified, and the entire work so arranged that the estimation does not require more than a total of 50 minutes in time.

The principle upon which the formaldehyde method depends is the estimation of reacting carboxylic-acid groups present in a digestion mixture. An amino acid, owing to its amphoteric character, cannot be directly titrated by a standard alkali solution in the presence of an indicator. If, however, formaldehyde in excess be added before the titration, the amino groups are converted into methyleneimino groups, losing their amphoteric character, whereupon they can be directly titrated with standard alkali in the presence of phenolphthalein.

The result of this titration is usually expressed as the percentage amount of total nitrogen in a mixture which enters into reaction with formaldehyde. For the purpose of malt valuation this is, however, not necessary, as we are not so much concerned with absolute values as with relative values. What we wish to determine is which malt or type of malt yields the greatest amount of amino acids, and also the extent to which this degradation of the proteids proceeds within a given time in different types of malt. It is, therefore, equally serviceable and far more convenient to make use of the titration figures as they are ob-

tained, rather than to first convert these into percentages of nitrogen, and then to make the comparison. A big saving in time and labor is thus effected.

The manner in which I operate is as follows: I prepare a cold water extract of malt with distilled water at room temperature in the proportion of 1 part of malt to 3 of water, using 50 grams of malt finely ground. The water and the malt are shaken at room temperature for a period of 30 minutes by means of some convenient shaking device, and then promptly filtered into a clean, dry flask. About 10 cc. are first permitted to pass through the filter and are then returned to the filter again, this procedure being repeated a second time. Exactly 45 minutes after the time of starting the extraction or 15 minutes after removing the solution from the shaking machine, a portion of the filtrate is titrated in the following manner:

Twenty cc. of the solution are placed in a beaker of 500 cc. capacity and about 20 cc. of distilled water and 0.5 cc. of standard phenolphthalein solution are then added, whereupon the mixture is titrated with $N/10$ NaOH. The number of cc. of the $N/10$ sodium hydrate required to produce a faint pink coloration are noted. This titration represents the natural acidity and can, if so desired, be figured over to a percentage basis and by multiplication with the factor 0.009 be stated in terms of lactic acid. However, this is not necessary, inasmuch as the titration figures themselves serve equally well for purposes of comparison. Ten cc. of the standard formaldehyde are next added and owing to the reaction with amino groups the mixture becomes strongly acid. The titration with $N/10$ hydrate is then continued until the solution has assumed a decided pink color. The additional amount of acid necessary to neutralize this increased acidity gives the measure of the amino groups which have entered into the reaction. For brewing purposes a malt having the greatest amount of amino groups is to be preferred, but only provided the original acidity has been fairly high, and the relation or ratio between the formol acidity and the natural acidity, obtained by dividing the number of cc. representing the amino acids by the number of cc. representing the natural acidity, is as 1 : 1.00 or greater. This ratio which I designate as the *acid ratio of malt* is an *entirely new factor in malt valuation*. A really good malt should be high in original acidity and should show an acid ratio of about 1 : 1.10, which for convenience sake I express simply as 110. There are some very good malts, especially low dried distillers' malts, which will have an acid ratio as high as 130, although I have failed to find any having a higher ratio. Large berried Western barleys (Bay Brewing, White Club, etc.) yield malts having a low acid ratio (about 88); two-rowed barley malts have an acid ratio of about 90 to 100, and regular six-rowed malts prepared from Manchuria barley about 110 to 120. It is quite likely, however, that these standards for the different types of malts are subject to change, like all other malt characteristics, from season to season.

In order to obtain comparative figures as to the proteolytic strength of different malts, the balance of the filtrate remaining from the 20 cc. used for the above determination is permitted to stand at room temperature for a given time, preferably over night for a period of 16 hours, after which time a second acid ratio determination is made. Malts showing the greatest increase in the acid ratio are those having the greatest peptic strength. This increase in the acid ratio may amount to from 5 to 30 or even more.

The reagents employed in the above determinations aside from the tenth normal alkali found in every laboratory are prepared as follows:

*0.5 per cent solution of phenolphthalein* in 50% alcohol to which is added a sufficient amount of tenth normal soda to impart to it a slightly pink color.

*40 per cent formaldehyde solution* (technical strength) to which is added 5 per cent by volume of the above phenolphthalein solution and a sufficient amount of tenth normal soda to impart to it a slight but decided pink color.

In conclusion, I wish to point out that the acid ratio method developed by me can be used to advantage in determining whether a certain malt has been prepared from a specific type of barley or whether it represents a mixture. Aside from its great simplicity it has the further advantage that one single determination suffices for the estimation of both the preformed amino acids present in the malt and the proteolytic strength, and furthermore, that all of the work can be carried out at room temperature and will yield reliable results without requiring special skill and a degree of accuracy which, owing to the time required, would render the method unsuitable for technical work.

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## A MODIFIED METHOD FOR DETERMINING CARBON-FREE ASH IN PLANT SUBSTANCES

By George E. Boltz

Received May 7, 1915

In the usual method for determining ash in plant substances, where no provision is made for purifying the ash, the error due to the presence of carbon dioxide in combination with bases present is, in many cases, quite large. The percentage of error is in proportion to the amount of basic material that is free to unite with carbon dioxide during combustion. Ash containing large amounts of calcium, magnesium and potassium should be corrected for the carbon dioxide it contains, while in most determinations of ash a correction for unburned carbon, and in some cases, a correction for sand, is necessary.

A procedure which has proved to be very satisfactory in determining the real ash in plant substances is as follows:

Weigh from 2 to 10 grams, depending upon the material, into a platinum dish. Ignite over a low flame until most of the carbon is burned off. Cool, cover the dish with a watch glass and add through the lip of the dish about 20 cc. of hot distilled water. Filter into a weighed 200 cc. Erlenmeyer flask, wash the residue 3 or 4 times with hot water, replace the filter paper with residue in the platinum dish, dry

and ignite until practically all the carbon is consumed. Transfer the remaining ash to the Erlenmeyer flask with hot water, using a policeman to loosen any particles that may adhere to the dish. Evaporate the moisture and dry the ash at 110° C. until thoroughly dry; weigh. The weight minus the weight of the flask represents the crude ash.

Connect the flask containing the crude ash to an apparatus[1] for determining the carbon dioxide, treat the contents of the flask with 80 cc. of distilled water free from carbonates and 20 cc. of dilute hydrochloric acid (1 : 10). Aspirate purified air through the apparatus while liberating the carbon dioxide. Boil for 30 minutes and absorb the gas in 50 cc. of a 4 per cent solution of sodium hydroxide. Drain the sodium hydroxide solution out of the absorption tower and wash the remaining caustic solution out of the tower with 250 cc. of $CO_2$-free water. Exactly neutralize with normal hydrochloric acid, using phenolphthalein as indicator. Add 2 drops of methyl orange solution (1 gram in 1000 cc.) and titrate with $N/20$ hydrochloric acid until the color of the methyl orange is just changed. From the number of cc. of $N/20$ hydrochloric acid used subtract blank: 1 cc. $N/20$ hydrochloric acid = 0.0022 gram carbon dioxide. The titration where phenolphthalein is used is ignored. The carbon, sand and silica are determined as outlined on page 22 in *Bulletin* **107,** U. S. Bureau of Chemistry. The carbon dioxide plus the unburned carbon and sand is subtracted from the weight of crude ash. The remainder represents the amount of carbon-free ash.

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## THE PRESENCE OF PROTEOSES AND PEPTONES IN SOILS

By E. H. WALTERS

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Recent investigators concur in stating that the chemistry of soil nitrogen is essentially the chemistry of protein undergoing hydrolysis. Proteins find their way into the soil in the form of plant and animal débris, manures and fertilizers. As soon as these substances are incorporated in the soil, hydrolytic decompositions ensue.

The investigations of Shorey,[2] Jodidi,[3] Robinson,[4] Suzuki,[5] Lathrop and Brown,[6] and Kelley[7] on the classification of the nitrogenous decomposition products as ammonia, monoamino acids, diamino acids, etc., and the work of Schreiner and Shorey,[8] Shorey,[9] Lathrop,[10] and Robinson,[11] on the isolation of a number of amino acids from soils indicate that the proteins are decomposed in a soil in much the same way as in acid hydrolysis or in animal digestion.

If this view is correct and the soil protein is hydrolyzed as in digestion by acids or enzymes we should expect to find in soils all of the intermediate products of protein hydrolysis provided the methods are sufficiently accurate for their identification. Up to the present time, however, only a few of the primary cleavage products have been found.

Although the complex, first stage, decomposition products of the proteins have not been found to occur or persist in soils, their presence has been anticipated. It is the object of this paper to report the presence of certain bodies, presumably proteoses and peptones, resulting either from partial hydrolysis of proteins or by the synthetic action of microörganisms.

The present methods for differentiating the various proteoses and peptones are unsatisfactory. These compounds are classified according to their varying solubilities, especially in ammonium sulfate solutions of different concentrations.

The differences in composition between the various members of the respective groups remain to be more accurately established. Because of the chemical similarity of these substances, the difficulty attending their separation, and the uncertainties in their identification, pure proteoses and peptones are not easy to procure, and in an investigation of this character where they are present in soil in comparatively minute quantities, only qualitative reactions can be employed to show their existence.

Numerous investigations[1] on the hydrolysis of proteins have shown that the protein molecule is gradually broken down into a series of long chains of amino acids. These chains are known as proteoses, peptones, and peptides according to the number of units in the chain. These still possess true protein characteristics. Further hydrolysis causes the ultimate splitting of these protein-like substances into amino acids of known chemical structure.

It would be beyond the scope of this paper to dwell upon the various proteoses and peptones which are described in detail in the literature. Only their general characteristic properties will be given.

The proteoses have been considered as the intermediate substances in the peptonization of proteins whose neutral or faintly acid solutions do not coagulate on boiling. They are subdivided into primary and secondary proteoses. The primary bodies possess a higher molecular weight and greatly resemble the proteins; they are precipitated and thus separated from the secondary proteoses by either completely saturating their aqueous solutions with sodium chloride or half saturating them with ammonium sulfate. According to Pick[2] and Haslam[3] the primary proteoses are represented by at least three substances: hetero-proteose, $\alpha$-proto-proteose, and $\beta$-proto-proteose.

[1] For general references see E. Abderhalden, "Biochemisches Handlexikon," Vol. IV; "Handbuch der Biochemischen Arbeitsmethoden," Vol. II and III; Gustav Mann, "Chemistry of the Proteids."

[2] E. P. Pick, *Ztschr. physiol. Chem.*, **24** (1897), 246.

[3] H. C. Haslam, *J. Physiol.*, **32** (1905), 262.

[1] THIS JOURNAL, **4** (1912), 611.

[2] E. C. Shorey, U. S. D. A. Hawaii Sta., *Ann. Rept.*, **1905**, pp. 25–38 and **1906**, pp. 37–39.

[3] S. L. Jodidi, Michigan Sta., *Tech. Bull.*, **4** (1909); Iowa Sta., *Research Bulls.* **I** and **III** (1911).

[4] C. S. Robinson, Michigan Sta., *Tech. Bull.* **7** (1911).

[5] S. Suzuki, *Bull. Coll. Tokio*, **7** (1907), 513.

[6] E. C. Lathrop and B. E. Brown, THIS JOURNAL, **3** (1911), 657.

[7] W. P. Kelley, *J. Am. Chem. Soc.*, **36** (1914), 429–444.

[8] Oswald Schreiner and E. C. Shorey, U. S. Dept. of Agr., Bureau of Soils, *Bull.* **74** (1910).

[9] E. C. Shorey, U. S. Dept. of Agr., Bureau of Soils, *Bull.* **88** (1913).

[10] E. C. Lathrop, *J. Am. Chem. Soc.*, **34** (1911), 1260.

[11] S. C. Robinson, *Ibid.*, **33** (1911), 564.

This classification is based upon differences in solubility in various solvents.

The hetero-proteose has a tendency to pass into an insoluble form on standing or when heated to about 50°. This insoluble form Kühne[1] termed "dysalbumose" (dys-proteose)

The secondary proteoses (deutero-proteoses) are in many instances divided from the peptones only by arbitrary definitions.[2] Chittenden and Hartwell[2] have found that the primary proteoses, proto- and hetero-, are only slowly converted into peptone by proteolytic ferments, since they must first pass through the intermediate stage of deutero-proteose.

Proteoses and peptones may also be formed by the hydrolysis of proteins by dilute acids or alkalies[3] and by the action of microörganisms.[4]

The proteoses in watery solution are precipitated at the ordinary temperature by nitric acid and by acetic acid and potassium ferrocyanide, and the precipitate has the peculiarity of disappearing on heating and reappearing on cooling. If a neutral proteose solution is saturated with sodium chloride, the proteose is partly precipitated, but on the addition of acetic acid it is more completely precipitated.

The proteoses give precipitates with ferric chloride, neutral and basic lead acetate, platinum chloride, phosphotungstic acid, phosphomolybdic acid, picric acid, tannic acid, trichloracetic acid, and metaphosphoric acid. The precipitates are all more or less soluble; some redissolve on the addition of an excess of the precipitant, and some dissolve on heating and reappear on cooling, while others are permanent on heating. Copper sulfate and copper acetate precipitate the primary but not the secondary proteoses, and are sometimes used to separate these bodies.[5] Acetic acid and potassium ferrocyanide precipitates all proteoses but the presence of peptone may interfere with the reaction. Nitric acid precipitates the primary proteoses in the absence of salts, the secondary proteoses only in the presence of sodium chloride, and the lowest members of the secondary proteoses only if the solution is saturated with salt. The precipitate is soluble in excess of nitric acid, especially on heating, but reappears on cooling.

The peptones are considered as the final products of the hydrolysis of proteins by means of proteolytic enzymes in so far as these products are still substances of a protein nature. They are readily soluble in water, glacial acetic acid, and in all salt solutions and are not coagulated by heat. The watery solutions are not precipitated by nitric acid, acetic acid and potassium ferrocyanide, picric acid, trichloracetic acid, potassium mercuric iodide, nor by neutral salts and acids. These reagents, however, precipitate peptones in concentrated solutions of calcium chloride, calcium nitrite, and ammonium sulfate. They are precipitated by phosphotungstic acid, phosphomolybdic acid, mercuric chloride (in the absence of neutral salts), absolute alcohol, and tannic acid, but the precipitate may redissolve on the addition of an excess of the precipitant. The tannic acid precipitate is soluble in acetic acid.

Proteoses and peptones give a red biuret reaction and the xanthoproteic reaction, while the other color tests may or may not be given according to the radicals contained in the individual molecules.

It is obvious that the names proteose and peptone do not indicate any definite compounds. They represent stages of decomposition between that of true proteins and amino acids. These terms will undoubtedly disappear, as acquisitions to our knowledge concerning the chemical nature of the polypeptides establish a more complete relationship to these cleavage products. In a few instances this relationship, both chemical and biological, has already been indicated for the lower members of the proteose-peptone group. The most interesting analogy in this connection is the fact that the tetrapeptide obtained from silk-fibroin by Fischer and Abderhalden,[1] consisting of two glycine molecules, one of alanine and one of tyrosine, shows properties with which many proteoses correspond.

EXPERIMENTAL

In a recent investigation of a sample of Norfolk sandy loam soil from Virginia a solution was obtained which responded to many of the color and precipitation reactions given by proteoses and peptones.

The solution was obtained in the following way: 50 lbs. of soil were extracted with a 2 per cent solution of sodium hydroxide for 24 hours. The alkaline extract was separated from the insoluble residue by decantation and made acid with sulfuric acid and filtered from the so-called humus precipitate. The acid filtrate was shaken out with ether to remove compounds soluble in this solvent and a solution of phosphotungstic acid in 5 per cent sulfuric acid added after removal of the dissolved ether, until no further precipitate was formed. After several days the phosphotungstic acid precipitate was filtered off and washed thoroughly with a dilute solution of sulfuric acid and phosphotungstic acid. The precipitate was then suspended in water and an excess of barium hydroxide added to precipitate the phosphotungstic and sulfuric acids. The excess of barium in the filtrate from the barium phosphotungstate and sulfate was removed by carbon dioxide and the barium carbonate filtered off.

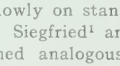
It frequently has been found in dealing with solutions obtained in a similar manner from many other soils that the barium is very difficult to remove by treatment with carbon dioxide.

At this point it is necessary to consider somewhat in detail the carbamino reaction of Siegfried.[2] This investigator has found that on saturating a mixture consisting of equal volumes of equinormal solutions of glycocoll and barium hydroxide at a low temperature (0° C.), an alkaline solution is obtained which remains clear when carbon dioxide is passed through it, and this continues to be the case till, for each volume

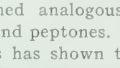
[1] W. Kühne and R. H. Chittenden, *Ztschr. f. Biol.*, **20** (1884), 11.
[2] R. H. Chittenden and J. A. Hartwell, *J. Physiol.*, **12** (1891), 12.
[3] Gustav Mann, "Chemistry of Proteins," p. 199.
[4] W. Kruse, "Allgemeine Microbiologie," p. 490.
[5] O. Folin, *Ztschr. physiol. Chem.*, **25** (1898), 152.

[1] E. Fischer and E. Abderhalden, *Ber.*, **39** (1906), 752.
[2] M. Siegfried, *Ztschr. physiol. Chem.*, **44** (1905), 85.

of glycocoll, nearly two volumes of equivalent barium hydroxide have been added. This solution gives off barium carbonate slowly on standing in the cold but quickly on boiling. Siegfried[1] and his students have subsequently obtained analogous results for several of the amino acids and peptones. An analysis of some of these compounds has shown that the amino acids contain the carbamino acid radical



and the barium salt would have the formula



These compounds are formed from the amphoteric amino acids by simply adding carbon dioxide.

This reaction has been recognized in dealing with the soil solution described above. However, it was found that these carbamino compounds are stable only at low temperatures (Siegfried's work was carried out at 0°) and that the barium could be completely removed by adding a slight excess of sulfuric acid after treatment with carbon dioxide and then boiling the solution with a slight excess of solid barium carbonate.

When a soil is treated with a dilute solution of sodium hydroxide a very dark-colored solution, the so-called humus extract, is obtained. When this extract is treated with an excess of acid a dark-colored precipitate is formed, the so-called humic acid. This precipitate usually contains the greater portion of the organic matter of the soil. The filtrate from this precipitate still contains a portion of the organic matter and is usually dark colored but much lighter than the original alkaline extract.

The extract obtained as described above, however, was a very light-colored solution which could be used very satisfactorily in any of the color and precipitation tests characteristic of the proteins, proteoses, and peptones.

This solution gave the following reactions: a red biuret reaction; Hopkins-Cole reaction; Millon reaction; Molisch carbohydrate reaction; a precipitate was formed with hydrochloric, nitric, and sulfuric acids which dissolved on warming and reappeared on cooling; a precipitate was formed upon the addition of an equal volume of absolute alcohol; a precipitate was formed when the solution was saturated with ammonium sulfate; a precipitate was formed in saturated sodium chloride containing acetic acid; and the tests for the presence of sulfur were negative.

On carefully evaporating the soil solution to dryness a yellow, sticky, gelatinous residue was obtained. No crystalline material could be observed. As there was not enough of this solution, upon which further tests could be made with any degree of certainty, a second sample of soil was obtained three months later and the solution was obtained again as described above.

This solution gave the following reactions: a red biuret reaction; Hopkins-Cole reaction; Millon reaction; Molisch carbohydrate reaction; Liebermann reaction; a precipitate was formed with hydrochloric, nitric, and sulfuric acids which dissolved on warming and reappeared on cooling. The solution containing the nitric acid changed from a light yellow to an orange upon the addition of an excess of potassium hydroxide; a precipitate was formed in 50 per cent alcohol; a precipitate was formed in saturated sodium chloride solution containing acetic acid; a precipitate was formed with picric acid, phosphomolybdic acid, acetic acid and potassium ferrocyanide, trichloracetic acid, silver nitrate, copper sulfate, copper acetate, ferric chloride (slight), tannic acid (soluble in acetic acid) and neutral lead acetate; a precipitate was formed when an equal volume of acetone was added to the soil solution; a slight precipitate was formed with mercuric chloride. The precipitate which was formed in half-saturated ammonium sulfate was filtered off and the filtrate saturated with ammonium sulfate when a further precipitate was formed.

Absolute alcohol was added to a portion of the soil solution until no further precipitate was formed. After standing for 24 hours the precipitate was filtered off and washed with 95 per cent alcohol.

The precipitate was then dissolved in warm water. This solution did not give the Hopkins-Cole reaction, thus indicating the absence of the tryptophane group. No precipitates were formed with acetic acid, picric acid, copper acetate, or mercuric chloride. All of the other reactions observed on the original solution were positive.

The filtrate, after removal of the alcohol, gave all of the reactions obtained on the original solution.

Weyl[1] has found that certain proteins, polypeptides, and amino acids are precipitated by acetone in certain concentrations.

To another portion of the test solution acetone was added until no further precipitate was formed. After standing for 24 hours the precipitate was filtered off and washed with a small quantity of acetone. After careful drying the acetone precipitate was dissolved in warm water. This solution gave the following reactions: A red biuret reaction; Millon reaction; Molisch test for carbohydrates; precipitates with tannic acid, picric acid, phosphotungstic acid, acetic acid and potassium ferrocyanide, lead acetate, and half-saturated and saturated ammonium sulfate solution. The Hopkins-Cole reaction was negative and no reactions could be observed with hydrochloric acid, nitric acid, or saturated sodium chloride and acetic acid.

The filtrate after removal of the acetone gave all of the above tests with the exception of the Hopkins-Cole reaction.

In order to determine whether or not these protein-like substances existed as such in the soil and were not entirely formed by hydrolysis of the protein by the dilute alkali used in making the extract, a water extract of the soil was obtained. This extract was made

[1] E. Abderhalden, "Biochemisches Handlexikon," Vol. 4, p. 198.

[1] Theodor Weyl, *Ztschr. physiol. Chem.*, **65** (1910), 246; *Ber.*, **43** (1910), 508.

acid with sulfuric acid to about 5 per cent and a slight excess of phosphotungstic acid added in the usual way. The phosphotungstic acid precipitate was treated exactly as described above and the solution finally obtained gave the following reactions: a red biuret reaction; Millon reaction; Molisch test for carbohydrates; the usual precipitates with hydrochloric, nitric, and sulfuric acids; precipitates with acetic acid and potassium ferrocyanide, saturated sodium chloride and acetic acid, half-saturated and saturated ammonium sulfate and a precipitate when an equal volume of alcohol or acetone was added.

A portion of the soil solution kept sterile by a few drops of toluol was observed after several days to contain a slight precipitate. It may be that this substance is similar to the dys-proteose which Kühne obtained from the hetero-proteose.

In an extensive examination of the nitrogen compounds of processed fertilizers, Lathrop[1] has reported the presence of certain protein-like bodies similar to those described above.

It is not the purpose here to enter into a discussion of the availability of the various forms of organic nitrogenous compounds. It may be stated, however, that in the light of recent extensive researches by Schreiner and Skinner,[2] which show clearly that most of the simple primary cleavage products of proteins, the amino acids, are readily available to green plants, that perhaps some of the simpler peptones and polypeptides (such as the tetrapeptide alluded to above) may also be used by green plants to a limited extent as a direct source of nitrogen.

From the nature of the reactions obtained in the various solutions described above it is clear that they contain a mixture of the various proteoses and peptones resulting from the hydrolysis of proteins and that they exist and persist in the soil as such for a considerable period, or, the original protein is only very slowly hydrolyzed. It is also clear that an attempt to make any further separation of these bodies, according to our present knowledge, would lead us beyond the limits of the ordinary laboratory equipment.

The experiments described above indicate that proteins undergo hydrolytic decompositions in the soil in much the same way as in digestion by enzymes, acids, or alkalies, in the laboratory.

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## THE DETERMINATION OF NITRATES IN SOIL

By R. S. Potter and R. S. Snyder

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C. B. Lipman and L. T. Sharp[3] have shown that such substances as alum, aluminum cream and bone-black for coagulating the clay and organic matter in obtaining the soil extract to be used for the determination of nitrates cause a decided loss in the amounts of nitrates found. They then recommend the use of quicklime for this purpose. It was found by them that no loss was induced when amounts of lime, varying from 1 to 5 g., were shaken with solutions (volumes not given) containing 1 and 5 mg. of nitrate nitrogen. Practically the entire amount of nitrate nitrogen in a soil of known[1] nitrate content was found by the use of 2 g. of calcium oxide with 100 g. of soil. Working with a soil whose content of nitrate nitrogen was not known, it was found that it made no difference whether the lime was added before or after the water.

The above investigators point out the fact that J. G. Lipman and P. E. Brown, in their "Laboratory Manual on Soil Bacteriology," give directions for the use of 2 g. of lime with 100 g. of soil in preparing the extract for nitrate determination, but Dr. Brown informs us that he has always used lime in the form of the carbonate. Since, during some preliminary work, the results with calcium oxide seemed inconsistent, it was decided to compare the action of these two flocculating agents. At the same time parallel tests were made with the colorimetric method and the aluminum reduction method as modified by Burgess,[2] who recommends the following procedure: 100 cc. of the soil extract are placed in a casserole, 2 cc. of 50 per cent sodium hydroxide added, the mixture boiled down to about 50 cc. to remove the ammonia, the residual solution washed into a large test tube, and made up to 100 cc. A strip of aluminum is then added and the test tube closed with a stopper bearing a glass tube drawn out to a capillary. By this means, with the amount of nitrate nitrogen less than 100 mg., Burgess states the loss of ammonia by diffusion is insignificant. After allowing the reduction to go on for 11 to 14 hours at about 20°, the solution is transferred to suitable flasks and the ammonia is distilled off into standard acid. The only difference from this of the procedure used by us has been to transfer from the casserole directly to the Kjeldahl flask of the aeration apparatus described by us elsewhere.[3] With the volume at 100 cc. aluminum strips were added; the flask was then connected to its absorption bottle which contained a suitable quantity of 0.02 *N* acid in 200 cc. of water. Either a slow stream of air may be run through the series for the required length of time, or the long tube in the Kjeldahl flask may be closed with a glass plug or a pinch cock. In either case, after 11 to 14 hours the pump is opened to give the maximum current of air. At the end of an hour, if the air current is sufficiently strong, the aeration will be complete, and the residual acid can be titrated. The use of this procedure effects a decided saving of time if the apparatus is at hand. Another advantage is that all danger of loss of ammonia by diffusion is avoided. As many as fifteen determinations have been run on one series. The colorimetric method used by us was the modification of the phenoldisulfonic acid method proposed by Chamot and collaborators.[4] Lipman and Sharp do not state just which modification of this method

[1] E. C. Lathrop, U. S. Dept. of Agr., *Bull.* **158** (1914).

[2] Oswald Schreiner and J. J. Skinner, U. S. Dept. of Agr., Bureau of Soils, *Bull.* **87** (1912).

[3] *Univ. Cal. Pub. Agr. Sci.*, **1** (1912), 21

[1] How the amount of nitrate nitrogen was found is not stated.

[2] *Univ. Cal. Pub. Agr. Sci.*, **1** (1913), 51.

[3] This Journal, **7** (1915), 221.

[4] *J. Am. Chem. Soc.*, **33** (1911), 381.

was used by them, except that ammonium hydroxide was used by them instead of potassium hydroxide.

Solutions of pure potassium nitrate were first experimented with. In each case, the respective flocculating agent was shaken with the solution at the rate of 2 g. per 100 cc. of solution. Where both methods were used, aliquot parts of the same filtrate were used. The results given are averages of closely agreeing duplicates.

TABLE I

| Flocculating agent | Parts per Million Nitrate Nitrogen Present | Found Colorimetric | Found Reduction |
|---|---|---|---|
| $CaCO_3$ | 1 | 0.97 | |
| CaO | 1 | 0.40 | |
| $CaCO_3$ | 10 | 9.0 | 9.94 |
| CaO | 10 | 6.6 | 9.66 |

The results show that while the use of calcium oxide gives low results with pure nitrate solutions by the colorimetric method, yet practically the entire amount is found by the reduction method.

Comparative experiments were next carried out on soils with high and low nitrate content, some with known amounts of nitrate added. In all cases, one part of soil was shaken for a half hour or less with two parts of water, and the flocculating agent was added at the rate of 2 g. per 100 g. soil. The results given in Table II were all found by the colorimetric method:

TABLE II

| Soil No. | Flocculating agent | Parts per Million Nitrate Nitrogen Added | Found | Recovered | Per cent recovered |
|---|---|---|---|---|---|
| 69 | $CaCO_3$ | None | 6.7 | | |
| | $CaCO_3$ | 3.0 | 9.6 | 2.9 | 97.0 |
| | CaO | None | 2.0 | | |
| | CaO | 3.0 | 2.9 | 0.9 | 30.0 |
| 268 | $CaCO_3$ | None | 14.7 | | |
| | $CaCO_3$ | 3.0 | 17.6 | 2.9 | 97.0 |
| | CaO | None | 7.6 | | |
| | CaO | 3.0 | 7.6 | None | 0.0 |
| 355 | $CaCO_3$ | None | 2.2 | | |
| | $CaCO_3$ | 3.0 | 5.0 | 2.8 | 93.0 |
| | CaO | None | 1.6 | | |
| | CaO | 3.0 | 3.1 | 1.5 | 50.0 |

The important point brought out by the above results is that calcium oxide gives decidedly low results with soils containing a small amount of nitrate nitrogen.

The reduction and the colorimetric methods were tried with soils which had been incubated 30 days with 0.150 g. ammonium sulfate per 150 g. soil. The extraction of the nitrates was carried out as usual. The results given represent the amounts found in duplicate incubations and not duplicates on the same incubation. For the two methods, aliquot parts of the same filtrate were used.

TABLE III

| Soil No. | Flocculating agent | Parts per Million Nitrate Nitrogen Colorimetric | Reduction |
|---|---|---|---|
| C | $CaCO_3$ | 152 | 183 |
| | $CaCO_3$ | 152 | 176 |
| | CaO | 135 | Lost |
| | CaO | 139 | 175 |
| D | $CaCO_3$ | 145 | 171 |
| | $CaCO_3$ | 149 | 170 |
| | CaO | 139 | 169 |
| | CaO | Lost | 169 |

The above results show, in harmony with the experience of others, that the colorimetric method gives somewhat lower results than the reduction method. With the former method, calcium oxide produces somewhat lower results than calcium carbonate, while there is no apparent difference by the reduction method.

From the data presented, one is forced to the conclusion that with soils low in nitrates the use of calcium carbonate is to be preferred to calcium oxide, and when the colorimetric method is to be used the carbonate is always better. Carbonate in all cases yields as clear and as nearly colorless a solution as the oxide. As to the reason for the low results by the colorimetric method with calcium oxide, we are not prepared to answer. Our results are not in harmony with those obtained by Lipman and Sharp. Some difference in the details of the colorimetric method might have caused the discrepancy. It is possible their use of ammonium hydroxide instead of potassium hydroxide might have made some difference. We have much more data than are here presented, on many types of soil, and in practically every case the calcium oxide gives lower results than the carbonate. While the subject is, no doubt, worth more complete investigation, since the calcium carbonate has proven entirely satisfactory, we have not seen fit to carry the subject any further at present.

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## A METHOD FOR THE DETERMINATION OF THE IMMEDIATE LIME REQUIREMENTS OF SOILS

BY W. H. MACINTIRE

Received July 9, 1915

At the November (1914) meeting of the Association of Official Agricultural Chemists[1] the writer gave the essentials of a method for the determination of the lime requirement of soils, and at that time stated that later he would give the results secured from experiments which led to the adoption of the method. The data and details of these investigations are to appear in bulletin form.

The study was begun in the spring of 1912, and was based upon an investigation of the various factors influencing the determination of the lime requirements of soils. At that time the laboratory methods of Veitch[2] and Tacke[3] and Suchting's[4] modification of Tacke's procedure were the only ones which involved the use of the substances which are used in practice to satisfy a soil's lime requirement. In this country the method of Veitch has been most generally accepted, in spite of the tedious manipulation attendant upon its use. In our initial studies, which included extensive basket experiments, the Veitch method was used as a basis of treatment. From the investigation of the factors influencing more particularly the Veitch method, it was hoped to evolve a method which would bear some relation to practice. After the evolution of the procedure given in this article, comparative studies were made with the Veitch, Tacke, and, later, the Hutchinson-MacLennan[5] methods.

[1] *American Fertilizer*, Nov. 28, 1914.
[2] *J. A. C. S.*, **24** (1902), 1120.
[3] *Chem. Ztg.*, **21** (1897), 174.
[4] *Z. angew. Chem.*, **4** (1908), 181.
[5] *Chemical News*, Eng., **1914**, p. 2854.

Without wishing in any way to detract from the priority of claim to publication of the innovation of using a solution of $CaCO_3$, which priority rightfully belongs to Hutchinson and MacLennan, the writer would state that the method given at the end of this article had been perfected for presentation to the A. O. A. C. before the appearance of their publication, which antedated the meeting of the Association by several weeks.

PRELIMINARY LABORATORY INVESTIGATIONS

The studies preliminary to the evolution of the method included a consideration of the relation of soil lime requirement to soil magnesia requirement. It was found that there exists a vast difference between lime and magnesia requirements of soils under laboratory treatments, as well as under contact treatments in baskets and in field cylinders. It was also determined that though a soil may be distinctly alkaline from contact with an excess of $CaCO_3$, this condition does not preclude the ability of a soil to effect extensive decomposition of $MgCO_3$. However, when soils had been treated with a large excess of $MgCO_3$ above lime-requirement indications and had effected complete decomposition of the excess of $MgCO_3$, they then effected no immediate reaction with $CaCO_3$. This was also found to be the case with an ignited soil. It was also found that this propensity of a soil to fix the magnesia upon evaporation of soil and $MgCO_3$ solution was not hindered by previous treatments with sodium and potassium carbonates.

It thus appears that the use of precipitated $MgCO_3$ may satisfy a soil's requirement for $CaCO_3$, while the long-continued presence of $CaCO_3$ in potted soils fails to satisfy a soil's requirement for magnesia. This difference was found to be due to the affinity of magnesia for $SiO_2$ and $TiO_2$, as well as for acid silicates.

The studies further led to the conclusion that there is a considerable difference between a soil's immediate ability to decompose $CaCO_3$ and its propensity to continue the decomposition when soil and an excess of $CaCO_3$ continue in moist contact. That this observation is to be found in practice is shown by the analyses of the lime-treated plots of the Pennsylvania Station.[1] Thirty-five per cent of the lime accumulated on these plots after 32 years of treatment is to be found as silicates.

In offering the method, the differentiation is, therefore, made between *immediate and continuous lime requirements of soils*. In paralleling the Veitch-method procedure the writer endeavored to determine the lime from an excess of lime-water, which was added to soils and subjected to evaporation, as in the Veitch procedure. It was thus intended to determine the lime requirement by difference between added lime and the residual caustic lime. The procedure followed was to evaporate soils with an excess of lime-water, and then to subject the evaporated soil and the excess of lime to treatment with carbonated water. The carbonated water extract was then filtered and titrated. It was found, however, that the lime silicates were very readily hydrolyzed, and that the recovery of lime was proportional to the period of extraction. Several hours' extraction, with agitation, effected greater lime recovery than was represented by the amounts of treatment. It was then decided to use C. P. precipitated carbonate instead of lime-water in the evaporations, and to determine original and residual carbonate before and after evaporation by the estimation of $CO_2$. Examination of the various C. P. precipitated carbonates showed the necessity, however, of converting hydrate impurities into carbonates before true lime absorption by soils from applied carbonate could be determined by $CO_2$ estimations. In thus treating precipitated $CaCO_3$ with carbonated water there were secured saturated $CaCO_3$ solutions. It was readily apparent that the use of aliquots of the solution of $CaCO_3$ afforded numerous advantages in speed and accuracy over weighed charges of the treated solid carbonate. Comparisons made between the activity of soil toward finely ground limestone and toward carbonate-water-treated precipitated carbonate showed that in a given time the finer and more soluble the precipitated carbonate was, the more extensively it decomposed. This proved true in controlled field treatments, as well as under laboratory conditions.

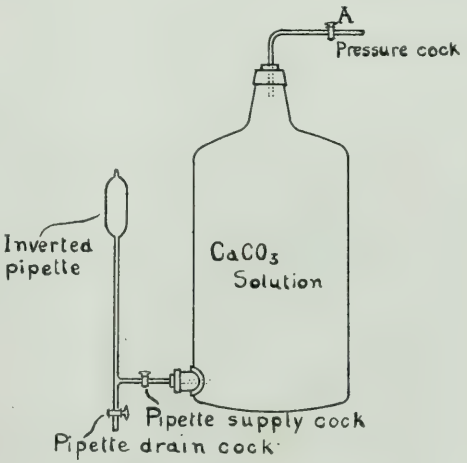


FIG. 1—PRESSURE CONTAINER FOR $CaCO_3$ SOLUTION

Further comparisons were then made between various treatments of soil and added solution of $CaCO_3$. The treatments included immediate evaporation, evaporation after 3 hours' agitation, precipitation of $CaCO_3$ from solution by heating on a water bath before adding soil, boiling for 5 minutes and for 30 minutes, and throwing out of solution by subjecting soil and solution to agitation with suction for various periods at room temperature. The results secured by immediate evaporation were the most uniform and the highest, and were almost identical with those secured by agitating for 3 hours before evaporation. The

[1] *Penn. Sta. Bull.* **107**, 19.

evaporation appeared to exert negligible activities upon soil organic matter, while the short period of contact between soil and carbonated water was responsible for no apparent hydrolysis of soil silicates.

Comparative studies between the proposed method and the methods of Tacke and Hutchinson and MacLennan demonstrated that their methods do not give the *maximum immediate lime requirement.* In order to eliminate the consideration of organic matter as being in part responsible for the continued decomposition of $CaCO_3$, through its further contact with soil, red clay subsoil was used, as well as surface soil. Repetition of the Tacke method upon the clay which had previously been treated with $CaCO_3$ for 3 hours gave further extensive lime-requirement indications. Residual clay, freed of atmospheric $CO_2$ after treatment according to the Hutchinson-MacLennan procedure, gave additional and appreciable lime-requirement indications by the Tacke procedure, and also by the method given in this article, and by repetition of the Hutchinson-MacLennan method itself. It was also found that the indications of the Hutchinson-MacLennan method varied appreciably with the charges, and that the indications were in no way proportional to variations in amounts of soil used. Repetition of the proposed method gave no further lime requirement, nor was any lime-requirement indication found by the Tacke procedure upon the clay after its evaporation with a solution of $CaCO_3$. Nine soils were then treated with the amounts of $CaCO_3$ indicated by the Hutchinson-MacLennan method plus 2 drops of saturated lime-water to offset any plus or minus analytical error, and the procedure of the Veitch method then carried out. In every case the soils failed to show alkalinity. The same soils were in like manner simultaneously treated with the indications of the proposed method, and in every case the Veitch test showed alkalinity.

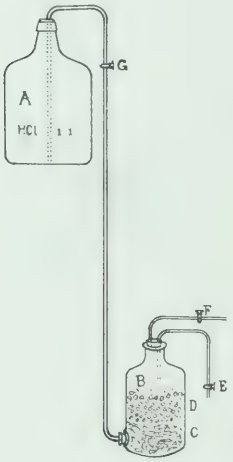


FIG. 2—$CO_2$ GENERATOR
A—16 Liter Acid Reservoir
B—4 Liter Generator
C—Broken Pottery
D—Marble-Sized Limestone Lumps
E—Geisler Cock Outlet for Spent Acid
F—Outlet for $CO_2$ to Purifiers
G—Safety Cock

To the writer it seemed that the results of the other methods depending upon quantitative determinations of residual lime gave but a fractional part of a soil's inherent ability to decompose $CaCO_3$ under laboratory conditions, and that it would be well to utilize a method which would give maximum decomposition of $CaCO_3$ in the laboratory. The method here given is believed by the writer to record a definite and complete reaction between soil and $CaCO_3$ under laboratory conditions. Its repetition at various times gives closely concordant results, and the technic is such as to permit considerable speed when making a number of determinations.

As before stated, when beginning the studies it was hoped to secure results from correlative basket studies which would afford opportunity to compare laboratory indications with field results. It appears, however, that this phase of the subject requires somewhat extensive field work under various seasonal conditions and various methods of cropping through more than one year. Such an investigation would be needed to show the relation of both immediate and continuous lime-requirement indications to field practice.

## PROPOSED METHOD

PREPARATION OF $CaCO_3$ STOCK SOLUTION—Pass purified $CO_2$ into one or more 4-liter cylinders containing distilled water and about 20 grams of "fluffy" C. P. precipitated $CaCO_3$ for 4 hours. Permit the $CO_2$ to enter with sufficient rapidity to keep considerable of the carbonate in suspension. At the same time prepare carbonated distilled water to the amount of about one-tenth that of the carbonate solution. Filter the carbonate solution through large gravity filters into the carbonated water. A large stock of 16 liters may be made and kept indefinitely without determinable change by use of the pressure-syphon bottle shown in Fig. 1. Upon withdrawal of each aliquot, pressure is maintained by blowing through the tube *A*. The $CaCO_3$ value of the solution is determined by first boiling and then liberating the $CO_2$ of the precipitated carbonate. *The value of the $CaCO_3$ solution should not be determined by direct titration, if the liquid absorption procedure be followed.*

The HCl used in generator to liberate $CO_2$ for preparation of $CaCO_3$ solution should not exceed 1:1 in strength. To insure complete removal of hydrochloric acid from the rapid flow of gas, it is necessary to force the gas through several columns of sodium carbonate solution when making large stock solutions of carbonate. A "Kipp" generator may be fitted with a 2-hole rubber stopper, a stand tube being inserted in one hole and in the other a stopcock-controlled tube for blowing to obtain pressure. A simple and more useful form of apparatus is that of Fig. 2.

PROCEDURE FOR THE DETERMINATION OF THE IMMEDIATE LIME REQUIREMENT OF SOILS—For the average soil, take 10-gram charges of soil and 150 cc. of $CaCO_3$ solution. This volume usually represents about 0.1500 gram of $CaCO_3$. For very heavy clays, or peaty or swamp soils, reduce the charge to 5 g. Evaporate to a paste in 150-cc. porcelain evaporating dishes. Transfer paste to a 300 cc. Erlenmeyer flask, by means of $CO_2$-free distilled water,[1] delivered by gravity from the reservoir. Do not have volume of transferring water to exceed 60 to 70 cc. In unusual cases of adhesion of soil to dish, scour with a little $CaCO_3$-free sand. The tendency of the carbonate

[1] Such water may be easily obtained in considerable quantities by slowly siphoning off boiling water, the volume of which is maintained by a gravity constant-level supply.

is sometimes to precipitate in a ring marked by the initial level of aliquot. Determine $CO_2$ by agitation and aspiration for 30 minutes, at room temperature, with 4 inches vacuum, using 5 cc. concentrated $H_3PO_4$ to effect liberation of gas.[1] Hydrochloric acid may be used instead of $H_3PO_4$, if proper precautions be taken for collection of volatile acid. The gravimetric method of absorption is decidedly preferable unless the analyst is thoroughly conversant with the technic of the liquid absorption and double titration procedure. Although absolute theoretical recovery of $CO_2$ cannot be secured in large amounts by the volumetric absorption, at room temperature, the factor is apparently uniform. However, the differential $CO_2$ values in the small charges used in the method may be very accurately determined at ordinary temperatures if proper precautions be observed.[2]

In this laboratory we have secured very satisfactory results, even on large amounts of $CO_2$, by the procedure of precipitating the alkali carbonate formed in the absorbent solution with a constant maximum amount of $BaCl_2$, and making to 500 cc. volume with $CO_2$-free distilled water. An aliquot of 250 cc. of the clear supernatant caustic liquid is then titrated directly with standard acid, using phenolphthalein as an indicator. From the determined strength of the absorbent is then deducted the blank obtained in the same manner upon the original solution.

Ten cc. of approximately $N/2$ NaOH, diluted to 50 cc. with $CO_2$-free water, is sufficient to absorb the liberated $CO_2$. If the double titration procedure be followed, the number of cc. of $N/20$ acid used in the methyl orange titration of the blank, minus that of the determined residual, will give, in terms of $N/20$ acid, the $CaCO_3$ decomposed by the soil. This number, multiplied by 0.005 g. and divided by the charge and multiplied by 100 will give the per cent of lime requirement in terms of carbonate of lime. If the barium chloride precipitation procedure be followed the difference between cc. of titration of one-half of original absorbent solution after its treatment with $BaCl_2$ and that of 250 cc. aliquot after absorbing $CO_2$ multiplied by the $CaCO_3$ value of titration-acid and divided by charge will give $CaCO_3$ requirement.

The small and nearly constant atmosphere blank of the apparatus is included in that of the added $CaCO_3$ and absorbent solution. This eliminates the necessity of rinsing the apparatus before each determination in order to remove any acid residual from the preceding determinations. This, together with the elimination of necessity for sweeping the apparatus free of atmospheric $CO_2$ prior to each analysis, greatly facilitates speed when making a large number of determinations. In very accurate work the slight action of the acid upon the soil organic matter in the cold should be recorded. The blank would then be run simultaneously upon the aggregate of a charge of the original soil equivalent to that used in the evaporation, the boiled $CaCO_3$ solution, the apparatus atmosphere, and the absorbent solution, if the volumetric absorbent method were used.

If the apparatus above specified for determination of residual carbonates at room temperature be not available, residual carbonates may be determined by bringing the soil and acid to boiling and continuing the boiling for *one minute*, with passage of purified air during boiling and for 30 minutes subsequently. A blank should then be run upon the acid soil in the same manner and correction made therefor. The boiling necessitates great care in order to prevent moisture being carried through the sulfuric acid into the soda lime tubes. Camp absorption towers will be found to be very efficient in the drying of the evolved gas.

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[1] Description of apparatus and detailed directions for manipulation of this determination were given in *Tennessee Station Bulletin* **100** and in This Journal **7** (1915), 227.

[2] See Lincoln and Walton, "El. Quant. Chem.," p. 64

## ON THE COMPOSITION OF THE SEEDS OF MARTYNIA LOUISIANA[1]

By E. H. S. Bailey and W. S. Long

Received June 9, 1915

Our attention was first called to the possible industrial value of this plant by Mr. J. A. Puntennay, of Granada, Colo., a locality just across the Kansas-Colorado, line. He estimates that under ordinary conditions of that climate the plant will yield 20 bushels of cleaned seed per acre, and under more favorable conditions this amount may be much increased.

The plant, which is found growing in waste places, escaped from gardens, from Maine to Georgia, and which occurs wild from Indiana west and southwest through Utah, Texas and New Mexico, is a coarse, diffusively branched, glandular, pubescent and viscid, strongly scented shrub. It is commonly known as *unicorn* or *Devil's Claws*. It has opposite, ultimate, long-petioled leaves, and large, violet-purple, whitish or mottled flowers in short terminal racemes. The seed-pod when inverted has the shape of an elephant's trunk, hence the name *Elephant's Trunk*, often applied to the plant. When dry the pod splits in the center and two horns or projections appear.

The Martynia grows abundantly as a weed in a climate that is so dry that few other plants will flourish, because it has a tap root that penetrates the soil to a great depth. The herb is very drought-resistant, and will mature its seed in localities where the moisture is not even sufficient to produce Mexican beans. With abundant moisture the yield is much increased. The seeds, of which as many as seventy are often found in a pod, are surrounded by a husk, and when this is removed, a comparatively soft, nearly white kernel remains. This is easily crushed, even when dry, and its oily character is apparent to the touch. The seed has the following percentage composition:

| Ether extract (Fat) | Protein (N × 6.25) | Starch | Crude fiber | Moisture | Ash |
|---|---|---|---|---|---|
| 60.63 | 24.41 | 4.55 | 3.05 | 2.91 | 3.80 |

[1] Presented at the 51st Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

The constants of the oil are as follows:

| | Refractive index (15.5° C.) | Iodine No. | Saponification No. | Specific gravity 15.5° C. |
|---|---|---|---|---|
| Sample I | 1.4760 | 122.3 | 197.1 | 0.9157 |
| Sample II | 1.4767 | 122.8 | 198.6 | |

The analysis was made from the oil expressed from the seeds, after warming. The seeds crushed very easily, but with the press that we were able to construct, only about 20 per cent of oil was extracted.

Comparing this oil with other edible oils, it has a high iodine number—between that of sesame oil and poppy oil, and much higher than ordinary oils. Its specific gravity is similar to that of olive oil and mustard oil; its saponification number is high—near that of poppy oil. The oil is readily hydrogenated, and a bland product is produced which has an iodine number, 72.8. Although experiments are lacking to prove that the oil is nonpoisonous, it seems to have no injurious effects from tasting small quantities. Feeding experiments are in progress with mice, to prove, if possible, the bland quality of the oil. It is a well-known fact that under the name of Martynia the green pods are often used as food and for making pickles.

If the plant is abundant enough, or if it can be grown cheaply enough in the arid regions, it may solve the question as to what to do with the otherwise barren land. Further experiments are in progress to test the quality of the oil. The press cake will no doubt prove to be valuable stock food.

UNIVERSITY OF KANSAS, LAWRENCE

## ON THE RATE OF EVAPORATION OF ETHER FROM OILS AND ITS APPLICATION IN OIL-ETHER COLONIC ANESTHESIA[1]

By CHAS BASKERVILLE

Received June 14, 1915

It is conceded that the anesthetic agent must get into the blood for distribution and for eventual elimination, whatever theory of general or central anesthesia one may support. The anesthetic agent has normally been introduced into the blood by inhalation or intravenously. It is normally eliminated *via* the lungs.

The intestinal mucous membrane of vertebrates is well known as an efficient transmitter of gases to and from the blood. Pirogoff[2] appears to have been the first to mention the administration of ether by this route. Liquid ether was used until Magendie gave warning as to the danger of its use and ether vapor was substituted. During the same year Roux,[3] y'Yhedo,[4] and Duprey[5] employed liquid ether or aqueous mixtures to induce complete anesthesia. Although Pirogoff's enthusiasm prompted him to predict the supplanting of the inhalation procedure by the rectal method, references to it disappeared from the literature until 1884. Then Molliers[1] revived interest in the method by using a hand bellows for forcing the ether vapor into the intestine. Variations in the technique were introduced during the same year, but the experiences of Yversen, Harter, Bull,[2] Weir,[3] Wancher[4] and Post[5] showed more or less diarrhea and melena as after-effects. These after-effects, with one case of death directly attributable to the procedure, caused the method to again fail in securing serious recognition until 1903 when Cunningham[6] employed air as a vehicle for sweeping the ether vapor into the colon. In 1909 Leuguen, Money and Verliac[7] used oxygen as the vehicle for the ether vapor. Buxton[8] in his splendid book on "Anesthesia" says that he found the procedure most satisfactory for certain operations, for example, those having to do with the mouth, nose, etc., but he remarks, "Deaths have occurred." Sutton's[9] introduction of a return flow tube for these gases introduced and unabsorbed constituted a distinct advance in anesthesia by colonic absorption.

In an effort to avoid certain well-known difficulties in intravenous anesthesia, Gwathmey experimented with mixtures of normal saline solution and ether per rectum. The concentration of ether in the aqueous solution was so small that excessive volumes of liquid were needed, and furthermore the ether parted from the solution so very rapidly that experimentation along those lines was abandoned. Gwathmey then applied a solution of ether in olive oil. As oil and ether make perfect solutions in all mixtures, it was his hope to reduce the total bulk of the fluid introduced into the colon by using a stronger solution of ether in oil than is possible with any known aqueous mixture. As oils are lubricants it was also hoped to avoid the irritation of the mucous membrane previously noted. The ether may always be separated from the oil by warming, but unless the temperature of the mixtures is suddenly raised to an excessively high point, the ether passes off deliberately. It was thought that the evaporation of the ether would induce some cooling of the mixture with a consequent checking of the evaporation and its absorption. These premises coupled with slow absorption by the colon in comparison with the rapid elimination by the lungs would automatically regulate any anesthesia that might be induced in this manner. As a result, Gwathmey presented a paper before the 17th International Medical Congress in London in 1913 on the work with animals done by himself and Wallace.

[1] Read before the American Philosophical Society, Philadelphia, April 23, 1915; the New York Section of the American Chemical Society, June 11, 1915; and the American Association of Anesthetists, San Francisco, June 21, 1915.

[2] "Recherches pratique et physiologiques sur l'etherization," St. Petersburg, 1847.

[3] *J. d. l'Academie d. Sciences*, **1847**, p. 18.

[4] *Gazette med. d. Paris*, **1847**.

[5] *Academie royale de medicine*, March 16, 1847.

[1] *Lyon Medical*, **1884**, p. 45.

[2] *N. Y. Med. J.*, March 3, 1884.

[3] *Med. Rec.*, **1884**.

[4] *Cong. internat. d. Sciences med.*, **1884**.

[5] *Boston Med. and Surg. J.*, **1884**.

[6] Cunningham and Leahy, *Boston Med. and Surg. J.*, April 30, 1905; *Vide* also Dumont, *Correspond. Bl. f. Schweitzer Aertze*, **1903**, **1904**, **1908**; Krugeline, *Wiener klin. Woch.*, Dec., 1904.

[7] *Compt. rend. soc. Biol.*, June, 1909.

[8] "Anesthesia," London, 1907.

[9] For full account of technique and literature, see "Anesthesia" by Gwathmey and Baskerville, Appleton, New York (1914): pp. 431–457.

At the request of my co-laborer, Gwathmey, I undertook an investigation on the rate of evaporation of ether from oils to secure the following information that might be of service to him in his further application of his ideas with human subjects:

1—A comparison of the rate of evaporation of ether from different mixtures of ether and the same oil.

2—A comparison of the rate of evaporation of ether from the same per cent mixtures of different oils and ether.

3—The influence of surface on the rate of evaporation.

As the result of much preliminary experimentation, the following mode of procedure was settled upon.

In the experiments to determine the influence extent of surface played upon the rate of evaporation, the same precautions were taken as to height of walls of the containing vessels. In the largest areas worked with, this involved using as much as 600 cc. of the mixture. As the 75 per cent mixture had been found most satisfactory clinically, this was determined with that mixture only.

The ether used was that prepared under my supervision and was 97 per cent absolute with 3 per cent absolute alcohol, being free from acids, aldehydes, and water.

The oils used were of three types, vegetable, animal

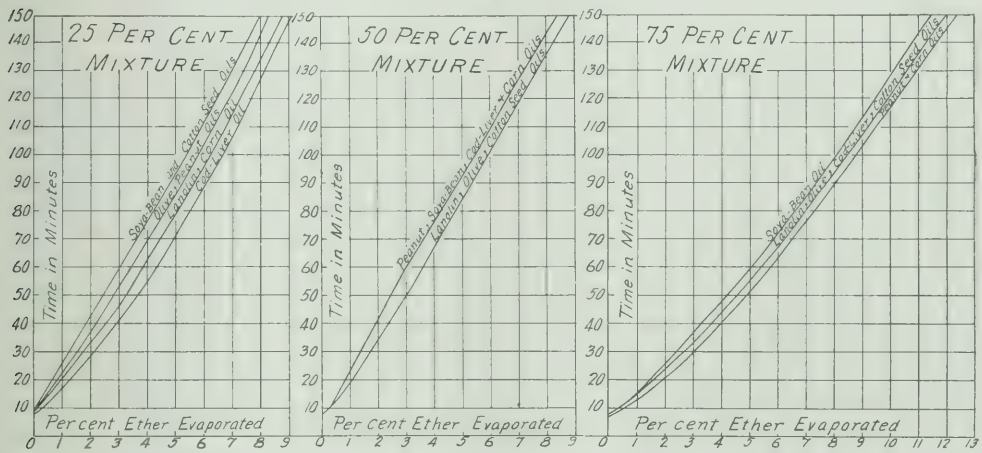



FIG. I FIG. II FIG. III

RATES OF EVAPORATION FROM 25, 50 AND 75 PER CENT MIXTURES OF OILS AND ETHER

Large glass tubes were calibrated to 1 cc. from 20 cc. to 105 cc. Mixtures of 25, 50 and 75 per cent of oil and ether were carefully placed in the tubes. The tubes were weighted with lead and placed in a thermostat, whose temperature was so regulated as not to vary more than ±0.03° C. from 37° C., the same being controlled by a toluene-mercury temperature regulator. All connections (gas, water, etc.) were made with lead pipes for safe use over night, as occasion arose. The water in the bath was stirred by a system of paddles and shaft operated through belt and pulleys by a small hot air engine. The tubes were immersed in the bath to within 2 cm. of the tops. During the first five minutes two readings were made in each case to get the highest point to which the volumes expand upon heating up to 37° C. After that readings were made every five minutes for two or three hours.

Since the evaporation of any liquid depends upon the partial pressure of that liquid at its surface, the higher the glass wall above the surface of the oil-ether mixture, the heavier the column of ether vapor resting on the surface of the mixture and the slower will be the evaporation; consequently the different oil mixtures with the different percentages of ether were experimented with in the same tube filled to the same height in all experiments.

and mineral, being, respectively, olive, cottonseed, corn, peanut and soya-bean; cod-liver and lanolin (anhydrous); and Russian mineral oil. All the vegetable oils, except olive, were refined by a process devised by the author[1] and were neutral. The other oils were purchased in the open market.

The experimental work was carried out by Mr. Hyman Storch, under my direction.

The data obtained for the 25, 50 and 75 per cent mixtures vegetable and animal oils are shown graphically in Figs. I–III. In the curves the abscissae show the percentage of ether evaporated (based on volume measurements) and the ordinates time of the evaporation.

Fig. IV (selected at random from charts made for each oil) shows the difference in rate of evaporation of 25, 50, and 75 per cent mixtures with one oil.

Fig. V shows the effect of increased surface on the rate of evaporation. One oil only was selected to show the principle, which is that the rate of evaporation bears a direct ratio to the surface exposed.

These experiments were made in glass, hence they do not disclose all the factors in the conduct of such mixtures in contact with the walls of the colon, for

[1] "Refining Oils," *Oil, Paint and Drug Reporter*, May, 1915.

there the principles of osmosis and diffusion are involved. But these observations demonstrated several striking facts:

1—While ether boils at 34.6° C., it does not escape violently from an oil-ether mixture, as from an aqueous

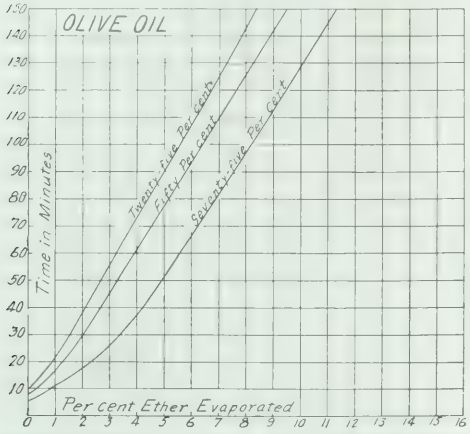



FIG. IV—COMPARISON OF RATES OF EVAPORATION OF DIFFERENT MIXTURES OF OLIVE OIL AND ETHER

mixture, when the mixture is heated higher, namely, to the body temperature of 37° C.

2—The *rate* of separation of ether from the oil quickly acquires a definite and fairly fixed speed.

The significance of this conduct cannot fail to be of great importance, for by this means the proper content of ether may be maintained in the blood to produce

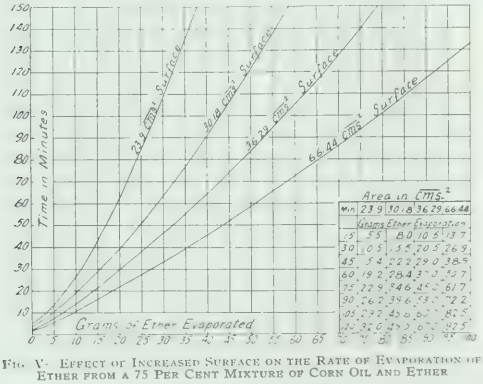



FIG. V—EFFECT OF INCREASED SURFACE ON THE RATE OF EVAPORATION OF ETHER FROM A 75 PER CENT MIXTURE OF CORN OIL AND ETHER

any desired physiological effect that has a quantitative relation thereto, for example, the third or surgical stage of anesthesia.[1]

The last mentioned has been demonstrated clinically by Wallace, who found respiration and blood pressure fully maintained, and Gwathmey and others with records to date of about 1000 human cases. So far, not a case of post-ether pneumonia has been encountered. The after-effects usually associated with inhalation anesthesia, unless induced by the most improved modern technique, are virtually absent, including post-anesthetic nausea. Its use for special cases involving the head, breathing passages, etc., is superior. Although having had the privilege of attending clinics, I am not qualified to pass judgment upon its value, but from what I have learned, if necessary, "Give it to me that way."

COLLEGE OF THE CITY OF NEW YORK

[1] In this connection it may be stated that about 30 mils of a 75 per cent mixture to 20 lbs. of body weight is administered as an enema.

## DISCUSSION[1]

By James T. Gwathmey

The rate of evaporation of ether from oil is the one all-important factor to be considered in oil-ether colonic anesthesia. If ether evaporated irregularly, either as to time or quantity, oil-ether colonic anesthesia would be a most dangerous procedure. The charts showing the percentage of ether evaporated during a period of two and one-half hours would convince the most skeptical that as far as this factor is concerned anesthesia colonically should be a very even and safe procedure. The whole medical profession owes a debt of gratitude to Dr. Baskerville for thus placing this method upon a scientific basis. Other factors to be considered would be injury to the colon, safety, and the time required for a patient to come out. All of these problems have been worked out satisfactorily and we can control a patient under this form of anesthesia just as readily as we can under inhalation anesthesia. If it were possible for the ether to leave the oil at any but a regular rate, which rate is determined by the per cent used, then this method of anesthesia would be very unsafe.

The fact that we have used it in over one thousand cases without any untoward effects and in not a single case have we had bloody stools or diarrhea following would seem to indicate that it is as safe as any other method of anesthesia when used in the proper way.

By placing a special rectal tube in position and massaging over the colon from right to left we can bring a patient out of a very deep anesthesia in fifteen to thirty minutes.

The charts show that the patient does not get a tremendous amount of ether at first and then gradually recover, which would mean anesthetic shock and recovery whenever this method was attempted but that the patient goes under very slowly and gradually, and on account of the rapid elimination from the lungs the depth of anesthesia is constant. The charts will have a tendency to inspire confidence in those who have not hitherto used this method. It is especially indicated in all operations upon the head and upper trunk where the anesthetist is usually in the way. For the insane, or wherever the element of fear is prominent, it is indicated in preference to all other methods. The fact that nausea, vomiting and other sequellae are reduced to a negligible quantity is also a factor in favor of this method.

40 EAST 41ST STREET, NEW YORK

[1] At Meeting of the New York Section of the American Chemical Society, June 11, 1915

# LABORATORY AND PLANT

## A NEW APPARATUS FOR FAT EXTRACTION

By I. Selecter

Received June 24, 1915

From the varied forms of apparatus for the extraction of fat that are upon the market, it would seem that there is not one in use that meets the approval of all laboratories. In laboratories for control work, the chief requisites of an apparatus of this nature are uniformity of results, better extraction and ease in manipulation. If the number of units in use is necessarily large, the cost and durability are also important.

FIG. 1

To meet these requirements, an apparatus was devised for use in the Feed Laboratory of the Louisiana Experiment Station. Some portions of this are similar to parts of an apparatus used in the laboratory of Prof. G. W. Cavanaugh in Cornell University, though the principle of extraction is somewhat different. Instead of soaking the sample in the liquid ether, or whatever the solvent may be, as is the case with most of the apparatus now in use, it is saturated with the vapors and is periodically flooded with the redistilled liquid.

The apparatus as shown in Fig. 1, consists in the main of three parts: (1) Condensing section, (2) flooding section, (3) reservoir.

The condensing section *E* is made of a tube 18 in. long and 1 1/2 in. in diameter. This is flanged slightly at the top and drawn out at the bottom into a ground glass end to fit the top of section *B*. Into this latter is first put a regular Soxhlet extraction tube, *D*, 6 in. long, having merely a siphon tube on the side. Above this is the condenser proper, *F*, which consists of a glass tube 12 in. long and 1 1/4 in. in diameter. This latter is also flanged at the top, and is suspended from the flanged part of the outer tube. Into the top of the condenser is fitted an ordinary two-holed rubber stopper, *G*. Through this are put the tubes *H* and *I*.

The advantage of this type of condenser instead of one with the sealed-in tubes is readily apparent. First, in the cost of making, since the former can easily be made in the laboratory by sealing one end of a 1 1/4 in. tube and drawing it out to a point, while the upper end is flanged so that it will hang suspended in the outer tube. There is the additional advantage of the rubber stopper in being able to clean the condenser when necessary without any difficulty whatever. Then, too, the tubes that extend into the condenser can be bent in the laboratory, so that broken parts can be replaced cheaply and readily.

The flooding section *B* is made of a straight glass tube 5 in. long and 1 in. in diameter. This is ground at the top to fit the lower part of section *E*. The ordinary Schleicher and Schüll capsule which contains the weighed sample of the feedstuff is placed in this part.

The reservoir consists of a 75 cc. Erlenmeyer flask ground to fit the end of section *B*.

The solvent is placed in the flask at the bottom and the vapors pass through the sample, thereby saturating it. Condensation takes place at the top, into the Soxhlet tube below, which on siphoning over floods the sample, thus leaching out the extract. The rate of flooding can readily be regulated by the amount of heat placed at the bottom.

One of the important features of this apparatus is the recovery of the ether that has been used in the extraction. This is a considerable factor in a control laboratory where large amounts are used. In a Soxhlet arrangement, where the condensation is good, there will be enough left in the tube to siphon over several times and one must wait until the solvent has evaporated sufficiently before the sample can be removed; there are also stopcock arrangements or mercury joints but these are either very delicate and liable to breakage or they work imperfectly. In the new apparatus when the extraction has gone on for the required length of time, the flooding section is detached and a glass capsule is substituted for the paper one. On flooding, this fills and the flask containing the extract can then be removed without any difficulty or loss of time.

As to arrangement in the laboratory, this apparatus can be set up either single or in sets of three or more, on either steam baths or electric hot plates.

For comparison of extractions with several kinds of apparatus, three methods were chosen: (1) The so-called straight extraction method, which has been in use in this laboratory for the past five years; (2) the Soxhlet, which is most commonly used; and (3) this new apparatus. The straight extraction unit consists of a long tube condenser, similar to any Liebig condenser, arranged with a cork stopper above a tube about 6 in. long into which the capsule containing the sample is placed. The extraction is carried on by having the condensed ether drop directly upon the sample which is covered with cotton within the capsule and thence draining into the fat bottle which is placed below. In this method there is neither flooding nor soaking. The Soxhlet was arranged with a reflux condenser. Here, of course, the principle is saturation.

Fat Extractions by Three Methods

| Commercial Feed | Straight Extraction | | | Soxhlet Apparatus | | | Author's Apparatus | | |
|---|---|---|---|---|---|---|---|---|---|
| | Duplicates | | Av. | Duplicates | | Av. | Duplicates | | Av. |
| Cottonseed meal | 7.95 | 7.75 | 7.85 | 7.80 | 7.85 | 7.83 | 8.03 | 8.05 | 8.04 |
| Rice polish | 8.25 | 8.10 | 8.18 | 8.10 | 8.20 | 8.15 | 8.18 | 8.13 | 8.16 |
| Wheat bran | 5.60 | 5.65 | 5.63 | 5.80 | 5.90 | 5.85 | 6.05 | 6.25 | 6.15 |
| Corn chops | 3.60 | 3.65 | 3.63 | 3.95 | 3.93 | 3.94 | 3.85 | 3.75 | 3.80 |
| Molasses feed | 4.00 | 4.04 | 4.02 | 3.85 | 3.80 | 3.83 | 4.90 | 4.70 | 4.80 |
| Chick feed | 5.10 | 5.05 | 5.08 | 5.10 | 5.30 | 5.20 | 5.95 | 5.90 | 5.93 |
| Meat crisps | 6.93 | 6.75 | 6.84 | 7.15 | 7.05 | 7.10 | 7.45 | 7.25 | 7.35 |
| Beef scraps | 11.10 | 11.00 | 11.05 | 10.60 | 10.77 | 10.69 | 11.75 | 11.55 | 11.65 |
| Digester tankage | 12.00 | 11.90 | 11.95 | 12.00 | 12.05 | 12.03 | 12.30 | 12.15 | 12.23 |
| Mixed bran | 4.00 | 3.80 | 3.90 | 3.95 | 3.80 | 3.88 | 4.10 | 4.30 | 4.20 |

Ten samples of commercial feeds were used and the results obtained for each of these feeds, using the official method for the determination, appear above.

It can readily be seen from the above results that the new apparatus gave better extraction in the greatest number of cases, and averages higher in 8 out of the 10 cases here noted. It was found, too, that there is a greater uniformity in the results obtained, it being necessary in several instances to make as many as six determinations with the straight extraction apparatus and four with the Soxhlet before checks within 0.2 per cent could be obtained.

To summarize, the apparatus gives better extraction than does either the straight extraction or the Soxhlet methods. It is easy to manipulate, presenting a smooth outer surface, reducing the danger of breakage to a minimum. The recovery of the solvent is easy and rapid and entails no loss of time. The cost of the apparatus is also comparatively small.

Acknowledgment should be made to Mr. A. P. Kerr, Assistant Director of this station, for his suggestions.

LOUISIANA AGRICULTURAL EXPERIMENT STATION
BATON ROUGE, LOUISIANA

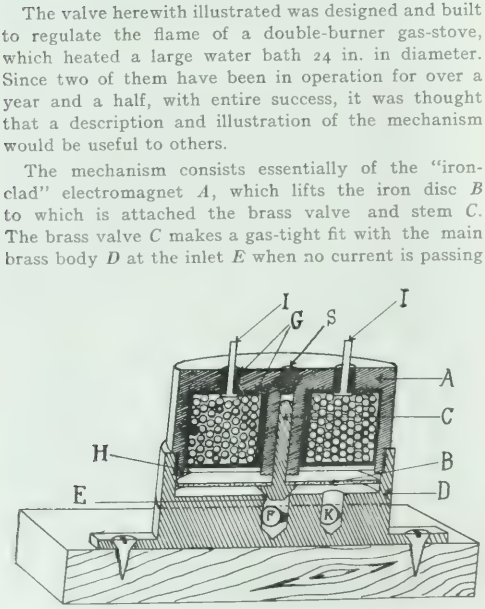
## A SIMPLE, DURABLE, ELECTRICALLY OPERATED GAS-VALVE

By ZENO OSTENBERG

Received June, 21, 1915

The valve herewith illustrated was designed and built to regulate the flame of a double-burner gas-stove, which heated a large water bath 24 in. in diameter. Since two of them have been in operation for over a year and a half, with entire success, it was thought that a description and illustration of the mechanism would be useful to others.

The mechanism consists essentially of the "iron-clad" electromagnet *A*, which lifts the iron disc *B* to which is attached the brass valve and stem *C*. The brass valve *C* makes a gas-tight fit with the main brass body *D* at the inlet *E* when no current is passing




through the magnet winding, but when current is sent through the magnet winding, the disc *B* and valve *C* are raised and thus gas is allowed to pass from *E* to *K*, which leads to the burner. *F* is the outlet to a pilot light. The disc *B* is prevented from sticking to the magnet *A* by the plug *S*, which may be screwed down to limit the travel of the valve stem *C*. *G* is insulation which must be able to withstand a rise of temperature up to about 100°, as the magnet sometimes becomes quite hot. The disc *H* is of brass and is soldered gas-tight to the magnet *A* to prevent moisture and gas from attacking the wiring and also to keep the wiring in place. The gas inlet tube (not shown) enters opposite to the pilot opening *F*. When operated from a 110 volt line, the winding consists of No. 26 d. c. c. copper wire with a 16 c. p. carbon lamp in series. This allows slightly less than 0.5 ampere to pass through the winding of the electromagnet. For use with a storage battery No. 30 wire is used.

The electrical circuit is opened and closed by a 75 ohm standard Pony relay, which is operated by a dry battery and thermoregulator. The dry batteries, which were originally put into the thermo-regulator circuits over a year and half ago, are still able to operate the relays as only about 0.02 ampere is used, and this amount of current is so small that no trouble whatever has been experienced from oxidation of the mercury at the contacts in the thermo-regulators.

Obviously the valve may be used on any size of burner, from the smallest micro-bunsen to one which has a gas inlet equal in size to the inlet and outlet of the valve. In the valves in use these holes are 0.25 inch in diameter.

2233 WEBSTER ST., SAN FRANCISCO

## PORTABLE TITRATING TABLE[1]

By R. E. OZIAS

Received June 16, 1915

Fig. I shows a convenient portable titrating table which has recently been installed in the United States Appraiser's Laboratory at New York. The burettes are operated by compressed air supplied by a Goodyear air bottle which rests on a shelf attached to the table.

The air is conducted through $^1/_8$ in. and $^1/_4$ in. brass pipe to the main pipe (1 in. diameter), on top of table, on which are seen the air pressure gauge and the individual taps fitted with $^1/_8$ Lunkenheimer brass spring key cocks.

The top of the table is 3 ft. × 6 ft. and is perforated with 8 circular openings, 5 in. in diameter, in which the bottles are placed, resting on a base board securely fastened 5 in. below the top.

The standard solution bottles are of dark glass, 2500 cc. capacity, and as shown are eight in number. Without necessarily increasing the size of the table, a second row of eight bottles could be placed in a similar position and thus give it a capacity of sixteen standard solutions.

No moisture or carbonic absorption apparatus is shown on the train, as the solutions employed did not require their use, but when necessary those accessories

[1] Published with the consent of the Secretary of the Treasury and United States Appraiser, Port of New York.

can be attached readily to any individual connection or placed at or near the outlet from the air supply.

To operate, air is admitted to the main pipe to about 15 lbs. pressure when the valve on the air bottle is

FIG. I

closed, followed by the closing of air valve on the vertical pipe leading from the supply.

To fill any burette, its corresponding air cock is opened cautiously until solution is moving into burette, when it is closed. After the solution has passed

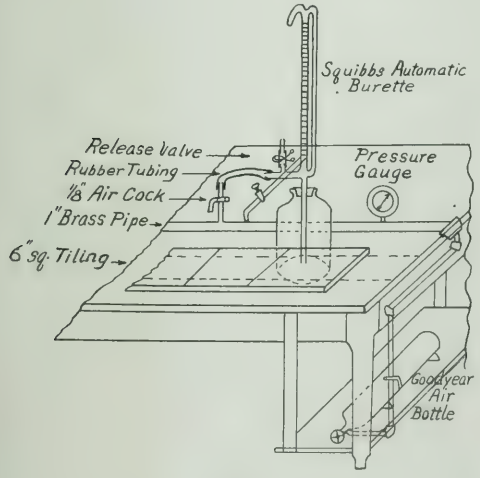



FIG. II

the zero mark, the relief valve attached to the side of burette is opened, when liquid flows back and automatically sets at zero.

The relief valve is made with a small piece of glass tubing with a nozzle end connected with rubber tubing to the air outlet attached to side of burette, using the pinchcock on the rubber tube connection. The glass tube outlet must be a nozzle of comparatively small orifice in order to release air pressure gradually, for if released suddenly there will be upward flow of solution through the relief valve.

The amount of air consumed is very small and as bottles are recharged at a cost of $1.00, the cost of air per annum in operating a table with eight solutions should not be over 50 cents.

White tilings 6 in. square are placed along the front of the bottles and under the spits of the burettes, the distance between tiling and spit of burette being about 7 in.

U. S. CUSTOMS SERVICE, TREASURY DEPARTMENT
641 WASHINGTON ST., NEW YORK

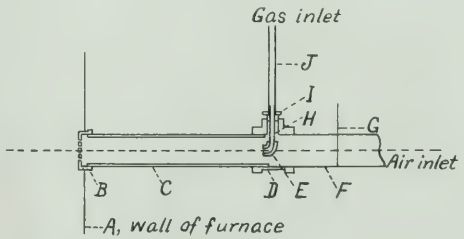
## A SIMPLE GAS BURNER FOR SMALL LABORATORY FURNACES

BY D L. RANDALL

Received June 21, 1915

The burner described below was devised to use natural gas instead of gasoline in heating a small assay furnace of the combined muffle and crucible type. Its merit lies in its simplicity and cheapness, as it can easily be made by any pipe fitter.

A section of the burner is given in the accompanying figure and it is constructed as follows: The part *C* is a piece of 2 in. iron pipe about a foot long. On one end of this is screwed a cap, *B*, and on the other a tee, *D*, 2 × 3 1/4 in. In the end of the cap as many 1/8 in. holes as possible are bored. The air is led into the burner through the large end of the tee. This air




is supplied by a centrifugal blower and is under a pressure of about 1/2 in. of water. Into the side opening of the tee is screwed a bushing, *I*, 3/4 to 1/4 in., and into this is screwed the 1/4 in. pipe that admits the gas. The lower end of this pipe, *J*, is tapped out to receive the 1/8 in. pipe *E* and to the lower end of this is screwed the 1/8 in. elbow *E*. A stopcock not shown in the figure regulates the gas supply while the air supply is regulated by the damper *G*.

The burner so constructed, when properly adjusted, burns very steadily at the openings at the end of the burner. There is no danger of it snapping back and a temperature sufficiently high for all assay purposes is easily obtained. This simple burner will doubtless be useful in heating other forms of apparatus and the writer sees no reason why it could not be used with any form of fuel gas.

CHEMICAL LABORATORY, BAKER UNIVERSITY
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# ADDRESSES

## CHEMICAL PATENTS[1]—II

### THE APPLICATION FOR AND PROSECUTION OF APPLICATIONS FOR UNITED STATES LETTERS PATENT

By Seabury C. Mastick

As to the requisites for the application, specification and claims, Section 4888 of the Revised Statutes prescribes as follows: "Before any inventor or discoverer shall receive a patent for his invention or discovery, he shall make application therefor, in writing, to the Commissioner of Patents, and shall file in the Patent Office a written description of the same, and of the manner and process of making, constructing, compounding, and using it, in such full, clear, concise and exact terms as to enable any person skilled in the art or science to which it appertains, or with which it is most nearly connected, to make, construct, compound and use the same; and in case of a machine, he shall explain the principle thereof, and the best mode in which he has contemplated applying that principle, so as to distinguish it from other inventions; and he shall particularly point out and distinctly claim the part, improvement, or combination which he claims as his invention or discovery."

The formal papers of an application comprise the petition, specification, oath, and, if the nature of the case admits it, drawings of the invention. The petition and oath are of stereotyped form and need not be considered further here.

The following order of arrangement should be observed in framing the specification:

1—Preamble stating the name and residence of the applicant and the title of the invention.

2—General statement of the object and nature of the invention.

3—Brief description of the several views of the drawings, if any.

4—Detailed description.

5—Claim or claims.

6—Signature of inventor, or if dead, of his executor or administrator.

The applicant must be the inventor personally or if insane, his guardian, or if dead, his executor or administrator. An application cannot be made by an assignee although the patent may subsequently be issued to an assignee.

A model or specimen of the thing invented will be required or admitted only as a part of the application when on examination of the case the Examiner of the Patent Office shall find it to be necessary or useful. As a rule models or specimens are neither asked for nor desired.

In discussing this general topic, we shall confine ourselves to applications for patents relating to chemistry—to compositions of matter and to chemical processes—taking up the general theory and requirements of applications for patents for compositions of matter and for chemical processes with illustrations from issued chemical patents, and using the history of the Charles M. Hall patent for the electrolytic production of aluminum as an illustration of the prosecution of an application through the Patent Office as well as an illustration of a form of patent for a chemical process.

In its essentials a specification of a composition case does not differ from that of any other class of invention. The specification must set forth the precise invention for which a patent is solicited and explain the principle thereof and the best mode in which applicant has contemplated applying that principle in such manner as to distinguish it from other inventions. A composition presents three essential subjects for description: the ingredients, the manner of combining them and the properties and nature of the resulting product. Each of the ingredients should be described in such manner that those skilled in the art may know exactly what is meant to be included. A great many applications are defective in this particular, owing to the use of indefinite and inaccurate terms in defining ingredients. This results in many cases from the loose use of chemical terms, such, for example, as using the word "soda" when referring to a salt or compound of sodium other than sodium carbonate, and it is difficult or impossible to tell from the context what particular compound is meant. When chemical substances are referred to, the safest rule is to designate them by their correct chemical names instead of their old or colloquial names. If thus defined or designated, or the formula stated, no question can thereafter arise as to what is meant. If a term has a definite accepted meaning in an art, though not strictly accurate, that is sufficient, since all that is required is that the substance be defined so that there is no question as to what is meant. Loose, indefinite terms are quite frequent in applications for paint compositions in such terms as "varnish," "drier," "japan," etc., and in alloy cases in such terms as "brass," "bronze," "white metal," to designate ingredients. When it is taken into consideration that there are many kinds of varnishes, japans, and driers and of brasses, bronzes and white metals, differing in composition and many of them in a great degree, it is seen that such terms do not meet the requirement of the rules as to definite disclosure. It would be possible to make up a composition having the ingredients named in such a description and in the same proportions, and yet the resulting composition would differ materially from that which the applicant had in mind, because his varnish, japan or drier, or his brass, bronze or white metal was different from the ones used by the other.

In specifying the ingredients none should be specified which is not essential to the composition. If any ingredient can be dispensed with it should be so stated in the description or no claim can properly be made for the composition with that ingredient omitted. Also the nature and number of the ingredients should be so stated that experiment is not necessary to determine what may be used.

In describing the manner of producing the composition, the proportions of the ingredients and the process of compounding them should be correctly and precisely stated so that one skilled in the art can produce it without the necessity of experiment.

It is not necessary that the theory of action of the ingredients be known or stated in the description, though if it is known it is preferable to state it.

The nature of the resulting composition should be defined by a statement of its peculiar physical or chemical characteristics if possible.

Usually compositions are devised for some particular use, such as a paint, fertilizer, explosive, etc., and the use or uses to which they are intended to be put should be set forth in the description.

In order to be patentable the composition must have utility. This may be assumed for some products such as new chemical compounds, but as to others the utility of the product should be specified.

The claims in composition cases often introduce questions which seldom or never arise in connection with the claims in machine and process cases, particularly the former. As a rule inventors devise or invent a specific composition to meet some definite want. The ingredients involved have to be mixed within certain limits or proportions or in a certain manner to get a composition which will have the desired properties. The description sets forth such a composition and too often says nothing

[1] Special lecturer on Chemical Patents, Department of Chemical Engineering, Columbia University, 1915.

about equivalents, whether or not proportions may be varied or whether or not some ingredient or ingredients may be omitted without any material change in the resulting product.

The person who has discovered that certain ingredients mixed in certain proportions will produce a certain composition of matter has not discovered every composition of matter which may be made from those ingredients nor is he entitled to the broadest possible claim for a composition containing those ingredients.

It is a good rule that in claims for compositions of matter in which proportions are essential the proportions be specified either directly or by reference to the specification, or the identifying and distinguishing characteristics of the composition should be stated in lieu of proportions. The latter is the better practice, though requiring more skill and care in drafting the claim, because it more fully protects the real invention.

Claims omitting ingredients which the specification does not state may be omitted are without basis in the case since they are not for the applicant's invention.

The omission of an essential ingredient makes a new composition. In a machine case whether an element is essential or not can be told by inspection. This, as a rule, is not so in composition cases, but only by experiment can the essentiality of ingredients be determined. Therefore, in the absence of a statement that it is not essential an element is considered essential unless it is obvious that it may be omitted, for example, one which is added for merely fanciful effect, such as a coloring or a flavoring ingredient. If an ingredient merely improves the composition and is not absolutely essential, claims may be drawn both including and omitting it. But even in such a case a proper basis for the omission of such an ingredient should be laid in the description.

If the specification lays a basis for the omission of certain ingredients the claims which do not include all the ingredients should be so worded as not to limit them to the ingredients enumerated therein.

In selecting terms to define ingredients of composition generically there is danger of choosing terms which are too comprehensive. In Bracewell *vs.* Passaic Print Works, 107 F. R., 467, the use of zinc oxide, hydrate, or carbonate seemed to be imperative to the success of the process. The applicant, however, stated that any zinc compound may be employed with good results, which statement was incorrect since it was proved that a large number of them could not be thus used. Judge Coxe said:

"It cannot be contended that the patentee knew that his statement that any zinc compound would operate successfully was false, but it is manifest that he did not know that it was true and he should have known it was true before he inserted it in his description and made his corresponding claim. He stretched his net to catch as infringers all users of zinc compounds and if he stretched it to the breaking point he has only himself to blame. The courts should be liberal in construing patents, but they cannot rewrite the description and claims, they cannot construct an entirely new patent even to save a meritorious invention. If the complainant's contention be correct a patentee can claim blindly an entire group of compounds, relying on the court, after subsequent investigation and experiment, to limit the claim to the one which gives the best results. This will not do."

In Matheson *vs.* Campbell, 78 F. R., 920, it was alleged by the patentees that any sulfo-acid treated by their process would give a "color producing black" and that, therefore, all sulfo-acids were equivalents. Judge Lacombe ruled that:

"The inventors did not make any such 'broad discovery.' They made the specific discovery that some disulfo-acids treated according to their process would produce their product. The broad discovery that all sulfo-acids may be thus transformed they certainly did not discover . . . since most of them cannot be thus transformed by the process of the patent. . . We are referred to no authority and know of no principle which will sustain applicant's contention that he can thus . . . speculate on the equivalents of his claimed invention, and thereby oblige the public to resort to experiments in order to determine the scope of the claims of the patent."

In defining ingredients generically, by statement of characteristics common to the several specific substances intended to be included, the characteristics or properties relied upon should be essential ones and not mere incidental ones which may be had in common by the substances but which are immaterial in so far as the particular composition is concerned. For example, in a non-corrodible alloy in which gold, platinum and iridium may be used interchangeably on account of their resistance to oxidation, and their specific gravity is unimportant, to define them in the claim as "heavy metals" is improper, since, while they *are* heavy metals, it is not this property which makes them equivalent in the alloy. Such a claim does not properly protect the invention since some heavy metals readily oxidize, and the claim would not cover alloys in which difficultly oxidizable metals not of high specific gravity are used. Essential, not non-essential, properties should be specified in identifying the ingredients.

The specification for a process patent also follows the usual rules as to making a full, clear and exact disclosure of the invention. As the practice of the process may be performed by various means, the claims are not to be restricted to the practice of the process in connection with the specific means disclosed. It is not necessary to disclose *every* mode or all the types of apparatus which may be employed but one particular mode or apparatus by which the process can be carried out should be set forth clearly and completely.

And this one means should be the best means known to the inventor at the time of making his application. If the specification sets forth a way of actually practicing the process and producing the result claimed, the theory of the inventor as to the mode of operation, if incorrect, may be disregarded, and will not be taken as limiting the invention. As such statement of mere theory is not necessary it had therefore better be entirely omitted, the specification setting forth the observed facts only.

It is better to always make a very full and detailed description of the way of practicing the process, even to the disclosure of apparently unimportant details. As a guide you might say that the disclosure should be just as detailed as a report of an important laboratory experiment. You may generalize, both in specification and claim from a detailed statement. The rules of the Patent Office, however, do not permit you to make more specific, mere general statements. In other words, if you have omitted an important detail, even if your whole process turns upon it, you may not afterwards add it to your specification. You might say that the specification may be subtracted from but may not be added to. These remarks apply as well to applications for all patents. The exclusion of an important originally omitted statement on the ground that it is "new matter" frequently wrecks the whole case.

Again, you may not always be able to tell at the beginning just what are the essentials of a process. You do not know what the prior art may show and on what you must rely in order to distinguish the invention in question from such prior art. Range of temperature, properties of substances employed, proportions of ingredients, pressures and all these and more may turn out to be of the utmost importance, yet if you have not made a definite statement in your specification you cannot claim it nor distinguish the invention from the prior art which may otherwise be a disclosure.

A process claim should not be for the *use* of a thing. Such claims are held to be invalid.

For example, in the famous ether case of many years ago wherein the use of ether as an anesthetic by inhalation of its vapors was claimed, the Court said:[1]

"It may not be amiss to speak of the character of the discovery upon which the patent is founded. Its value in securing insensibility during the surgical operation, and thus saving the patient from sharp anguish while it is proceeding, and mitigating the shock to his system, which would otherwise be much greater was proved on the trial by distinguished surgeons of the city of New York. They agreed in ranking it among the great discoveries of modern times; and one of them remarked that its value was too great to be estimated in dollars and cents. Its universal use, too, concurs to the same point. Its discoverer is entitled to be classed among the greatest benefactors of mankind. But the beneficent and imposing character of the discovery cannot change the legal principles upon which the law of patents is founded, nor abrogate the rules by which judicial construction must be governed. These principles and rules are fixed, and uninfluenced by shades and degrees of comparative merit. They secure to the inventor a monopoly in the manufacture, use, and sale of very humble contrivances of limited usefulness, the fruits of indifferent skill, and trifling ingenuity, as well as those grander products of his genius which confer renown on himself, and extensive and lasting benefits on society. But they are inadequate to the protection of every discovery, by securing its exclusive control to the explorer to whose eye it may first be disclosed. A discovery may be brilliant and useful, and not patentable. No matter through what long, solitary vigils, or by what importunate efforts, the secret may have been wrung from the bosom of Nature, or to what useful purpose it may be applied, something more is necessary. The new force or principle brought to light must be embodied and set to work, and can be patented only in connection or combination with the means by which, or the medium through which it operates. Neither the natural functions of an animal upon which or through which it may be designed to operate, nor any of the useful purposes to which it may be applied, can form any essential parts of the combination, however they may illustrate and establish its usefulness."

Obviously, the claim must be limited to some art involving a particular material or group of analogous materials. For example, the process of heating a *substance* to 1000° Centigrade to melt it, and then crystallizing it by cooling to 800° could be applied neither to water nor to platinum. The process is necessarily limited in scope to a few particular materials, and should not be claimed in any broader application.

Of course, one may claim his invention as broadly as the limits of the art allow, provided the claim is not broader than the original disclosure, which disclosure, in turn, must be sufficiently clear that one skilled in the art may be able to utilize the same. For example, a method involving coating canes with varnish and subjecting to a temperature of 240 to 300 degrees for not less than 3 hours was held void, because the limits of temperature stated were so wide apart that the process could not be carried out throughout the whole range claimed; hence, the claim was too broad in the sense of being inaccurate, vague and indefinite.

A patentable process claim must include all steps necessary to produce the stated or any useful result.

This seems to be clear, following the precedents of the decisions covering claims to structure. Each claim must define an operative process, however broadly stated. For example, in making a battery plate involving the four steps of pasting lead oxide on a grid, treating it with sulfuric acid, drying it and then electrolyzing as a cathode in a suitable bath to form a spongy lead electrode—if these four steps are all essential steps in making the electrode, then the first two steps alone, for example, are not patentable, since a finished and useful product is not produced thereby.

Of course, one is entitled to subprocess claims where they can be properly drawn.

An applicant may properly in one case have claims covering the principal or essential steps of his process, and other claims including these steps together with other specific steps which are not absolutely necessary to the performance of the process, but which add to its efficiency or make its operation more perfect.

For example, a claim omitted the intermediate step, in a process of making sugar, of "agitating and reducing the temperature." It was contended and held that the omitted step was not essential to the performance of the process, although it was an improvement and rendered the process more practical.

Similarly, in the example covering the making of a battery plate referred to, if the step of drying the plate is not essential, but merely works toward greater efficiency and a better product it may be left out of a broad claim. The claim without this additional step covers a complete, useful and operative invention by itself, and therefore is a true subprocess claim under the specific process. As a rule a process claim should be expressed independently of the specific structure of the article treated and independently of the structure of the apparatus in which the process is carried out. So far as the steps of the process are concerned, it is clear that it is immaterial whether a battery grid, or plate, for example, is made of woven lead wire gauze or of a reticulated lead plate made of V-shaped bars cast together, since the steps of pasting, treating with acid, drying and electrolyzing can be carried out with the one electrode structure as well as with the other. Similarly, if the claim specified "applying the lead oxide paste with a *trowel* and treating the electrode with acid in a *rubber-lined wooden tank*," it would be objectionable. These structures have no patentable relation to the process steps.

Again, it was held that "it is better form in a method claim to state that a mixture is heated at a moderate temperature than to state that the same is heated over a water bath."

This rule cannot always be applied, however, in individual cases, especially in mechanical processes. Here the best we can say is that whatever structure is essential should be set forth to the minimum extent and only in the broadest possible terms, since no patentability is involved over the broad proposition in specifying particular structure.

Coming now to certain patents which we shall consider as illustrating the application of the principles heretofore set forth, showing different forms of statement in the specifications and different modes of claiming both compositions of matter and processes, together with other points which will be referred to in connection with the particular illustration, let us examine

(*a*) The "Calcium Carbide" Patent number 541,138, issued to Thomas L. Willson on June 18, 1895.

(*b*) The "Aspirin" Patent number 644,077, issued to Felix Hoffman, assignor to the Farbenfabriken of Elberfeld Company, on February 27, 1900.

(*c*) One of the "Adrenalin" Patents, number 753,177, issued to Jokichi Takamine, on February 23, 1904.

(*d*) Patent number 977,053, issued to Ludwig Taub, assignor to the Farbenfabriken on Nov. 29, 1910, for an amid of beta-beta-diethyl-propionic acid.

(*e*) Patent number 1,053,300, issued to Georg Korndörfer and Baptist Reuter, assignors to Farbwerke vormals Meister, Lucius & Brüning on Feb. 18, 1913, for derivatives of diamino-dioxyarsenobenzene and

(*f*) The Reissue of the latter patent.

(*g*) Hamilton Young Castner's Patent for the process of

[1] Morton :: N. Y. Eye Infirmary, F. C. No. 9865

manufacture of sodium and potassium, No. 452,030, issued May 12, 1891, and

(*h*) Charles M. Hall's Patent for the process of reducing aluminum by electrolysis, No. 400,766, issued April 2, 1889.

(*a*) THE "CALCIUM CARBIDE" PATENT

This patent describes the manufacture of commercial calcium carbide in which finely divided coke and pulverulent lime, mingled together, are subjected to the action of an alternating current in an electric furnace. A drawing illustrates the furnace diagrammatically in vertical section.

The patent reads as follows:

"This invention relates to the production of *a new form* of crystalline *calcium carbide*.

"Before my invention calcium carbide has existed in an *amorphous* condition, due either to the method of its preparation, or to the impurities contained in it.

"By my invention herein described, calcium carbide is produced in a new form, namely, in *crystalline* condition, having a bluish or purplish iridescence. The carbide so existing is in a condition particularly applicable, on account of its purity, for conversion into other compounds.

"In order to produce this product, I proceed as follows: I take very finely divided coke and lime, mechanically reduced to a pulverulent condition, and I mingle them thoroughly mechanically in the proportion of thirty-five per cent of coke and sixty-five per cent of lime. I then subject them to the action of the electric current in a furnace, such as that shown in the accompanying drawing, which is a vertical section, and in which

"A represents an inclosing brick work; B, an internal lining, preferably of carbon, which, though *preferable*, is *not* in all cases *necessary;* C, one of the conducting poles, by preference of broken carbon; D, a removable pole of compacted carbon; E, a tap hole for removing the melted product, if desired; F, adjusting mechanism for raising the carbon pole D; and G an alternating current dynamo, which may, therefore, be made commutatorless.

"In starting this furnace, the carbon pole D and the conducting bodies C are connected to the poles of an alternating current dynamo having a mean potential, say, of fifty-five volts, and sufficient amperage to produce the amount of material required, having regard to the size of the furnace. Using, *for instance*, a pole having eight inches on the side, an amperage of about fifteen hundred is desirable. Under these conditions, by reason of the alternation of the current, a feeding in of the mingled lime and carbon between the poles is effected to an extent which does not occur when a direct current is used. Furthermore, it has been generally understood that the production of calcium carbide was due to an electrolytic action and not due to a smelting action. I have demonstrated that the action is purely a smelting action, under the conditions of the process here described. Furthermore, that the block of molten calcium carbide which forms beneath the elevating pole is itself a good conductor of electricity and can be built up from the bottom to any desired height without preventing the operation of the process. A height, *for instance*, of two or more feet is entirely practicable in the apparatus above described. *If preferred*, of course, the fused calcium carbide may be tapped out as the same is formed, in the ordinary way, as applied to iron and steel. The liquid calcium carbide thus produced, when allowed to cool, crystallizes into the form above described, and when broken exhibits the iridescent surfaces above named. By this process, likewise, the yield of calcium carbide per electric horse power is almost doubled over a process of using a direct current, which is, evidently, a matter of the utmost importance, while, at the same time, the process proceeds uniformly and without break, by reason of the substantial uniform feeding in of the material.

"*It is essential*, in order to produce the new material here described, to have the lime and coke very finely divided. This is done by a powdering machine, and then the powdered lime and coke are thoroughly mingled by a grinder or mixer so as to bring these bodies into most intimate contact. The action of the alternating current is likewise essentially different from that of a direct current, producing a series of explosions, the effect of which seems to be to feed the pulverized material into the arc. This is very important in accomplishing a rapid and uniform conversion.

"What I claim as my invention, and desire to secure by Letters Patent, is

"As a new product, crystalline calcium carbide existing as masses of aggregated crystals, substantially as described."

It will be noted that the patentee sets forth in the order given: (1) the object of his invention; (2) the prior art; (3) the properties of his new product; (4) a general outline of his manner of producing his product; (5) the essentials of his process; and (6) his claim.

The use of the words "preferable," "necessary" and "for instance" should be noted as implying what is and what is not essential and what is purely illustrative.

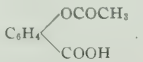
The distinctive property of the product over the art, *viz.*, "crystalline" as contrasted with "amorphous," is the basis of the claim. The property of "having a bluish or purplish iridescence" is incidental rather than essential and is therefore omitted in the claim.

It will be noted that the word "crystalline" in the first paragraph had better been omitted—the invention related to a new form of calcium carbide, not of *crystalline* calcium carbide. "Crystalline" calcium carbide was what was new, and there was no previous form of "crystalline" calcium carbide.

(*b*) THE "ASPIRIN" PATENT[1]

This patent describes the making of a compound having certain properties which distinguish it from the prior art.

"In the *Annalen der Chemie und Pharmacie*, Vol. 150, pages 11 and 12, Kraut has described that he obtained by the action of acetyl chlorid on salicylic acid a body which he thought to be acetyl salicylic acid. I have now found that on heating salicylic acid with acetic anhydride a body is obtained, the properties of which are perfectly different from those of the body described by Kraut. According to my researches the body obtained by means of my new process is undoubtedly the real acetyl salicylic acid,



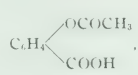
Therefore the compound described by Kraut cannot be the real acetyl salicylic acid, but is another compound. In the following I point out specifically the principal differences between my new compound and the body described by Kraut.

"If the Kraut product is boiled even for a long while with water (according to Kraut's statement), acetic acid is not produced, while my new body when boiled with water is readily split up, acetic and salicylic acid being produced. The watery solution of the Kraut body shows the same behavior on the addition of a small quantity of ferric chlorid as a watery solution of salicylic acid when mixed with a small quantity of ferric chlorid—that is to say, it assumes a violet color. On the contrary, a watery solution of my new body when mixed with ferric chlorid does not assume a violet color. If a melted test portion of the Kraut body is allowed to cool, it begins to solidify (according to Kraut's statement) at from 118° to 118.5° Centigrade, while a melted test portion of my product solidifies at about 70° Centigrade. The melting points of the two compounds cannot be compared, because Kraut does not give the melting point of his compound. It follows from these details that the two compounds are absolutely different.

"In producing my new compound I can proceed as follows:

[1] Kuehmsted *vs.* Farbenfabriken, 179 F. R., 701.

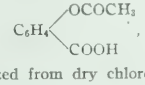
(without limiting myself to the particulars given): A mixture prepared from fifty parts of salicylic acid and seventy-five parts of acetic anhydride is heated for about two hours at about 150° Centigrade in a vessel provided with a reflux condenser. Thus a clear liquid is obtained, from which on cooling a crystalline mass is separated, which is the acetyl salicylic acid. It is freed from the acetic anhydride by pressing and then recrystallized from dry chloroform. The acid is thus obtained in the shape of glittering white needles melting at about 135° Centigrade, which are easily soluble in benzene, alcohol, glacial acetic acid, and chloroform, but difficultly soluble in cold water. It has the formula



and exhibits therapeutical properties.

"Having now described my invention and in what manner the same is to be performed, what I claim as new, and desire to secure by Letters Patent, is

"As a new article of manufacture the acetyl salicylic acid having the formula



being when crystallized from dry chloroform in the shape of white glittering needles, easily soluble in benzene, alcohol and glacial acetic acid, difficultly soluble in cold water, being split by hot water into acetic acid and salicylic acid, melting at about 135° Centigrade, substantially as hereinbefore described."

The patentee sets forth the nearest prior art product and compares its properties with the properties of his new product, showing that the two compounds are different. He then describes the process by which he prepares his new product and sets forth the characteristic properties of his new product including the structural formula.

The claim describes the product by the use of its structural formula and by a statement of characteristic properties. The enumeration of characteristic properties in the claim should be especially noted as a good form for such a claim.

### (c) THE "ADRENALIN" PATENT

This patent relates to a substance consisting of the blood-pressure-raising principle isolated from the suprarenal glands chemically combined with a nonsuprarenal substance whereby the stability of a water solution of said principle is maintained.

It is cited because it contains a *Disclaimer* "to so much of claims 3 and 4 as cover the benzoylated compounds."

Claims 3 and 4 read as follows:

"3—As a new article of manufacture, a substance having the properties of the hemostatic, astringent and blood-pressure-raising principle of the suprarenal glands substantially free from non-blood-pressure-raising constituents thereof, which is soluble in water and the water solution of which is practically inert to the oxygen of the air and gives a green coloration with ferric chlorid and a red coloration with iodin.

"4—As a new article of manufacture a compound of the crystallizable blood-pressure-raising constituent of the suprarenal glands substantially free from the non-crystallizable constituents thereof which is soluble in water and which when in water solution is practically inert to the oxygen of the air and gives a green coloration with ferric chlorid and a red coloration with iodin."

The law provides that whenever, through inadvertence, accident or mistake, and without any fraudulent or deceptive intention, a patentee has claimed as his invention or discovery more than he had a right to claim as new "he may make disclaimer of such part of the thing patented and thereby render valid the part which is truly and justly his own."

In a case concerning this adrenalin patent[1] one of the references related to a certain monobenzoylated salt physiologically active comparably with adrenalin. This was the salt of a base constituted in part by the atoms which together make up the active principle of adrenalin and for the remainder by a benzoyl radical. The Court found that Takamine was therefore not the first to broadly discover a stable and pure salt having the physiological activity of the suprarenal gland and held claims 3 and 4 to be anticipated on the broad construction. Hence Takamine disclaimed the broad construction as we have seen thus in so far validating the claims held to be invalid.

[1] Parke-Davis & Co. *vs.* Mulford, 189 F. R., 95; 196 F. R., 496.

### (d) TAUB PATENT NO. 977,053

This describes the making of and claims by its characteristic properties the amid of beta-beta-diethylpropionic acid. The specification sets forth succinctly the process and the properties of the resulting product, giving the equations according to which the reaction proceeds. It is a good example of a well-drawn specification.

The salient features of the specification read as follows:

"The new product is a crystalline compound soluble in hot alcohol and hot benzene. When reacted upon by hot alkalies it is split up into the beta-beta-diethylpropionic acid and ammonia.

"In carrying out my process practically I can proceed as follows (the parts being by weight): 390 parts of beta-beta-diethylpropionic acid are heated to 100° C. with 140 parts of $PCl_5$, the product of the reaction is separated from the phosphoric acid by decanting of the formed acid chlorid and the chlorid is distilled *in vacuo*. The chlorid of beta-beta-diethylpropionic acid is then treated with an excess of ammonia, the amid is filtered off and crystallized from benzene."

Another reason for referring to this patent is that it contains the statement:

"The present application is a division of my application serial No. 523,805, filed October 21, 1909," *i. e.*, an earlier application.

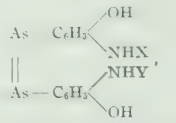
If several inventions claimed in a single application are of such nature that a single patent may not be issued to cover them, two or more separate inventions not being claimable in one application, the inventor is required to limit himself to whichever invention he elects, the other inventions being made the subject of *divisional* applications. He must file a new separate application for each division but the filing date of the original or parent application is taken as the filing date of the division.

### (e), (f) KORNDÖRFER PATENT NO. 1,053,300

This patent relates to improvements in derivatives of diaminodioxyarsenobenzene and is referred to, first, because of the form of the claims, and second, because it has been reissued.

When the original patent is inoperative or invalid by reason of a defective or insufficient specification, or by reason of the patentee claiming as his invention or discovery more than he had a right to claim as new, provided the error arose through inadvertence, accident, or mistake, and without any fraudulent or deceptive intention, the patent may be surrendered and a "reissue" granted in its place to run for the remainder of the life of the original patent.

In this case the original patent stated that the general formula of the compound was



wherein "X" and "Y" stand for "the residue known as methylene-sulfinic acid (—$CH_2SO_2H$) and "X" may be replaced by hydrogen, whereas the Reissue states that either "X" or "Y" may be replaced by hydrogen.

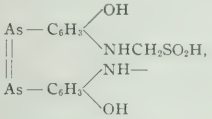
In accordance with the original statement the claims of the

original patent covered the acid *per se* and the acid radical in but one form while in the Reissue (No. 13,848) the claims cover the acid radical in two forms and the sodium salt specifically.

A comparison of claim 2 of the original with claim 2 of the Reissue will indicate the line of difference, a different form of the radical being claimed in each case.

Claim 2 of the original reads:

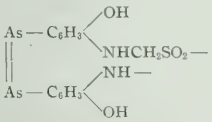
"2—As new products, the derivatives of diaminodioxyarsenobenzene, the radicals of which have the general formula



said derivatives being yellowish powders, difficultly soluble in water, insoluble in alcohol, ether and acetone, dissolving in alkalies with formation of salts, these alkali-salts being yellowish powders readily soluble in water."

Claim 2 of the Reissue reads:

"2—As new products, the derivatives of diaminodioxyarsenobenzene, the radicals of which have the general formula



the acid derivatives being yellowish powders, difficultly soluble in water, insoluble in alcohol, ether and acetone, dissolving in alkalies with formation of salts, these alkali salts being yellowish powders readily soluble in water."

It will be noted that, besides the change in the radical, the word "acid" is inserted before "derivatives" in the Reissue claim. The error of statement in the original was thus corrected and the damage repaired.

The rules for drawing up a specification and claims for a process patent do not differ materially from those heretofore given when considering product patents. The apparatus used is nearly always capable of illustration by drawings, either diagrammatic or of the actual apparatus.

I shall call your attention to but two process patents.

### (*g*) THE CASTNER PATENT

This patent (No. 452,030 of May 12, 1891) is for a process of manufacturing sodium and potassium from caustic soda or potassa without distillation by treating the caustic alkali, while constantly maintained at a temperature of not more than 20° C. above its melting point, to the action of the electric current.

The specification is illustrated with a drawing showing in section an electric furnace or cell suitable for the process. The specification first sets forth the prior art, the reasons for the commercial failure of the processes of the prior art and outlines the process of the patent and the reasons for its commercial success. The particular feature accented is that the processes of the prior art were not and had never been proved to be commercially practicable while the process of the patent possessed this characteristic. The subsequent commercial success of the Castner process proved that these assertions were well founded. The law recognizes a patentable difference between a laboratory experiment not capable of commercial utilization or a bare statement of a scientific fact and a commercially successful process. It is clear that the latter would require more than the average expected skill of one skilled in the art in order to bring it into being, even starting from the previous disclosures.

Having set forth the foregoing statements the specification then describes the process, with reference to the drawing, setting forth a practical means of practicing the process, even giving specific directions as to size and as to the amount of current required in a typical apparatus.

It is unusual in a patent drawing to have it drawn to scale but when it is done and the process described as having been actually carried out, the argument of inoperativeness cannot be made against it. This was particularly valuable in a case like the present where the argument as to patentability rested on the commercial inoperativeness of the prior art.

The frequent use, throughout the specification, of such words as "preferably," "suitable," "as described," and "conveniently" indicates that the matter set forth is subject to variation and is not essential to the invention in the form described. These words are in sharp contrast to the feature which is said to be "necessary," *viz.*, the limit of temperature which should not be exceeded.

The specification concludes with the statement that "I do not of course confine myself to the particular form of apparatus shown, but simply describe it as one of the forms which may be employed," thus bringing out the fact that his descriptive statement is illustrative only and not limiting.

The claims are but two in number, illustrating that a great number of claims is not always necessary to adequately protect an invention. The claims read as folllows:

"1—The hereinbefore-described process of manufacturing the alkaline metals, which consists in treating the caustic alkali while constantly maintained at a temperature of not more than 20° Centigrade above its melting point to the action of the electric current, substantially as described.

"2—In an apparatus for the manufacture of alkaline metals, the combination, with positive and negative electrodes, of the gauze or screen interposed between said electrodes and a superposed vessel or dome for collecting the separated metal, substantially as set forth."

### (*h*) THE HALL PATENT

This patent (No. 400,766, April 2, 1889) is the basic patent which led to the present electrolytic production of aluminum: to that wonderful commercial success which reduced the price of aluminum from $12 a pound to 19 cents and which was instrumental in building up a business from practically nothing to a production of 160,000,000 pounds a year, giving employment to 45,000 men in its various branches and involving an invested capital of $175,000,000. Of course this was not all due to this particular patent but this patent was the root of the industry.

I have chosen this patent to illustrate Patent Office procedure and the history of a Patent through the Courts.

Hall made his first button of aluminum according to this process on February 23, 1886, less than a year after he was graduated from Oberlin College and when he was but two months and a half past 22 years of age. He filed his patent application July 9, 1886.

When an application is filed in the Patent Office it is given a Serial No. and a date of filing. Hall's application received the application serial No. 207,601. The Patent Office, for the examination of applications, is divided into 43 divisions. Those relating primarily to applications for chemical products and processes are Division 2, Medicines; Division 3, Electrochemistry-Metallurgy; Division 6, Bleaching and Dyeing; Chemicals; Explosives; Fertilizers; Liquid Coating Compositions; Plastic Compositions; Preserving; Sugar and Salt; Substance Preparation; and Division 31, Alcohol; Ammonia, Water and Wood Distillation; Mineral Oils; Oils, Fats and Glue, etc. The Hall application would fall into and be assigned for examination to Division 3, Electrochemistry-Metallurgy, where it would be filed to await its turn for examination, the applications coming up *seriatim* in order of date of filing.

The prior art U. S. patents are all classified into classes and sub-classes, the patents of each sub-class being kept in separate compartments so that they may be readily inspected in the course of a search. As the issued U. S. patents now number upwards of 1,125,000 the search is a formidable affair in any conspicuous art. In addition to the U. S. patents, the Examiners of each Division have a classified, and more or less complete, set of certain foreign patents, generally only the English, French and German as well as a rather incomplete reference list to literature other than patent publications. With the present equipment of the Patent Office it is practically impossible, both from the standpoint of the references at hand, and from the standpoint of time and men to make the searches, to make a complete and final search in any art. The wonder is that the hard-working and hard-worked officials of the Patent Office do as well as they do

When the application comes up for examination, if correct as to form, a search is made and the applicant (or his attorney) is informed by mail of the result. This result is almost invariably a rejection of some or all of the claims on the references named and it is then the duty of the applicant to amend his application and to distinguish, if he can, his invention from what is shown in the references cited. This procedure goes back and forth until either the application based on the amended claims is allowed or finally rejected as being unpatentable. If finally rejected by the Primary Examiner an appeal may be taken to the Board of Examiners-in-Chief; from them to the Commissioner of Patents and from him to the Court of Appeals of the District of Columbia. After this a still further appeal lies to the U. S. District Court with an appeal from it to the U. S. Circuit Court of Appeals.

Hall, in his original application, set forth his invention, generically as follows:

"My invention consists in a process and apparatus for the reduction of aluminum by electrolysis from alumina dissolved in melted anhydrous salts or compounds; and the means employed are:

"*First*, suitable solvents for alumina in the form of chemical compounds and combinations which fuse at a moderate heat and, when melted, dissolve alumina so as to bring it into a liquid or dissolved condition which will admit of electrolysis.

"*Second*, suitable crucibles and receptacles for containing the solvents and dissolved alumina at a melting temperature; and

"*Third*, suitable electrodes or poles for the purpose of transmitting electricity through the fused and liquid mass in order to reduce from alumina the metal aluminum."

He then describes his solvent, stating the proportions of fluorides of aluminum actually used by him and that cryolite possesses the qualities desired, describing how he proceeds to melt the solvent, dissolve the alumina therein and reduce the aluminum therefrom.

The manner in which the invention may be carried out is described by reference to a drawing, particular attention being paid to the construction of the crucibles and of the electrodes.

As to the prior art he says:

"I am aware that aluminum has been produced by the electrolysis of fused masses containing the chloride of aluminum or other haloid compounds of that metal; and I am aware that in these operations it is alleged that rods or plates made of alumina and carbon have been introduced into the crucibles so as to be acted on by the evolved chlorine or other gas and thereby regenerate the chloride or other corresponding compound so as to produce aluminum from alumina indirectly.

"But my device differs from the above mentioned in that melted solvents are employed to dissolve alumina, and that alumina is added in a condition to be readily dissolved by and in the melted mass, and being dissolved is acted upon and decomposed in solution by electricity; and thus aluminum is reduced or liberated from alumina dissolved in melted anhydrous compounds or salts. .... I believe that I am the first to produce aluminum from solutions of alumina dissolved in melted anhydrous compounds or salts."

The original application contained 16 claims of which 1–10 inclusive were directed to the process and 11–16 to the apparatus. The issued patent contains but three claims, all relating to the process, the first claiming a bath of "fluorides of aluminum and a metal more electro-positive than aluminum" without reference to the anode; the second being restricted to the fluoride of sodium as the metal more electro-positive than aluminum and to a carbonaceous anode, and the third like the second excepting that the fluoride of lithium is added to that of aluminum and sodium.

Let us put ourselves in the mental attitude of Hall at the time of filing his application. He had dreamed about and worked upon the problem of how to produce aluminum cheaply even when he was a boy in the high school and all through his college course he had kept this goal in sight. Now after all these years and all his work, in the enthusiasm of youth, he had reached his goal. He believed himself to be the first to reach the goal, the first, as he says in his application "to produce aluminum from solutions of alumina dissolved in melted anhydrous compounds or salts" so that the alumina may be decomposed electrolytically.

What a shock he must have had when he received the first action from the Patent Office on October 28, 1886, after nearly four months of impatient waiting, stating that all his process claims seemed to be anticipated by a French patent—that to Héroult, for electrolyzing a solution of alumina in molten cryolite, the very thing which he had done specifically, and that all his claims for apparatus were likewise anticipated upon various cited U. S., English and French patents.

It was furthermore stated that the apparatus claims should be divided out and submitted in a new application and that the process claims 2–9 set forth such modifications of the generic process that they were inadmissible in the case, which should comprise but the broad generic process and one specific modification.

But it was not as bad as first sight would make it seem. In the first place the Héroult French patent was dated April 23, 1886, and we have seen that the disclosure in a foreign patent is not to be considered unless the subject matter is patented prior to the making of the invention in question or more than two years prior to the filing of the U. S. application for patent. Now the Héroult patent was dated less than three months prior to the filing of Hall's application and we have seen that Hall made his first button of aluminum according to his invention on February 23, 1886, just two months before the issue of the French patent.

Accordingly Hall took advantage of this rule of law and, as prescribed by the Rules of Practice of the Patent Office, filed an affidavit setting forth, among other formal requirements, that he had completed his invention in the United States before the date of the French patent. This disposed of Héroult for the time being.

He then amended his application by striking out all of his original claims and substituting 9 new claims in place of the original 16, 4 of the new claims relating to the process and 5 to the apparatus, the requirement for division as to the apparatus claims having in the meantime been taken up to the Commissioner of Patents on appeal and the Examiner's holding on the point reversed.

To this amendment the Examiner replied:

"The claims presented in this application are objectionable, being so broad as to include subject matter substantially different from that described in the specification. Rule 37 requires

the claims to set forth specifically the actual improvement described.

"Applicant's invention consists in fusing a compound composed of the fluorides of aluminum and sodium, with or without the fluoride of lithium, adding alumina to the same, and passing a current of electricity through the fused mass, and the claims should be restricted accordingly. With reference to the apparatus claims, it is denied that there is any combination between the vessel and its contents. These claims are held to be mere aggregations of well-known apparatus. Claim 7 is objected to, as alternative in form, and, as presented, covers merely an oxidized copper plate. If applicant desires to cover the use of copper anodes in the process described, he should present a claim giving the steps of the process above quoted, specifying the use of copper anodes therein."

The new apparatus claims were further objected to as being informal. For example, new claim 5 reads as follows:

"In apparatus for the reduction of aluminum by electrolysis, the combination of a metal receptacle lined with carbon, a solution of alumina dissolved in a melted anhydrous salt or compound contained in said receptacle, and means for passing a current of electricity through the said solution, substantially as and for the purpose described."

Concerning these claims the Examiner said "The clauses in the various apparatus claims describing the process are thought to be unnecessary and should be cancelled. The various parts of the apparatus should not be described by their functions in the process, but by their construction and relation to the other parts of the apparatus."

New claim 7 objected to as being alternative in form and, as presented, covering merely an oxidized plate, which was not patentable read as follows:

"In apparatus for the reduction of metals by electrolysis, an anode of copper or its equivalent coated with oxide or its equivalent which at a red heat protects the underlying metal and transmits an electric current, substantially as described."

To this latter Hall made reply:

"The Examiner says that my 7th claim as amended February 2, 1887, covers only an oxidized copper plate. I would like to know what he means and what he wishes. An *anode* composed of an oxidized copper plate is new. An oxidized copper plate is old. It cannot be used in aqueous solution as the copper oxide is an insulator at ordinary temperature. Such an anode is an anode only when used as such and at a red heat, or the temperature of the melted compound."

And to this the Examiner rejoined:

"The Examiner means just what was said, that the 7th claim is alternative in form, and, as presented, covers merely an oxidized plate. Applicant admits that an oxidized copper plate is not, *per se*, new, and accordingly not patentable. The mere statement that it is used in an apparatus for electrolyzing aluminum does not add any new feature which invests it with patentable novelty. As stated, it must be claimed as one element of a combination, which as a combination, is new and patentable. The claim as drawn appears to be an attempt to cover any metal plate which becomes covered with oxide, and can be used as an electrode at the temperature employed, which is more than the applicant is fairly entitled to."

Hall responded to this by again cancelling his claims, submitting 14 claims in place of the 9 cancelled, of which 14 claims 1, 2 and 3 were broadly for the process; claims 4 to 7 were an attempt to protect his oxidized copper anode; claim 8 an attempt to protect a carbon-lined metal receptacle as a cathode and claims 9–14 for the apparatus.

In the 18th communication between the applicant and the Patent Office, dated April 9, 1887, the Examiner replies to this last amendment of Hall's as follows:

"Applicant's apparatus consists of an anode of oxidized copper, and a carbon-lined iron crucible used as a cathode, with means for heating the same. The applicant admits that the oxidized copper plate is not *per se* new, the iron carbon lined vessel is old, the carbon cathode is old and the apparatus is held to be a mere aggregation anticipated by the references of record. .... There seems to be an unnecessary multiplicity of claims. The apparatus claims are informal. The words 'with or without lithium' make the claims in which they appear alternative. Claims 4, 5, 6, 7 and 8 cover the 'use' of various parts of the apparatus, which use is not patentable. .... The claims describing an 'anode of oxidizable metal coated with a protecting compound, which at red heat transmits an electric current' are functional ..... Claims 11, 12 and 13 which introduce the solution as one element of the combination are improper. There seems to be no combination between the vessel and its contents."

To this Hall replied again, for a third time cancelling all of his claims, this time submitting eight claims instead of the fourteen cancelled, of which eight claims 1–3 related to the process and claims 4–8 to the apparatus.

He does not seem to have changed his process claims much during his various amendments and substitutions but to have directed his efforts mostly towards the apparatus. One cannot but wonder whether, at this stage of the proceedings, he did not regard the apparatus claims as the more important. We have seen that the various parts of his apparatus were all old and that the essence of his invention consisted in fusing a compound composed of the fluorides of aluminum and of a metal more electropositive than aluminum, dissolving alumina therein and passing an electric current through the fused mass. It may be that at this point of time Hall himself did not appreciate that the process, regardless of the form of apparatus used, was the broad and valuable invention.

However that may be, the Patent Office again rejected all the apparatus claims and the patent finally issued without any such. One of the peculiar things about the case is that although Hall made such a fight over his oxidized copper anodes, when his claims were finally formulated, the only ones referring to anodes were for carbonaceous anodes, no written explanation appearing in the file for the sudden change. This point was afterwards brought up in the litigation over this patent.

The claims as finally issued read as follows:

"1—As an improvement in the art of manufacturing aluminum, the herein-described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum and a metal more electro-positive than aluminum, and then passing an electric current through the fused mass, substantially as set forth.

"2—As an improvement in the art of manufacturing aluminum, the herein-described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum and sodium, and then passing an electric current, by means of a carbonaceous anode, through the fused mass, substantially as set forth.

"3—As an improvement in the art of manufacturing aluminum, the herein-described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum, sodium, and lithium, and then passing an electric current, by means of a carbonaceous anode, through the fused mass, substantially as set forth."

About the time of the last above-referred-to action by the Patent Office, an interference was declared between the application of Hall and one which had been filed by Héroult, the patentee of the French patent which we have seen Hall had overcome by affidavit in the first instance.

An interference is a proceeding instituted by the Patent Office for the purpose of determining the question of priority of invention between two or more parties claiming substantially the same patentable invention. The Patent Office first formulates

a "declaration of interference" setting forth and defining the issue in interference; the parties are then each required to file an affidavit or "preliminary statement" setting forth the date of conception, disclosure and reduction to practice, if any, of the invention. If the invention has not been actually reduced to practice, the date of filing the application is taken as the date of constructive reduction to practice. The parties then take their testimony to support their respective cases, the limits of time within which the testimony of each is to be taken, being fixed by the Patent Office, but the exact time within such limits and the place of taking the testimony being fixed by the party himself upon due notice to his adversary who is entitled to attend and cross-examine the witnesses produced. The testimony is generally taken by question and answer upon a typewriting machine or stenographically, before a Notary Public, who swears the witnesses.

The testimony of each is then printed and the case argued orally upon printed briefs before the Examiner of Interferences, who sits as a Judge in such cases. From his decision there is an appeal to the Board of Examiners-in-Chief, a tribunal of three members; from them an appeal lies to the Commissioner of Patents; from him to the Court of Appeals of the District of Columbia. If the litigant is still unsatisfied he can bring the case up afresh in the District Court of the United States whence an appeal lies to the United States Circuit Court of Appeals.

But Hall did not have to go through with all this because his interference was with one who had made his invention abroad and in such case, in the absence of a printed publication issued prior to the date of the U. S. invention or more than two years prior to the filing of the application therefor, the only thing that counts is, when was the foreign invention introduced into this country. And as the date of Héroult's application was later than February 23, 1886, the date of Hall's actual reduction to practice, the interference was decided in Hall's favor.

After this Hall once again cancelled his specification and claims and submitted new ones, the patent finally issuing with the claims as above quoted.

Altogether there were over 30 communications between the inventor and the Patent Office. Neither the final specification nor the claims bear any resemblance to the original specification and claims. Yet the germ of a great invention was present at the beginning and the final form, as we shall see later, gave adequate protection when the patent came before the Courts.

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## PROXIMATE ANALYSIS OF NITROCELLULOSE SOLUTIONS AND SOLVENTS[1]

By A. D CONLEY

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The purpose of this article is to give a few rapid approximate methods which the writer has found useful in the analysis of commercial nitrocellulose solutions. They are intended for use in laboratories where apparatus is limited. No claims for originality are made.

### CONSTITUENTS OF NITROCELLULOSE SOLUTIONS

Although many nitrocellulose solvents are known, comparatively few of them find commercial use. These are mostly the ketones and acetates of the methyl, ethyl, propyl, butyl, and amyl groups. The commercial solvents are mixtures of two or more of the above compounds and include: amyl acetate, ethyl acetate, acetone, wood alcohol, ethyl methyl ketone, and light acetone oil. Amyl acetate, the best all-round solvent, is high in price, and for this and other reasons, non-solvents are nearly always used in connection with the solvents. The most important of these are fusel oil, denatured alcohol, benzol and toluol, and petroleum benzine. Some of these materials will be found in practically every nitrocellulose solution, and in individual cases there may be found some of the amyl acetate substitutes, or some material intended to mask the odor, or perhaps some material designed to raise the flash point. In the pure state all the material may be readily identified by the ordinary methods of organic analysis, but mixtures of impure commercial materials with nitrocellulose offer considerable difficulty if a quantitative analysis is necessary.

### USES OF NITROCELLULOSE SOLUTIONS

LEATHER FINISHING—C. A. Higgins[1] and Thomas Callan[2] have discussed the use of nitrocellulose solutions in leather finishing.

METAL LACQUERS—For objects where there is little need of handling, or where only a temporary protective coating is desired, nitrocellulose solutions make a very satisfactory lacquer. They are easily and rapidly applied, they may be air-dried, or if speed is desirable, oven-dried at almost any temperature below 100° C. This does away the baking necessary with japans or with some of the synthetic resin lacquers, such as Bakelite. Ordinarily a nitrocellulose film will not stand washing with water to any extent and this renders it unsuitable for many purposes.

Lacquers may be classified: by the surface for which they are designed, as brass or silver lacquers; by the method by which they are applied, as brush, dip, or spray lacquers; or by the surface which they produce, as matt, satin, or glossy lacquers. Brush lacquers are usually the highest in total solids and in resin content. The same lacquer will often serve both as a dip or a spray lacquer. In the latter case the lacquer is blown on the work in the form of a fine spray by the use of a jet of compressed air in a suitable apparatus.

Resin lacquers, sometimes called gum lacquers, are thus defined by Worden.[3] "Resin lacquers are solutions of gum resins or resins in fusel oil and pyroxylin solvents without linseed or other drying oil and hence are not varnishes." Many of the same solvents are found here as in nitrocellulose solutions.

### DETERMINATION OF NITROCELLULOSE

Worden[4] suggests precipitating the nitrocellulose with fusel oil but this method was not found satisfactory as it does not give a complete precipitation.

Benzine, carbon tetrachloride, chloroform, and water all precipitate nitrocellulose. Water and benzine are less satisfactory because they precipitate the resins as well. Chloroform is convenient because it does not precipitate many of the resins and is also easily removed from the precipitated nitrocellulose by drying at moderate heats.

A simple way is to take a 200 cc. stoppered graduated cylinder and place in the neck a small funnel, capable of holding the desired amount. The funnel can be quickly removed when the solution has reached the mark without danger of spilling any of the solution on the sides of the cylinder. The chloroform should be added in small amounts with vigorous shaking. It will be necessary to thin very heavy solutions and to use the diluted solution for this determination. Since the amount of nitrocellulose is usually stated in terms of ounces per gallon, it is convenient to take 10 cc. when

$$\text{ounces per gallon} = \frac{\text{weight precipitate in grams} \times 378.5}{28.35}.$$

This amount usually gives a precipitate convenient to handle. When nitrocellulose is dissolved there is an increase in volume, so that the result obtained is the amount actually present in a gallon and not the amount that must be added to a gallon of

[1] Abstract of thesis presented at University of Maine in part fulfilment of requirements for degree of Chemical Engineer, June, 1914.

[1] "The Uses of Collodion in Leather Finishing," C. A. Higgins, *Leather Trades Year Book*, **1914**, pages 148–151; *J. Soc. Chem. Ind.*, **33**, 704.

[2] "The Constitution of Collodion Enamels for Leather," Thomas Callan, *Leather World*, **4**, 523.

[3] "Nitrocellulose Industry," Vol. I, p. 305, D. Van Nostrand Co., 1911.

[4] *Ibid.*, Vol. I, p. 358.

solvent in order to obtain that concentration. When 4 ounces are added to a gallon of solvent the increase is about 2 per cent of the volume; when 8 ounces, about 3.5 per cent; when 12 ounces, about 5 per cent; when 16 ounces about 6.6 per cent.

If no resins are present it is necessary only to filter, using suction, and weigh this precipitate. The wet precipitate is very voluminous and the amount that may adhere to the sides of the cylinder is not so serious as would appear at first glance. Since the precipitate is likely to stick to the filter paper on drying it is best to remove it to a watch glass. The precipitate is inflammable when dry and hence may not be dried over a flame. It may be heated, however, in almost any oven without risk of ignition.

If only a few ounces of gum are present to each gallon of solution practically none of the gums will be precipitated. With large amounts, however, the precipitate will be contaminated with and usually colored by resin. In this case decant the liquid, redissolve the precipitate in the smallest possible amount of solvent, and again precipitate. If the resin-containing precipitate is allowed to dry before redissolving, the difficulty of separation is greatly increased. The resins may often be held in solution by adding 10 cc. of fusel oil to the 10 cc. of the solution taken before adding the precipitating agent. But this is to be done only when necessary, as where little nitrocellulose is present it would hinder the precipitation of the nitrocellulose.

### DETERMINATION OF RESINS AND OILS

The resins are obtained by the evaporation of all or a part of the filtrate from the nitrocellulose determination. If more than a few ounces are present it is necessary to evaporate only a portion. Just enough to form a thin film of residue must be taken as a thick film will form a skin on the surface and prevent complete drying. The odor during evaporation will indicate the presence of camphor (usually introduced by the use of scrap celluloid in place of nitrocellulose) and the character of the film will tell if it be oil or resin. Castor oil is sometimes found and is distinguished by its well known insolubility in benzine. Oil may also be determined by making a thick film of the solution on a glass plate, and when it is dry stripping and burning. There will be left an oily residue and the burning will usually be accompanied by smoke. The chloroform itself will often leave a visible residue but of negligible weight.

It seems to be practically impossible to identify the resins. The amount obtained is so small that no very extensive tests can be carried on and moreover the resins are often decomposed during the process of separation. It is no uncommon thing for a residue to be insoluble in its original solvent. Hicks[1] gives some color reactions based on Halphen's Reagent for Colophony, and some methods for shellac analysis. Some resins may be eliminated when the solvent is known. For instance, bleached shellac will not work satisfactorily in solutions containing amyl acetate. Others may be too highly colored. Gum benzoin is recognized by its chocolate-like odor. Different grades of the same resin will often work differently and some can be put into solution only by fusion or other special methods. The solubility of bleached shellac is quickly reduced on exposure to summer heat. The solubilities of the various grades of copal vary greatly. Rosin, probably on account of its acid nature, is not suitable for lacquers, but a synthetic product, Ester Gum, which closely resembles it in appearance, is much used. This gum is said to be a glycerine ester: it is soluble in amyl and ethyl acetates, acetone, benzol, chloroform and other solvents. Since nitrocellulose solutions containing fusel oil often acquire a yellow color on standing, the color alone cannot be taken as proof that resins are present.

[1] "New Color Reactions with Some of the Resins with Halphen's Reagent for Colophony," THIS JOURNAL, **3** (1911), 86. "Shellac Analysis and the Detection of Small Amounts of Colophony in Shellac," *8th Intern. Congr. Appl. Chem.*, **12**, 115.

Resins are added to nitrocellulose solutions in the form of solutions since the dry resins would be practicably insoluble. Such resin solutions are usually first clarified by filtration or settling. The solubility of resins in carbon tetrachloride is summarized by Baskerville and Riederer,[1] and in acetone by Worden.[2]

### DETERMINATION OF TOTAL SOLIDS AND OF PIGMENTS

Enamels may contain a pigment. The precipitate is burned, which destroys the nitrocellulose, leaving the pigment. Aniline dyes are frequently used in colored lacquers.

Total solids are determined by evaporating just enough to cover the bottom of a weighing bottle.

### SEPARATION OF THE SOLVENT

To a certain extent some nitrocellulose solutions may be distilled over a direct flame, but as soon as the solution becomes concentrated the nitrocellulose will stick onto the flask and breakage will result. The writer has never had an explosion during distillation and has made a practice of heating the solution to about 120° C. in a paraffine bath and then continuing the distillation with steam (by simply pouring water into a flask and continuing the distillation). This latter part may be done on a direct flame but in the long run fewer flasks will be broken if the paraffine bath be used for the entire operation. Most of the water-soluble material will be distilled below 120°, so that the distillation with water or steam is not inconvenient. The solution may froth when it first begins to boil, but after it is boiling steadily it may be left to itself.

The distillate with water is separated and dried. The separated water is again distilled to recover dissolved solvents. Amyl acetate and fusel oil are nearly entirely insoluble in a saturated solution of potassium carbonate so that by adding potassium carbonate to the water these may be recovered. Calcium chloride is the best drying agent but it is too soluble in fusel oil to be satisfactory. It may be necessary, if much alcohol or ethyl acetate be present, but it will dissolve out much of the alcohol. It is interesting to note the time required for drying. The distillate from a solution containing only amyl acetate and fusel oil will probably be slightly milky and will clear on the addition of a small amount of potassium carbonate and be entirely "dry" with an indefinite volume of benzine in a few minutes. This is the most satisfactory way of drying but if alcohol be present the process is very slow and the calcium chloride may be necessary.

This dried distillate may or may not be mixed with the distillate obtained before the addition of water. Whether or not it is advisable will depend upon the relative amounts and the nature of the solution. But the dried distillate must be distilled to remove dissolved solids and then the specific gravity may be taken. Consideration of gravity and boiling points will often indicate rather clearly just what materials are present. Limiting values will be placed upon the proportion of various materials by their solubility and their price. Hence for many simple solutions the analysis will stop here. But usually it will be necessary to go further and consider each of the possible ingredients.

FUSEL OIL is the mixture of higher alcohols secured along with ethyl alcohol in the fermentation industries. The crude oil, which normally contains 5 to 10 per cent of water, is the starting point in the manufacture of amyl acetates but is not used in the manufacture of nitrocellulose solutions. Foreign crude oils are usually dark colored and are likely to contain considerable residue. Domestic oils are much cleaner in appearance. Boswell and Gooderham[3] have analyzed a sample of

[1] "Chlorides of Carbon as Solvents: I. Carbon Tetrachloride," THIS JOURNAL, **4** (1912), 647.

[2] "Nitrocellulose Industry," Vol. I, p. 165.

[3] THIS JOURNAL, **4** (1912), 667.

Canadian fusel oil from beet molasses and quote LeBel's analysis for fusel oil from corn. .

Refined fusel oil is the crude oil redistilled to remove water, low boiling alcohols, dirt, etc. It has a specific gravity of about 0.814 at 15° C. and distills between 100 and 135°, the bulk of the distillate being between 120 and 130°. It receives its name on account of its oily appearance.

Fusel oil is not a nitrocellulose solvent though it does dissolve it to a very limited extent. This same solvent effect is shown by ethyl alcohol. It may be mixed in equal parts with amyl acetate without injuring its solvent power for ordinary uses but such a solution is more viscous than one in amyl acetate alone. By reason of the slowness of fusel oil to evaporate as well as its oily nature it is of great advantage in metal lacquers because it aids in securing a film free from the distortion produced by too rapid drying and, in the case of a brush lacquer, allows time for the natural flow of the solution to cover the brush marks. Where a film would have a tendency to whiten, a little fusel oil will help to keep it transparent. This is particularly true in the case of amyl acetate-benzine mixtures. Fusel oil is also a good resin solvent and it is frequently convenient to add these in the form of a fusel oil solution. Another advantage of fusel oil is that it enables methyl and ethyl alcohols to unite in any proportion with petroleum benzine. It shares this property with other liquids which are soluble in alcohol but not in water, but has advantages over most if not all of them. Masland[1] has patented the use of chlorinated hydrocarbons, such as chlorolefins, as a substitute for fusel oil for this purpose.

Fusel oil may often be detected by its odor. It has a peculiar irritating action on the throat which causes a desire to cough. By pouring a mixture on a blotter this odor may often be detected after the other ingredients have evaporated.

In solutions which are designed to be diluted the fusel oil might be present in any proportion but in metal lacquers it will almost never exceed 15 per cent. Knowing the uses of it a study of the film will usually show about how much should be added to the solvent mixture. In solutions for leather finishing the amount of fusel oil may be considerably greater.

According to Allen[2] and Worden[3] the amount of fusel oil in amyl acetate can be approximately determined by agitating it with 50 per cent acetic acid. The amyl alcohol is supposed to be soluble. This method the writer has found so very approximate as to be quite useless, as amyl acetate is itself partially soluble in 50 per cent acetic acid and entirely soluble in the glacial acetic acid. Ethyl acetate is entirely miscible with the 50 per cent acid, but the lower boiling fractions of amyl acetate showed no important difference in solubility as compared with the higher boiling ones.

AMYL ACETATE—Amyl acetate is the best general solvent for nitrocellulose known but its cost encourages the addition of the maximum amount of cheaper materials. It is of course composed of the acetic acid esters of the alcohols contained in fusel oils. The specific gravity may vary from 0.865 to 0.875 at 15° C. and is usually about 0.870. Zimmer[4] gives pure amyl acetate as 0.856 and commercial amyl acetate as 0.850 to 0.860 at 20° C. This corresponds to 0.855 to 0.865 at 15° C. and would seem to indicate a less complete esterification in the German product.

The boiling points of amyl acetate vary considerably with different samples but will lie between 100 and 145° with the bulk of the distillate between 120 and 140°.

Saponification is of course the real test. Commercial amyl acetate saponifies 80 to 100 per cent amyl acetate. Some low boiling samples will give considerably higher results. A sample saponifying 89.91 per cent gave the following results upon distillation and the saponification of each fraction:

| Fraction | 90–100° | 100–110° | 110–120° | 120–130° | 130–140° C |
|---|---|---|---|---|---|
| Per cent amyl acetate | 91.1 | 89.3 | 88.1 | 84.8 | 83.4 |

For the determination of the saponification value a 10 per cent alcoholic potash solution has been found satisfactory. Fifty cc. of this solution were used with 10 cc. of the sample and the tests kept at least one hour in boiling water. The mass was then diluted to one liter and 50 cc. titrated. When working in this manner it was repeatedly noticed that a yellow layer was often formed which floated on the top. As this layer was apparently neutral the liter flask was filled so that all of this layer came above the mark. Several known mixtures were saponified both to determine the accuracy of the test and to determine the cause of this yellow layer.

| No. | Per cent Used in Mixtures: Amyl acetate | Fusel oil | Benzine | Benzol | Wood alcohol | Acetone oil | Per cent amyl acetate found |
|---|---|---|---|---|---|---|---|
| 1 | 40 | 10 | 25 | 25 | .. | .. | 36.2 |
| 2 | 40 | 10 | 25 | 25 | .. | .. | 38.0 |
| 3 | 60 | .. | 40 | .. | .. | .. | 51.6 |
| 4 | 50 | .. | .. | .. | 50 | .. | 47.3 |
| 5 | 50 | .. | .. | .. | .. | 50 | .... |

Nos. 1 and 2 were different samples of amyl acetate.

A yellow layer was formed in each case except the last two. The layer was equal to 2 or 3 cc. which is considerably less than the total amount of benzine and benzol present. The results obtained for amyl acetate by the saponification were satisfactory as amyl acetate itself would saponify only 80–100 per cent and the results obtained were in about that proportion to the amount of amyl acetate known to be present.

ETHYL ACETATE—The presence of ethyl acetate in any amount will be noted by the odor and gravity of the proper fractions. The fractions containing the bulk of the ethyl acetate are then separated and saponified in the same manner as for amyl acetate. Methyl acetate is a solvent but is so low boiling and so hydroscopic that it finds little use in lacquers. A product selling under the name of trimethylacetate is said to be a commercial acetone containing 40 per cent of methyl acetate.

ACETONE—Acetone is perhaps the best nitrocellulose solvent known and will sometimes, when added in small amounts, complete a solution which has been only partially effected by other solvents. Its solutions give ragged white films which makes it useless for transparent lacquers. In connection with wood alcohol it is available for mantle dips.[1] An impure acetone having a somewhat yellow color is sold under the name of methyl acetone. Commercial acetone has a gravity of about 0.800 and 80 to 90 per cent distills below 60°. Methyl acetone has a higher gravity and a less constant boiling point. Two samples had the following properties:

| | | | |
|---|---|---|---|
| Specific gravity | | 0.808 | 0.824 |
| Per cent distillate | 56 to 60° C. | 84 | 83 |
| | 60 to 62° C. | 16 | 13 |

The standard method for the determination of the acetone in the wood alcohol used for the denaturing of grain alcohol is as follows: To 1 cc. of a mixture of 10 cc. wood alcohol and 90 cc. water, add 10 cc. of a $2N$ soda solution; then add 50 cc. of $N$ 10 iodine solution with shaking. After three minutes make acid with dilute sulfuric acid. Titrate the excess of iodine with $N/10$ sodium thiosulfate.

If $x$ = grams acetone in 100 cc., $y$ = cc. $N/10$ iodine required, and N = volume of spirit taken for the titration,

$$x = y \times 0.096672/N$$

Allen[5] gives a gravimetric method for carrying out this iodoform reaction. The iodoform reaction occurs also with ethyl alcohol or any other compound having the group $CH_3CO$- in union with O. Another method adapted from that of Deniges[5] consists of heating in a water bath for 10 minutes with a 5 per cent solution of mercuric oxide and sulfuric acid. Acetone gives a white precipitate.

[1] U. S. Patent 1,082,543.

[2] "Commercial Organic Analysis," 3rd Ed., Vol. I, p. 210; 4th Ed., Vol. I, p. 249.

[3] "Nitrocellulose Industry," Vol. I, p. 211.

[4] "Analysis of 'Zapon' and Celluloid Lacquers," *Kunststoffe*, **3**, 323–5.

[1] Welsbach mantles are dipped in nitrocellulose solutions before packing in order to make them less likely to break in shipment.

[2] "Commercial Organic Analysis," 3rd Ed.

[3] *J. Soc. Chem. Ind.*, **1899**.

WOOD ALCOHOL—Wood alcohol is a solvent because of the acetone contained therein. With some samples of wood alcohol it will be found necessary to add 5 to 10 per cent of acetone before a satisfactory solution can be made. Wood alcohol solutions give a dense white film when dried under ordinary conditions, but much smoother than that produced by acetone. It may be distinguished from acetone by the iodoform reaction given above, or in the absence of acetone, from ethyl alcohol, in the same manner. For a qualitative test salicylic acid may be added and heated in acid solution. The characteristic odor of methyl salicylate is evidence of wood alcohol although its absence cannot be taken as absolute proof of the absence of wood alcohol. Many methods are given for the detection of methyl and ethyl alcohols in the presence of each other, but most of them deal with their determination in distilled liquors; some of them are colorimetric, and usually are much too delicate to be of service in the analysis of nitrocellulose solutions. Unless these alcohols are present to the extent of 5 or 10 per cent it is hardly worth while to determine them. Impurities in other materials are almost sure to introduce traces. Wood alcohol is seldom used in lacquers since it gives a white film. Most commercial wood alcohol has been found to have a specific gravity ranging from 0.804 to 0.808 though some samples were as high as 0.812 at 15° C. The bulk of the distillate was between 64° and 66° with the temperature of the last portions going as high as 70° C.

ETHYL METHYL KETONE AND THE ACETONE OILS—Many of the constituents of these acetone oils are described by Worden.[1] Many of these acetone oils have a pronounced yellow or even red color and a disagreeable odor; this it is sometimes possible, but seldom profitable to remove by chemical treatment. The high boiling fractions are poor nitrocellulose solvents and of little use in lacquers. The lower boiling fractions are excellent solvents. Frequently they are sold under some fancy meaningless name.

The heavy acetone oils may boil anywhere between 80° and 200° C. but the light oils, which are the only ones of much importance, will boil about 75 per cent below 100° and not go above 130° C. The specific gravity varies from 0.810 to 0.820 at 15° C. They have the characteristic ketone odor, are about one-third water-soluble, and although some will mix with an indefinite volume of benzine, most become cloudy with 1 to 3 volumes. Some products of an indefinite nature are sometimes found, for instance, one with a boiling point similar to wood alcohol but with a specific gravity of 0.840.

The ethyl methyl ketone of commerce is practically a light acetone oil but is colorless and different lots will run much more constant in composition. It distills mostly between 75 and 90° and has a specific gravity between 0.812 and 0.814. The bulk of the distillate is at about 80°. The solutions give a transparent film.

DENATURED ALCOHOL—Denatured alcohol is not a nitrocellulose solvent but will dissolve it to the extent of one or two per cent. That this is not entirely caused by the presence of the wood alcohol added as a denaturing agent is shown by the fact that pure ethyl alcohol has the same slight solvent effect. Some instances of complete solubility are on record but these may have been due to slight impurities. This is discussed by Schwartz.[2] It is not certain, however, that the material dissolved is really nitrocellulose and not some by-product. It offers an interesting analogy to the solvent effect of acetone diluted with water upon guncotton which has been described by Luck and Cross.[3] Washing nitrocellulose with alcohol probably increases its stability and the material dissolved seems to be different from the nitrocellulose itself. The amount of alcohol in ethyl acetate may be determined by agitation with a calcium chloride solution as described in Allen's "Commercial Organic Analysis"[1] but this method cannot be applied to nitrocellulose solutions as a class. Since acetone is seldom found the iodoform reaction is available for the detection of alcohol.

BENZOL, TOLUOL AND XYLOL—The choice between these non-solvents depends upon the rate of evaporation desired in the solution. The sulfuric acid test referred to under benzine may be used here as well, as the great difference in specific gravity would prevent any confusion of the two. The formation of nitrobenzol with its characteristic odor is sometimes helpful but not conclusive. These two non-solvents are of great value because they can be added in very much larger amounts than can benzine. By careful selection of the nitrocellulose it is possible to make a solution directly in a solvent mixture consisting of 60 per cent benzol and 40 per cent amyl acetate. It is always important to be sure that the nitrocellulose used is suited to any given solvent mixture before concluding that such a mixture is not a solvent. The properties of these materials, as well as their rates of evaporation, have been described by Weiss in his article, "Commercial Benzol in the United States."[2]

BENZINE—Benzine is important because cheap. It is usually a little heavier and higher boiling than automobile gasoline; it boils at about 85 to 140° C. and has a specific gravity of about 0.735.

It is not a nitrocellulose solvent, though it is possible to add an equal volume of benzine to an amyl acetate solution containing a pound of nitrocellulose to the gallon. In more dilute solutions it is sometimes possible to add as much as 65 per cent of benzine. But solutions containing such large proportions as these are of practically no value as the solution would leave a white film on evaporation, would be cloudy, and probably the nitrocellulose would precipitate in a few days or weeks. In all cases it is easier to add benzine to a solution already made if it be stirred in while adding small portions at a time than it is to dissolve the nitrocellulose in the mixture of the solvent and the benzine. Or the solution may be made in a mixture of the solvent and part of the non-solvent and then the remainder of the non-solvent stirred in. In general more benzine may be used with the higher nitrated nitrocelluloses and these may often be distinguished by the longer and stronger fibers. The character of the film will usually limit the amount of benzine before the actual limit of solubility is reached. Benzine can usually be detected in any fraction of the distillate by reason of its insolubility in water and its low specific gravity. It may be detected together with benzol and toluol by its insolubility in concentrated sulfuric acid but this method like most of the other extraction methods is not quantitative. The benzine is supposed to rise to the top and form a colorless layer. This upper layer will contain both the benzine and the benzol but the specific gravity will settle the question as to which is present. This method is very convenient but not very accurate. Zimmer publishes some results in his article, "Analysis of 'Zapon' and Celluloid Lacquers."[3]

This same sulfuric acid test is frequently given for the detection of small amounts of benzine in amyl acetate or fusel oil. It is supposed to be a means of detecting adulteration, but unfortunately a colorless layer is sometimes formed in cases where no benzine has been added. Hence it is not reliable for amounts of only 2 or 3 per cent. The amyl acetate or fusel oil is supposed to be mixed with 1.5 to 2 times its volume of concentrated sulfuric acid, care being taken to avoid heating, and allowed to stand for several hours.

Hammelman[4] states that amyl acetate may be decomposed

[1] "Nitrocellulose Industry," Vol. I, p. 151.

[2] "Solubility of the Nitrocelluloses in Ethyl Alcohol," *Kunststoffe*, **3**, 341–3, 370–2; *Cantschuk and Gutta-Percha*, **12** (1914), 8859–60.

[3] "A Reinvestigation of the Cellulose Nitrates," *J. Soc. Chem. Ind.*, **1900**, "Researches on Cellulose," Cross and Bevan, Vol. I, p. 45.

[1] Third Edition, Vol. I, p. 186.

[2] THIS JOURNAL, **3** (1911), 10.

[3] *Kunststoffe*, **3**, 324.

[4] "Examination of Amyl Acetate," *Farben. Ztg.*, **18**, 2594–5.

by sulfuric acid and that readily polymerizable ethylenes are formed which remain as insoluble residues and give a high value for the benzine and benzol present. Wolff and Rosumoff,[1] while admitting this, claim that if not more than 1.5 volumes of acid are used and the reading taken before a cloudy separation takes place (about 3 hours), the method gives good results and is the best yet devised.

The writer has also obtained this colorless upper layer in an attempt to form amyl sulfuric acid by the action of sulfuric acid upon fusel oil but could not obtain it a second time even with the same fusel oil. The method used is given in Liebig's *Annalen der Chemie*.[2]

DIACETONE ALCOHOL ("ALCO DEO")—This material, which was first described by Hoffman, is well described in U. S. Patents 1,082,424 (A. Hoffman) and 1,075,284 (an apparatus for making diacetone alcohol granted to C. W. Crockett). The material as sold has a gravity of about 910 and distills between 60 and 170° C., about one-half the distillate being between 160 and 170°. Since it is made by the polymerization of acetone with calcium hydroxide, its gravity and boiling point will obviously depend upon the concentration of the diacetone and its freedom from acetone. The writer has secured samples with a specific gravity of 0.930. It is an excellent nitrocellulose solvent and may be mixed with equal volumes of benzol. It will mix in some proportions with benzine but not in all. The odor is mostly due to the contained acetone; it has an oily feel, and the combination of solubility in water, high specific gravity with these will readily suggest its presence. Under continued heating it will revert to acetone but the consideration of the film would show that acetone was not the original constituent. It has some serious disadvantages as compared with amyl acetate and the extent of its use would naturally be limited by the relative prices of amyl acetate. Its film is transparent.

### FLASH POINT

Nearly all nitrocellulose solutions have a flash point below room temperature. A small amount of carbon tetrachloride will raise the flash point greatly but will also make the film turn dark. This is said to be due to the presence of sulfur in the carbon tetrachloride. It is possible that trichlorethylene, known commercially as "tri," might serve a similar purpose.

### ACIDITY OF SOLUTIONS

The acidity is best determined by titration of the water extract. Shake one volume of amyl acetate with 10 volumes of hot *freshly distilled* water, separate and titrate the water layer as soon as sufficiently cool. The writer has found $N/10$ alkali, with phenolphthalein as an indicator most satisfactory for this purpose. In the case of solutions, 10 to 12 grams are shaken with 100 to 150 cc. water and filtered. The material on the filter is then washed twice with about 50 cc. of water. A nitrocellulose solution should not exceed 0.05 per cent acid, calculated as acetic acid, according to some specifications. Since some, if not most of the acid is certainly derived from the nitrocellulose, it cannot all be acetic acid but it has been convenient to calculate it as such. When proper care is taken consistent results may be easily obtained by this method. Care must be taken to secure water as free as possible from $CO_2$, which according to Stein[3] will be that containing the equivalent of 0.09 cc. of $N/10$ alkali for each 100 cc. Stein gives a rather elaborate way for preparing such water. The writer has secured equally good water by condensing high pressure steam. Live steam was first blown through the coil, and then the water distilled hot so that a mixture of steam and boiling water came from the coil. This is a very rapid way. The titration must be made very rapidly as there is enough amyl acetate dissolved in the separated water to be saponified by the alkali, and the first red color must be taken as the end point for this reason. The acidity of the solution increases with age.

VISCOSITY OF THE SOLUTION—No very satisfactory method of determining the viscosity of nitrocellulose solutions has as yet been suggested. Commercial solutions vary from those which are almost water-thin to others which are a thick paste and scarcely flow at all. They vary from those containing one ounce to a gallon of solvent to those which may contain two pounds. Most of the published work on viscosity has been done with very thin solutions so that the methods described have practically no commercial value. Some thin solutions may be tested by the time required to run a given amount through an orifice of known size. The flow must be fairly rapid on account of evaporation and it is extremely important to consider the effect of temperature. A good deal of experimental work would need to be done in order to make this method satisfactory. For ordinary work an ordinary four ounce sample oil bottle may be nearly filled with the solution, and the time required for the bubble to rise when the bottle is inverted may be noted or the sample to be tested may be compared with a standard sample. Care must, of course, be taken to have the bubbles of equal size. Some allowance must be made for a possible change of viscosity with age in a standard sample. Such a change has been mentioned by several observers but no really definite information regarding it has been given. C. Piest[1] claims that a considerable decrease in viscosity of 2 per cent acetone solutions was noticed after long standing. Analysis for total solids showed that this was not due to the settling out of material. He states that this decrease may be due to the contamination of the solution by an ester of oxycellulose formed during nitration, or by the nitration of a highly bleached cotton. The treatment of cotton with oxidizing agents (bleaching) yields alpha and beta oxycellulose, the former insoluble and the latter insoluble in 5 per cent NaOH solution. This beta cellulose, which is evidently an addition product, he considers to be the cause of the lowering in viscosity. This change in viscosity does appear to take place sometimes but not always in samples which the writer has kept. This bottle method for determining viscosity is simple and cheap and perhaps no more unsatisfactory than the more elaborate ones.

The same sample of nitrocellulose will give different viscosities in different solvents. The reason for this is as yet unknown, but in a general way the better the solvent the lower the viscosity. Acetone, wood alcohol, ethyl methyl ketone, and ethyl acetate all give much thinner viscosities than amyl acetate. In general a low boiling amyl acetate gives a slightly thinner viscosity.

But two samples of nitrocellulose that give the same viscosity in wood alcohol do not necessarily give the same viscosity in amyl acetate. A nitrocellulose that forms a thick heavy solution in wood alcohol will nearly always give a much thicker solution in amyl acetate, but it is quite possible to have two samples of nitrocellulose, both having a thin viscosity when dissolved in wood alcohol, one of which will be thin and the other thick when dissolved in amyl acetate. This proves that the boiling point of the solvent is not the factor which determines viscosity even though the lower boiling solvents do appear to be the ones which give the thinnest viscosities. Where a sample is very heavy when dissolved in amyl acetate but very thin in wood alcohol it is evidently a case of very low nitration, and when it is very heavy in both it appears to be a case of high nitration. But the nitrogen content *does not* determine the viscosity.

F. Baker[2] says that the viscosity of cellulose nitrate solutions

[1] "Examination of Amyl Acetates," *Farben Ztg.*, **18**, 2641–2.

[2] L. Pasteur, "Ueber den Amyl Alcohol," *Liebig's Annalen der Chemie*, **96**, 288; Kekulé, "Ueber die Amyloxydschwefelsaure und ihrem Salze," **76**, 275; Cahours, "Ueber das Kartoffelfuselöl und seine Verbindungen," **30**, 291.

[3] "Some Fatty Acid Esters of Hydrocellulose and Their Saponification," A. Stein, *Ztschr. angew. Chem.*, **26** (1887), 91, *Aufsatzteil*, pp. 673–7.

[1] "Cellulose," *Ztschr. angew. Chem.*, **26**, 24–30.

[2] *J. Chem. Soc.*, **103**, 1653–78.

depends to a large extent upon the cellulose from which the nitrate was derived. Oxy- and hydroxycelluloses give nitrates, the solutions of which possess extremely low viscosity. As has been mentioned above, Piest gives the cause of these oxycelluloses as being the nitration of a high bleached cotton. Nishida[1] states that the lower the nitrogen content the higher the oxycellulose and that a dilute nitrating bath is favorable to the formation of beta oxycellulose. This agrees very well with the theory that, within limits, low nitrated products are likely to produce thin viscosities, as does the statement of H. Barthelemy,[2] that "the more highly polymerized the cellulose molecule the higher the viscosity." Continuing, he states, "The viscosity of nitrocellulose is less, the higher the temperature of the nitrating bath, and is greater, the less water in the acids, with a short period of immersion."

T. Chandelon[3] notes that a 5 per cent solution made from cellulose nitrated with an acid containing 20 per cent nitric acid gave a viscosity equal to that of a solution containing 5.74 per cent nitrocellulose made from an acid containing 15 per cent nitric acid. The weaker acid involved a loss of 11 per cent in yield. The character of the cellulose used also affects the viscosity. Noyer[1] says: "Cellulose from different sources, whether in the form of hydro- or oxycelluloses, or the hydrate, while it has identical chemical composition, yields entirely different products when subjected to identical treatment. The difference is not only in viscosity and elasticity but in other physical qualities. Cellulose being formed by successive polymerization of HCHO by chlorophyll in sunlight with starch as an intermediate product, there should be as many celluloses as there are isomeric forms of starch." Berl[2] found that the nitrates of mercerized cellulose gave solutions of much less viscosity than the nitrates of normal cellulose prepared under the same conditions. Baker, whose article has already been mentioned, deduces from this that viscosity does not depend upon the size of the molecule. As a hypothesis he sets forth this: Residual affinity is a characteristic common to all associated liquids. The nitrate in solution is associated with the solvent, the true solute being a complex of a cellulose nitrate and the solvent. The viscosity then varies according to the residual affinity.

1302 COMMONWEALTH AVE., ALLSTON, MASS.

# CURRENT INDUSTRIAL NEWS

## PAINTS CONTAINING LEAD IN ENGLAND

A British Government Blue Book has just been issued which contains the report of the Departmental Committee, appointed in 1911 to investigate the danger attendant on the use of paints containing lead. The report contains a summary of the evidence considered by the Committee, followed by an analysis of this evidence, and details of the action taken with regard to lead in paints by foreign governments.

The recommendation of the Committee is that a law should be introduced prohibiting the importation, sale, or use of any paint material which contains more than 5 per cent of its dry weight of a soluble lead compound. For the determination of soluble lead, a weighed quantity of the dried or dry material, freed as far as possible from oil, or other vehicle, or adhesive substance, is to be continually shaken for one hour at the common temperature, with 1000 times its weight of an aqueous solution of hydrochloric acid containing 0.25 per cent of acid. This solution is to be allowed to stand for one hour, and to be passed through a filter. The lead salt contained in an aliquot portion of the clear filtrate is then to be precipitated as lead sulfide and weighed as lead sulfate. In conjunction with this restriction the Committee state that it would be necessary to exempt specifically certain classes of colors, such as those used by artists; and in addition it would be desirable to provide powers of granting exemptions applicable only to very special branches of the general painting industry, where it could be shown to the satisfaction of the Secretary of State that the use of lead paints containing more than 5 per cent of soluble lead, calculated as above, cannot as yet be dispensed with; in such cases the Secretary of State should have power to enforce adequate precautionary measures, *viz.*, abolition of dry rubbing down, provision for overalls, mess rooms, cloak rooms, lavatories, medical examination and the like. The supply of lead materials to any user to whom such an exemption is granted could be controlled by permitting paint manufacturers to supply the materials in question only on condition of sending written notice of the customer's name and address to the proper Government Department.

To give adequate time for paint grinders and others to arrange for supplies of non-poisonous materials, and also to facilitate the introduction of modifications in painting methods where special work necessitates such changes, the Committee recommend that the restriction of the amount of lead in paints to not more than 5 per cent of soluble lead should not be brought into force until three years have elapsed from the date of publication of this report.

While the terms of reference to the present Committee deal only with the use of lead compounds, the Committee desire to call attention to possible dangers to health arising from the vapors of media used equally in all paints—whether compounded with lead or leadless pigments—and to the consequent importance of investigating the possible effect on health of vapors arising from the linseed oil and turpentine, or turpentine substitutes, used in ordinary paints.

One member of the Committee, Mr. W. G. Sutherland, dissociated himself from the conclusions arrived at by his colleagues, and issues a "minority report."—D. G. ANDERSON.

## MANUFACTURE OF CHEMICALS IN INDIA

According to the *Chemical Trade Journal*, 1464 (1915), in January, 1913, the Eastern Chemical Company, Ltd., was formed to manufacture in Bombay sulfuric acid and other chemicals used in the textile trade and in agriculture, and also to manufacture Epsom salts.

Works have been erected, and the manufacture of sulfuric acid was commenced experimentally last August. The entire acid plant has been got to work, and an excellent quality of acid has been produced; it has been sold at prices which at the present rate of production leave a good margin of profit. Epsom salts, Glauber's salts, copperas, etc., are now being made in increasing quantities, and are being sold at good prices.

Orders and inquiries for considerable quantities of Epsom salts have been received from Europe. At the special request of the Bombay Government, experiments have been made on a large scale with the object of manufacturing magnesium chloride, for which there is a local demand. An order for 500 tons of sulfuric acid has been received from the Anglo-Persian Oil Company, Ltd., and it is anticipated that this will lead to more business

[1] H. Nishida Aboshi, "Determination of the Oxycelluloses by Titration with Titanium Trichloride and Its Practical Application in the Celluloid Industry," *Kunststoffe*, **4**, 266–8.

[2] "The Measurement of Viscosities and the Cellulose Ester Industries," *Caoutchouc and Guttapercha*, **10**, 7202–13.

[3] "Viscosity of Collodions," *Bulletin de société chimique de Belgique*, **28**, 24-32.

[1] "The Measurements of Viscosities and the Cellulose Ester Industries," *Caoutchouc and Guttapercha*, **10**, 7202–13.

[2] *Ztschr. Schiess Sprengstoffwesen*, **4** (1909), 81.

with that company. For plant extensions and to provide working capital the directors contemplate issuing 2,500 ordinary shares for which application has been received. In the event of negotiations with the Anglo-Persian Oil Company, Ltd., resulting in an agreement, the Anglo-Persian Company will take an interes in the Eastern Chemical Company, in order to provide the capital necessary to increase the sulfuric acid plant and to erect a plant for producing other chemicals required by the Anglo-Persian Company.

## THE BRITISH ALKALI ACT

The report of the Chief Inspector, of the work done during the year 1914, in carrying out the provisions of the alkali Works Regulation Act 1906 has just been issued. It shows that the number of works in England, Ireland, and Wales registered was 1,356, in 68 of which salt was decomposed with evolution of muriatic acid, defined in the Act as "Alkali Works." There was thus, compared with 1913, a decrease of 2 in the number registered as alkali works and an increase of 31 in the number otherwise registered, the net increase being 29. There were also 170 works in Scotland registered under the Act, making in all an aggregate of 1,526 for the United Kingdom.

The following figures supply a concise statement of the registered and scheduled processes under inspection:

| | 1913 | 1914 | | 1913 | 1914 |
|---|---|---|---|---|---|
| Alkali waste | 10 | 9 | Bisulfide of carbon | 4 | 4 |
| Arsenic | 50 | 53 | Copper (wet process) | 18 | 18 |
| Bisulfite | 30 | 31 | Cylinder muriatic acid | 12 | 11 |
| Cement | 60 | 50 | Muriatic acid: | | |
| Chemical manure | 155 | 151 | Other than alkali works | 65 | 63 |
| Chlorine | 27 | 25 | Tinplate flux | 73 | 70 |
| Gas liquor | 54 | 56 | Salt | 45 | 47 |
| Lead deposit | 33 | 33 | Nitrate & chloride of iron | 31 | 32 |
| Nitric acid | 76 | 70 | Sulfate and muriate of ammonia | 595 | 624 |
| Picric acid | 5 | 8 | Sulfuric acid | 146 | 150 |
| Salt cake | 48 | 47 | Sulfuric acid (class 2) | 90 | 93 |
| Smelting | 75 | 75 | Wool carbonizing (decomposing salt) | 1 | 1 |
| Sulfide | 83 | 83 | Zinc extraction | 13 | 12 |
| Tar | 192 | 205 | | | |
| Venetian red | 12 | 12 | | | |

These figures show an increase of 47 processes under inspection as compared with 1913. The increase is associated largely with the manufacture of sulfate of ammonia and with the distillation of tar.

Considerable improvement occurred during 1914 from extended adoption of mechanical appliances in place of manual labor in certain of these operations which are liable to cause local escape of acid gases or fumes. This was especially the case as regards bleaching powder manufacture, superphosphate manufacture, and extraction of copper by the wet process. The mechanical devices put into operation in these cases improved very greatly the environment of the men employed, and remove cause for complaint in the vicinity from local escapes of acid gases, while they are more reliable for uniformity of working.—A.

## INDIAN OILSEEDS CROP

The Department of Statistics, India, has now issued the final forecast of the Winter oilseeds (rape, mustard, and linseed) crop for the season 1914–15. This forecast is based upon reports received from provinces where rape, mustard, and linseed are grown to any extent.

These provinces contain 99.2 per cent of the total area under rape and mustard, and 99 per cent of the total linseed area in British India.

Of the native states, estimates are furnished by Hyderabad and the States in the Bombay Presidency (including Baroda). No report is made by any other native states.

The total area under rape and mustard is now reported to be 6,402,000 acres, which is 136,000 acres or 2 per cent larger than the finally revised area of last year. The total estimated yield is 1,195,000 tons, as compared with 1,087,000 tons, the revised final figures of last year, or an increase of 10 per cent.

The total area under linseed amounts to 3,332,000 acres, which is 301,000 acres or 9 per cent larger than the area of last year.

The total estimated yield is 396,000 tons, as against 386,000 tons, the revised final estimate of last year, or an increase of 2.5 per cent.

In addition to the areas for which particulars are given above, the crops are grown in certain other tracts in British India, and the average areas so grown for the last five years have been some 47,000 acres of rape and mustard and some 33,000 acres of linseed.

An addition of approximately 0.8 per cent (9,000 tons) should be made to the estimated total yield of rape and mustard, and of 1 per cent (4,000 tons) to that of linseed on this account.

The condition of the crop on the whole is reported to be from fair to good, except in Bihar and Orissa and Bengal, and in the southern and eastern districts of the United Provinces, where the crops were adversely affected by drought.—A.

## USE OF SILICA-GRAPHITE PAINT

A practice that is fast gaining adoption in progressive power plants is the use of paint for the inner surface of steam boiler drums. The paint is said to afford protection against pitting. Silica-graphite paint is used for this purpose. For a number of years the manufacturers of this paint have coated the steam drums of five B. & W. boilers developing 1800 H. P. and as a result the drums are in almost perfect condition. In another instance, the interiors of the drums of B. & W. boilers developing 8400 H. P., were scalded, painted both above and below the water line and allowed 48 hours to dry thoroughly. This treatment was repeated every ten months and not only did it stop pitting but where it had previously taken six men seven days to clean the drums of one boiler, two men now clean them in a day. This latter experience is quoted from a letter of the Chief Engineer of the New York Life Insurance Company, in the April issue of *Graphite*.

## EXPLOSION IN ENGLISH CORDITE FACTORY

The report of Major A. Cooper-Key, H. M. Chief Inspector of Explosives, on an explosion which occurred at a Stowmarket factory has just been issued. The report states that on the morning of the accident cordite M. D. was in the course of manufacture, and at the moment of the accident two men in the building were on the point of handing out to two bogie runners the bags of cordite paste for removal to the hand-mixing house. Before being placed on the bogie the bags are wiped down to get rid of the guncotton dust, and also to remove to some extent the water from the bottom of the bags, due to their having been standing on a wet floor. In order to avoid the use of a loose implement of any kind this operation was done by hand and not with a brush. It was a fine, dry, cold morning and the two men in the building were wearing stout rubber overshoes, which would completely insulate them from electric contact with "earth." The bags were of rubber-impregnated canvas, a marked dielectric, and in the case at any rate of a man with a naturally dry skin, the operation of wiping the bags would undoubtedly have the effect of generating in his person a statical charge of electricity which might well be sufficient to cause a spark to pass as soon as he should happen to "earth" himself by touching an uninsulated article.

The Chief Inspector adds that this explanation may appear at first sight to be a somewhat far-fetched one, but that he is convinced that it is the true one. He quotes a case at Ardeer Explosive Works where a workman wearing rubber shoes fired acetone vapor by a spark from his fingers after merely allowing the thin strands of rifle cordite to pass over his hand —A.

## THE TRUMBLE OIL REFINING PROCESS

According to the *Petroleum World*, 1915, 178, the Trumble refining process, invented by Mr. M. J. Trumble and formerly owned by the Trumble Refining Company, a $5,000,000 corporation controlled by the General Petroleum Company, has been purchased by the Shell Company of California for the benefit of the Royal Dutch and Shell group. The Simplex Refining Company with an authorized capital of $2,000,000 has applied to the Commissioner of Corporations for permission to issue $1,000,000 stock to Mr. W. Meischke-Smith in exchange for the rights to the patents covering the Trumble process for refining petroleum. Mr. W. Meischke-Smith is the California representative of the Shell interests.

The Trumble process was originally financed by the General Petroleum Company which bought a half interest for $75,000 and assumed certain obligations to carry on the work. The payment for this half interest was used in securing patents in seventy-two countries. The General Petroleum Company was unable to fulfill the obligations toward the Trumble Company and finally consented to turn over its interests to the Royal Dutch and Shell.

The Trumble process thereupon sold for $1,000,000 of which $900,000 has been paid and $100,000 is withheld pending the final action on certain patent applications. Of this sum the General Petroleum Company receive one-half, less $50,000 owing to the Trumble concern. In other words, the General Petroleum Company has received $400,000 in cash for an investment of $75,000, and will receive another $50,000 upon the completion of the deal. In addition the General Petroleum retains the right to use the process in the state of California. The special feature of the Trumble system is the tall tower-like still, in contrast to the usual horizontal still. It is claimed that this keeps the oil longer in contact with the heating surface and prevents the vapor from recondensing and falling in drops back into the oil that is being evaporated.—A.

## METAL CLOTHS AND FELTS FOR SWEDEN

The *Paper Maker* (V. L. No. 1) states that Swedish paper mills are getting uneasy with reference to their supplies of machine wires and other metal cloths. Even in ordinary times the Swedish industry could not entirely meet the requirements of the domestic market in these articles, particularly in certain widths and finer numbers, while at present the prohibition of exports from Germany and England interferes with trade. Some wires, it is remarked, might be imported from England under guarantee of not being re-exported to Germany, were the British wire works not so busy for the home market to replace the imports from Germany before the war. It has been suggested for the Swedish metal works to make paper wires from phosphor bronze, but doubts have been expressed as to the sufficiency of the demand to absorb such production.

Wool suitable for paper felts is reported scarce in Sweden, while German and English felts cannot at present be obtained.—A.

## COPPER SMELTING IN CANADA

Arrangements have been completed for the refinement in Canada of Canadian-produced copper and zinc. The London *Times Engineering Supplement*, p. 490 (1915), remarks that the copper-smelting industry of the Dominion is so great as long ago to have warranted the establishment of the necessary plant for refining the metal within the Dominion, instead of sending it across the border into the United States. Apart from the importance of the copper industry in Ontario, it may not be generally known that the Granby Smelter at Grand Forks, British Columbia, is claimed to be the largest copper smelter within the British Empire. It has a capacity of 5,000 tons of ore per day; but a new plant erected at Anyox, B. C., by the same company is intended to equal this capacity if not to exceed it. At present the capacity of the Anyox smelter is about 2,500 tons per day. In addition to these smelters, there are exceedingly important copper smelters at Trail and Greenwood, B. C., each with big outputs and both actively employed, and also well-equipped smelters at Ladysmith, B. C., and one or two other points in the province which it is proposed to put again into blast as soon as a steady tonnage of "customs" ore can be relied upon from the numerous copper properties awaiting or under development. The Pacific Coast province of the Dominion could probably keep going on with its own ores a zinc and copper refinery established at or near the coast, and would also draw some custom from the adjacent States of the United States.

Unfortunately the zinc ores of Canada are usually highly refractory, but it is believed that, as the result of the attention paid to their reduction by the Dominion Department of Mines, a satisfactory solution of a difficult problem has been found. It is also noteworthy that early in 1914 it was stated before the Vancouver Chamber of Mines by Mr. J. C. Nettel that the old-fashioned Swansea method applied to the British Columbian zinc ores would result in a satisfactory reduction of such ores. The "Coast" district of British Columbia, as well as some of the internal districts, are extremely rich in copper and zinc ores, and coal for coking purposes is also abundant and near at hand. It would not be surprising, therefore, if the proposed refinery were established near the coast of British Columbia.—A.

## STORAGE OF CALCIUM CYANAMIDE

According to the *Chemical Trade Journal*, p. 1475 (1915), manufacturers of cyanamide have adopted the practice of treating it with mineral oil, which surrounds the particles with an oily film, and diminishes the loss of nitrogen which it undergoes when stored. Burgess and Edwardes-Ker have conducted experiments on this treated material, in order to determine the part played respectively by moisture and carbon dioxide in causing these losses of nitrogen. Weighed samples of cyanamide were exposed under various conditions and their nitrogen content tested from time to time, with the following results:

| | Conditions under which sample was sfored | No. of days stored | Nitrogen test per day Parts per 100 of original weight |
|---|---|---|---|
| 1 | In the open air | 25 | 0.0776 |
| 2 | In moist air free from $CO_2$ | 28 | 0.0077 |
| 3 | In dry air containing excess of $CO_2$ | 25 | 0.0113 |
| 4 | In moist air containing excess of $CO_2$ | 20 | 0.025 |
| 5 | In a corked bottle | 42 | 0.0 |

While the sample exposed to the air had lost nitrogen at the rate of 0.07 per cent per day, the losses when the fertilizer was exposed in a closed vessel to the action of moist air, to that of carbon dioxide, or to that of the combined effect of both of these factors, were always much smaller, showing that neither of the factors could be held responsible for the losses of nitrogen; nevertheless, as the nitrogen content of the sample kept out of contact with the air, in the corked bottle, underwent no change, it would appear that some atmospheric agent, other than moisture or carbon dioxide, must be the cause of the nitrogen losses.—A.

## DEVELOPMENT OF A TAR SAND REGION

The *Petroleum World*, p. 179 (1915), mentions that it is announced by representatives of Mr. D. A. Thomas, the Welsh coal magnate, acting for the Athabasca and Fort Vermilion Railway, that a survey will shortly begin at Athabasca preliminary to actual construction of 300 miles of railway between the two points named.

Mr. Thomas has spent considerable money in prospecting the region along the big waterways north of Edmonton and believes that coal is plentiful; the railway, when completed, will also facilitate to some extent development of the oil possibilities of the region north of Edmonton. It is in this area that the famous and extensive "tar sands" are found.—A.

# SCIENTIFIC SOCIETIES

## FIFTY-FIRST MEETING AMERICAN CHEMICAL SOCIETY SEATTLE, WASHINGTON, AUGUST 31 TO SEPTEMBER 3, 1915

### PROGRAM OF PAPERS

#### GENERAL PUBLIC MEETINGS, AUGUST 31

**Address of Welcome.** HENRY SUZZALO, President of University of Washington.

**Response.** CHARLES HOLMES HERTY, President of American Chemical Society

**Opening Address. Chemical Industry.** LEO H. BAEKELAND

**Industrial Resources and Opportunities of the Pacific Northwest.** H. K. BENSON.

**Public Symposium.** DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

**Part I. Continuation of series of papers first presented at New Orleans on the Chemists' Contributions to American Industries.** (See below and also *April issue*, pp. 273–304.)

**Part II. Symposium on the Chemistry of Wood Waste.** (See below.)

**Evening Address. Coöperation in Matters Chemical.** PRESIDENT CHARLES HOLMES HERTY.

#### AGRICULTURAL AND FOOD CHEMISTRY DIVISION

FLOYD W. ROBINSON, *Chairman* GLEN F. MASON, *Secretary*

1. **The Activity of Proteolytic Enzymes in Breadmaking.** ARNOLD WAHL.
2. **The Spontaneous Decomposition of Butter-fat.** C. A. BROWNE.
3. **The Analysis of Maple Products. Paper V. "Miscellaneous Observations on Maple Syrup Incidental to a Search for New Methods of Detecting Adulteration."** J. F. SNELL.
4. **The Analysis of Maple Products. Paper VI. "A Volumetric Lead Subacetate Test for Purity of Maple Syrup."** J. F. SNELL, N. C. MACFARLANE AND G. J. VANZOEREN.
5. **The Analysis of Maple Products. Paper VII. "The Electrical Conductivity Test for Purity of Maple Syrup." Corrections and Supplement to Paper I.** J. F. SNELL.
6. **Determination of Total Solids in Milk by Open-Air and Vacuum Methods.** GEO. GRINDROD.

#### BIOLOGICAL CHEMISTRY DIVISION

CARL L. ALSBERG, *Chairman* I. K. PHELPS, *Secretary*

1. **Mutual Action of Similarly Charged Colloids.** W. D. BANCROFT.
2. **Adsorption of Colloids by Liquids.** W. D. BANCROFT.
3. **Formation of Surface Films.** W. D. BANCROFT.
4. **A Search for Hydrocyanic Acid among the Caprifoliaceae.** C. L. ALSBERG.
5. **The Reaction of the Pancreas.** J. H. LONG AND FREDERICK FENGER.
6. **On the Digestive Activity and Composition of Separate Fractions of the Pancreas.** J. H. LONG, MARY HULL AND H. V. ATKINSON.
7. **Kelp.** F. K. CAMERON.
8. **The Inadequacy of Schultz's Valency Rule.** W. D. BANCROFT.
9. **The Evolution of the Yeast Type Especially Adaptable for Breadmaking.** A. WAHL.
10. **A Theory Regarding Protoplasmic Structure, Based on the Study of Emulsion Equilibrium.** G. H. A. CLOWES.
11. **Alleged Abnormal Adsorption of Filter Paper.** W. D. BANCROFT.
12. **Adsorption of Acids by Cellulose.** W. D. BANCROFT.
13. **Oxycellulose.** W. D. BANCROFT.
14. **Chemical Investigation of Eggs Preserved in Waterglass and Lime Solutions.** F. C. COOK.
15. **Boron, Its Absorption and Distribution in Plants and Its Effect on Growth.** F. C. COOK.
16. **A Study of the Calcium and Magnesium Metabolism in a Case of Chronic Gout.** JACOB ROSENBLOOM.
17. **Metabolism Studies in a Case of Bronchial Asthma.** JACOB ROSENBLOOM.
18. **Note on Semipermeable Membranes.** W. D. BANCROFT.
19. **Dilute Solutions of Gelatine.** W. D. BANCROFT.
20. **Nephelometric Estimation of Phosphorus.** P. A. KOBER AND G. EGERER.
21. **Spectrographic Study of Amino Acids and Polypeptides.** P. A. KOBER AND W. EBERLEIN.
22. **Citric Acid Production by Black Aspergillus.** J. N. CURRIE.
23. **Oxalic Acid Production by Aspergillus ficuum, Schiemann.** J. N. CURRIE.
24. **An Oxalic Acid Producing Penicillium.** J. N. CURRIE AND CHARLES THOM.
25. **Quantitative Changes during Growth of the Human Brain.** E. A. DOISY AND C. G. MACARTHUR.
26. **Quantitative Differences between Normal and Pathological Human Brain.** E. A. DOISY AND C. G. MACARTHUR.
27. **Nitrogenous Hydrolysis Products of Brain Lecithin.** J. E. DARRAH AND C. G. MACARTHUR.
28. **Some Physico-Chemical Properties of Several Brain Lipoids.** G. NIEDERMAN AND C. G. MACARTHUR.
29. **Respiration of Nerve Tissue.** O. C. JONES AND C. G. MAC ARTHUR.
30. **The Effect of Large Applications of Commercial Fertilizers upon Carnations.** GEO. D. BEAL AND FRED WEAVER MUNCIE.
31. **Improved Methods for the Separation of the Higher Saturated Fatty Acids and the Properties of Alfalfa Seed Oil.** C. A. JACOBSON.

#### INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

GEO. P. ADAMSON, *Chairman* S. H. SALISBURY, JR., *Secretary*

**Part I—Symposium on the Contributions of the Chemists to American Industries. Continuation of series of papers first presented at New Orleans:** (See *April issue*, p. 273.)

1. **The Naval Stores Industry.** JOHN E. TEEPLE.
2. **The Iron and Steel Industry.** GEORGE W. SARGENT.
3. **The Iron and Steel Industry.** A. S. CUSHMAN.
4. **The Art of Soap Making.** M. H. ITTNER.
5. **The Perfumery and Essential Oils Industry.** E. T. BEISER.
6. **The Lead Industry.** G. W. THOMPSON.
7. **The Paint and Varnish Industry.** MAXIMILIAN TOCH.
8. **The Photographic Industry.** FRANCIS C. FRARY.
9. **The Pharmaceutical Products Industry.** FRANK R. ELDRED.
10. **The Hardwood Distillation Industry.** S. W. KATZENSTEIN.
11. **The Packing House Products Industry.** ARTHUR LOWENSTEIN.
12. **The Electrochemical Industry.** W. S. LANDIS.
13. **The Explosives Industry.** CHAS. E. MUNROE.

**Part II—Symposium on the Chemistry of Wood Waste:**

1. **Chemical Engineering of the Hardwood Distillation Industry.** JAMES R. WITHROW.
2. **What Chemistry Has Done to Aid the Utilization of Wood.** S. F. ACREE.
3. **The Study of the Tannin Content of Douglas Fir and Western Spruce Sawmill Waste.** H. K. BENSON AND THOMAS G. THOMPSON.
4. **Yield of By-Products from the Destructive Distillation of Some Western Conifers.** H. K. BENSON AND MARC DARRIN.
5. **The Extraction of Resinous Wood by Ammonia.** H. K. BENSON AND NEWTON CRITES.
6. **Discoloration of Maple in the Kiln.** ROY C. JUDD.
7. **The Chemical Composition of the Light Oil from the Destructive Distillation of Resinous Woods.** R. E. ROSE AND A. G. BISSELL.
8. **Manufacture of Ethyl Alcohol from Wood Waste. II. The Hydrolysis of White Spruce.** F. W. KRESSMANN.
9. **The Application of the Davis Spot Test in the Preliminary Examination of Creosotes.** HOMER CLOUKEY.
10. **Isoprene from Beta-pinene.** A. W. SCHORGER AND RALPH SAYRE.
11. **The Distillation of Douglas Fir at High Temperatures.** BAILEY TREMPER.
12. **The Manufacture of Ethyl Alcohol from Wood Waste. III. Western Larch as a Possible Raw Material.** F. W. KRESSMANN.
13. **The Production of Acetone from Pyroligneous Acid.** MARC DARRIN.
14. **Waste Pine Wood Utilization.** J. E. TEEPLE.

**Part III—Additional Papers not Read in Symposiums:**

1. **Refining Vegetable Oils.** CHAS. BASKERVILLE.
2. **The Relation of Water Power to Chemical Industry.** HENRY J. PIERCE.
3. **"Viscosimeters."** R. F. MACMICHAEL.
4. **The Function of Cooking Fossil Resins in Varnish Manufacture.** W. L. JEFFERIES AND CHAS. H. HERTY.
5. **A Test of a Surface Combustion Furnace.** E. SCHRAMM AND J. R. CAIN.

#### ORGANIC CHEMISTRY DIVISION

F. B. ALLAN, *Chairman* C. G. DERICK, *Vice-Chairman and Secy.*

1. **The Chemistry of Enzymic Action.** J. U. NEF.
2. **The First of the Enzymes and Its Evolutionary Significance.** R. G. ECCLES.

3. **A New Form of Absorption Bottle for Use with Either Calcium Chloride or Soda Lime in Organic Combustion.** H. L. Fischer.

4. **Spectrophotometric Study of Copper Complexes and Biuret Reaction.** P. A. Kober and A. B. Haw.

5. **The Constitution of the Three Nitro-α-carbopyrrolic Acids.** W. J. Hale.

6. **The Oxidation of Ethyl Alcohol with Alkaline Potassium Permanganate.** W. L. Evans and J. E. Day.

7. **The Oxidation of Certain Lactates with Potassium Permanganate.** W. L. Evans, P. A. Davis and P. Cottringer.

8. **The Condensation Products of Menthone Formed by the Action of Aluminium Chloride.** G. B. Frankforter and A. L. Newman.

9. **The Polymers of Pinene.** G. B. Frankforter and C. J. Frankforter.

10. **The Electron Conception of Valence. A Laboratory Search for Electromers.** O. Kamm.

11. **The Hofman Rearrangement of (N) Alkyl Anilines.** C. G. Derick and J. W. Howard

12. **The Synthesis of 1-Phen-3-phenoxy-propane by the Grignard Reaction.** C. G. Derick and L. O. Potterf.

13. **The Isomeric Tetracetates of Xylose and Observations Regarding the Acetates of Melibiose, Threhalose and Sucrose.** C. S. Hudson and J. M. Johnson.

14. **The Preparation of Melibiose.** C. S. Hudson and T. S. Harding.

15. **A Second Crystalline *d*-Fructose Pentacetate (*α-d*-Fructose Pentacetate).** C. S. Hudson and D. H. Brauns.

16. **Bromoacetylxylose and Beta Triacetylmethylxyloside.** J. K. Dale.

17. **Undissociated Organic Acid in the Role of a Catalytic Agent.** I. C. Biddle.

18. **The Isomerism of 1,4,5,6-Tetrahydroxynaphthalene.** A. S. Wheeler and V. C. Edwards.

19. **The Bromination of 1,4,5,6-Tetrahydroxynaphthalene.** A. S. Wheeler and V. C. Edwards.

20. **Simple and Mixed Alkyl Phosphates.** W. A. Drushel.

21. **The Preparation and Properties of Hydracrylic Esters.** W. A. Drushel and W. H. T. Holden.

22. **The Synthesis of Glycocoll and Diethyl Carbonate.** W. A. Drushel and D. R. Knapp.

23. **Further Studies upon the Resene of Pinus Heterophylla.** Chas. H. Herty and V. A. Coulter.

24. **The Occurrence of Inosite-triphosphoric Acid in Cottonseed Meal.** J. B. Rather.

25. **Balys Theory of Chemical Reactions.** W. M. Dehn.

26. **Study of the Common Bean.** W. M. Dehn.

27. **A Case of Steric Hindrance in Enzymes.** W. M. Dehn.

28. **Colorimetric Studies of Picrate Solutions.** W. M. Dehn.

29. **Certain Noninterchangeable Radicals.** W. M. Dehn.

### PHARMACEUTICAL CHEMISTRY DIVISION

F. R. Eldred, *Chairman* A. P. Sy, *Secretary*

1. **The Alkaloidal Content of Hyoscyamus Grown in Minnesota.** E. L. Newcomb.

2. **Some Notes on Sandalwood, Its Assay, Yield of Oil, and Changes in the Oil during Distillation.** C. H. Briggs.

3. **Iso-Pulegol Phosphonic Acid.** F. D. Dodge.

4. **Note on the Use of the White Mouse as a Test Animal for Determining the Toxic Coefficients of Various Drugs.** J. H. Beal, C. G. MacArthur and E. A. Doisy.

5. **Color Standards and Colorimetric Assays.** H. V. Arny.

6. **Electrolytic Determination of Mercury in Mercury Oleate.** B. L. Murray.

7. **Electrolytic Determination of Bismuth in Bismuth Beta-naphthol.** B. L. Murray.

8. **Electrolytic Determination of Mercury in Mercury Salicylates.** B. L. Murray

9. **Hardness, Weight and Thickness of Medicinal Tablets.** A. D. Thorburn.

10. **The Rate of Evaporation of Ether in Oil-Ether Anesthesia.** Chas. Baskerville.

11. **The Identification of the Emodin Containing Drugs.** Geo. D. Beal and Ruth E. Okey

12. **Some New Laboratory Methods.** Albert Schneider.

### PHYSICAL AND INORGANIC CHEMISTRY DIVISION

G. A. Hulett, *Chairman* R. C. Wells, *Secretary*

1. **Anodic Relations of Passive Iron.** H. G. Byers and Seth C Langdon

2. **Electrolytic Endosmose.** Ruby Clift and George Glockler.

3. **The Stabilizing Influence of Hydrogen Sulfide on Colloidal Metallic Sulfide Solutions.** S. W. Young.

4. **The Interpolation of the Equilibria Curves in Systems of the Higher Alcohols, Water, and Salts.** G. B. Frankforter and Sterling Temple.

5. **Equilibria in Systems of Ketones, Water, and Salts with a Method for the Determination of Methyl Alcohol in the Presence of Acetone.** G. B. Frankforter and Lillian Cohen.

6. **The Influence of Dissolved Substances on the Velocity of Crystallization of Under-cooled Water.** James H. Walton, Jr., and A. C. Brann.

7. **The Partition Coefficients of Hydrogen Peroxide between Water and Certain Organic Solvents.** James H. Walton, Jr., and H. A. Lewis.

8. **The Preparation of Pure Iron and Iron Carbon Alloys.** J. R. Cain, E. Schramm and H. E. Cleaves.

9. **The Oxides of Iron. I. Solid Solution in the System $Fe_2O_3$–$Fe_3O_4$.** Robert B. Sosman and J. C. Hostetter.

10. **The Water Correction in Conductivity Determinations.** James Kendall.

11. **Conductance Data and Empirical Equations.** Stuart J. Bates.

12. **A Quantitative Measure of the Deviation from the Law of Mass Action.** Stuart J. Bates.

13. **Ion Concentration and the Law of Mass Action.** Stuart J. Bates.

14. **The Calorimetric Determination of Ferrous and Ferric Iron.** O. L. Barnebey.

15. **Differential Iodimetry. I. The Titration of Periodates, Iodates, Bromates, and Chlorates in the Presence of Each Other and in the Presence of Perchlorates.** O. L. Barnebey.

16. **Molecular Weights by an Evaporation Method. (Preliminary Report.)** H. L. Trumbull.

### WATER, SEWAGE AND SANITATION DIVISION

Edward Bartow, *Chairman* H. P. Corson, *Secretary*

1. **The Seattle Water Supply.** John Weinzirl.

2. **The Composition and Properties of Activated Sludge.** Edward Bartow and W. D. Hatfield.

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## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS SEVENTH SEMI-ANNUAL MEETING LOS ANGELES AND SAN FRANCISCO AUGUST 18 AND 25-28, 1915

The Eastern delegation to the meeting of the American Institute of Chemical Engineers left New York August 6th *via* Pennsylvania R. R., the first stop being made at Colorado Springs, where the interesting rock formations in the Garden of the Gods were visited and Pike's Peak ascended. The Cripple Creek mining district was visited, the trip being made by the Cripple Creek Short Line, the beautiful Canyon scenery being particularly enjoyable.

A day was spent at the Grand Canyon of the Colorado where some of the party studied the geology of the Canyon during the trip, on mule back, to the Colorado River by the Bright Angel Trail. Others enjoyed the magnificent views to be obtained from the rim.

The trip through the desert being made at night, no hot weather was experienced, the party arriving at San Diego August 13th. Two days were spent in visiting the San Diego Fair and inspecting the beautiful harbor of this charming southern California city.

#### LOS ANGELES

Three days were then spent in Los Angeles where the party was entertained by the local committee of the Institute, consisting of Messrs. Edgar Baruch and D. B. W. Alexander, assisted by members of the Southern California Section of the American Chemical Society of which Mr. Baruch is Chairman, and Mr. Henry L. Payne, Secretary. For the various automobile trips which had been arranged for the entertainment

of the visitors, cars were provided by Messrs. E. Baruch, N. M. Hill, R. B. Peters, H. J. Reese, M. P. Waite, Mark Walker and F. C. Winter.

On Monday, August 16th, a 120 mile automobile trip was taken. Redondo Beach was first visited where the oil-fired power station of the Pacific Light and Power Company was inspected. It contains reciprocating sets of 15,000 kw. and turbine sets of 24,000 kw. Salt water was used for the condensers, the kelp being removed by means of screens. The kelp was examined with interest in view of the possibility of utilizing it as a commercial source of potash.

After luncheon at the Huntington Beach Hotel, the beet sugar plant was visited under the guidance of Mr. Jos. Varra and the chief chemist, Mr. A. C. Horn. The return trip to Los Angeles was made *via* Santa Ana and Orange through extensive walnut and fruit orchards.

The evening was spent seeing the Mission Play at Alhambra. This was of special interest on account of its vivid presentation of the early exploration and settlement of California by the Spanish Missionaries and their very successful work in Christianizing the Indians. Several of the Missions still standing between San Diego and San Francisco were visited with great interest during that portion of the trip.

On Tuesday the party took the trip to the Catalina Island, seeing flying fish, a whale, and the marine gardens through the glass bottom boats.

On Wednesday the party was taken by automobiles to the Fullerton oil fields where the methods in use for drilling oil wells were shown and also the freezing out of gasoline from the natural gas. A very volatile oil obtained in this manner was shown. The refrigerating agent used was the gas itself: the extreme cold produced was illustrated by the production of a snowball of solid gasoline which, when placed on the ground and ignited, burned with a long flame for a considerable time. The process was described by Mr. A. Yost, superintendent of the Brea Canyon Oil Company, and Mr. W. A. Culp, superintendent of the Pacific Gasoline Company. The informal lunch of watermelons and figs was very much enjoyed.

In the afternoon the electrolytic plant at Santa Monica for the purification of sewage was inspected. At this plant 500,000 gallons of sewage are treated. The current used was 440 amperes and 2.5 volts. The sewage flows through an open flume containing iron plates, the time required being 35 seconds. Before the electrolytic treatment, the sewage passes through a receiving tank of 22,000 gallons capacity.

### MEETING WITH SOUTHERN CALIFORNIA SECTION A. C. S.

On Wednesday evening a well attended joint meeting was held with the Southern California Section of the American Chemical Society preceded by a dinner at the University Club. Mr. Baruch presided at the meeting. He first introduced the Secretary, Dr. J. C. Olsen, who read a letter from the President, Dr. Geo. D. Rosengarten, expressing his regret at being absent on account of sickness in his family. Professor J. M. Stillman of Leland Stanford University, Vice-President of the Institute, who had come especially from Palo Alto to Los Angeles to welcome the Institute to California, also made a few remarks.

The first paper, presented by Mr. W. C. Hanna of the California Portland Cement Company at Riverside, described the Fleming dust collecting system which is successfully used at that plant for collecting any dust and preventing damage to the surrounding orange groves. Briefly, the installation consists of normal rotary kilns using dry process and oil for fuel. The draft for the kilns and driers is produced by fans sucking at the ends of separate flues. Instead of discharging gases into the atmosphere, the same exhauster fan blows the dust and fumes into a large "dry dust settling chamber," the velocity of the gases being reduced about 90 to 95 per cent, resulting in a large amount of dust being deposited. The extremely fine dust which does not settle, and the gases, then go to the "wet washing chambers," where the gases are forced up and down several times while following a serpentine course through a system of seven baffle chambers, and the last of the original so-called cement dust is captured by sprays of water which are in each chamber. These sprays of water also bring into solution much of the gases, lime and alkalies. In connection with both the dry and the wet chambers there are means provided for the removal of the captured dust to the cement kilns.

Secretary J. C. Olsen read a paper on "A New Electrolytic Method of Sewage Disposal." This process is in operation at Elmhurst, New York City, and has proved very successful. The process includes electrolyzation with iron electrodes in a closed box, thorough agitation and precipitation with lime. A very pure, stable effluent is produced.

On Thursday the large beet sugar factory of the American Beet Sugar Company at Oxnard was visited. The entire day was spent in this factory, which produces about 10,000 bags of sugar daily. Great interest was shown in the operation of the Steffen process by which the sugar is extracted from the molasses and especially in the efforts being made to recover the very large amount of potash in the waste liquors from this process. Small amounts of this potash were being recovered and utilized.

The immense and unique high-grade kieselguhr deposits at Polnoc were also visited by some of the party.

Sight-seeing auto rides at Santa Barbara and Del Monte were found very enjoyable.

### SAN FRANCISCO

The meeting at San Francisco was opened on Monday morning at the Civic Center Auditorium. Professor J. M. Stillman, of Stanford University presided in the absence of President Geo. D. Rosengarten, of Philadelphia.

The reports of the officers of the Institute showed a satisfactory increase in membership and a substantial surplus in the treasury with all bills paid.

An amendment to the Constitution permitting the re-election of a President for one term of one year was favorably acted upon.

An invitation to hold the winter meeting in December in Baltimore was presented and referred to the Committee on Meetings.

A paper on "The Improvement of High Boiling Petroleum Oils and the Manufacture of Gasoline as a By-Product therefrom by the Action of Aluminum Chloride" was presented by A. M. McAfee of the Gulf Refining Co. at Port Arthur, Texas. By the use of aluminum chloride as a catalytic agent, the amount of gasoline obtained from petroleum was increased from 15 to 40 per cent. Typical samples of crude oil from various districts were refined by the new process with satisfactory results. Methods for the recovery of the aluminum chloride were described. Samples of the crude oils and the products obtained were shown.

Dr. Arthur L. Lachman gave a very complete description of the methods of handling grapes and the manufacture of wine in California. This industry is carried on with great advantage in California because on account of the very favorable climatic conditions the second fermentation necessary in other localities is obviated.

On Wednesday afternoon the party were taken by autos to Protrero where the manufacture of illuminating gas from petroleum oil was explained by Mr. Edw. C. Jones and the plant visited under his guidance. This process has been developed to a point where all but a very small percentage of the carbon of the oil is converted into gas in a single operation. This result was obtained by the practical application of physical chemical principles to manufacturing processes. The simplicity, ease and accuracy of control of the process as well as the cleanliness of the entire plant were very much admired.

On Thursday the sessions were held at the University of California at Berkeley where the members were welcomed by Professor Edmund O'Neill.

At the morning session a paper on "Costs as Applied to Professional Businesses" was presented by Ralph A. Gould, of San Francisco. Careful records of an experience of several years showed that the overhead charges of a carefully managed business of this kind cannot be much less than 35 per cent.

A paper on "Resources and Possibilities of Chemical Industry in the Southwest" was presented by Edgar Baruch, of Los Angeles. In this paper the possibilities of developing the kelp industry and the Searles Lake deposit were discussed and the opinion expressed that when the technical problems involved have been worked out these industries will be a success. The large amount of water power available presents opportunities for electrolytic industries.

After luncheon at the Faculty Club the laboratories and grounds of the University were visited as well as the famous Greek Theatre.

On Thursday evening at Waites Restaurant a typical California dinner was served. With his characteristic good humor and geniality, Professor Stillman acted as Toastmaster. The Secretary responded to the toast "Our Absent President Rosengarten," and explained the unfortunate combination of circumstances which prevented the President and other members of the Institute from attending the meeting, the chief cause being the unsettled and active condition of chemical manufacture produced by the war. Mr. A. M. McAfee, in responding for the Southern States, related how he was compelled to use his bathing suit in order to leave the flooded districts of Texas and reach the meeting. Dr. Samuel P. Sadtler, as the first President of the Institute, congratulated the California members on the progress made in chemical industry on the Pacific Coast and the cordial hospitality extended to the Eastern members. Others who responded were Professor O'Neill and Professor James R. Withrow.

The meeting on Friday was held at the Stanford University at Palo Alto. Professor S. W. Young in a paper on "The Present State of the Thiogen Industry" showed how the essential conditions for the absorption of sulfur fumes by means of lime or alkaline earth hydroxides has been worked out and the possibility of economically recovering the sulfur demonstrated. The cost of recovering the sulfur was stated as $7.00 per ton.

Professor J. P. Mitchell presented a paper on "The Injury to Vegetation by Sulfur Fumes" in which he showed that the sulfur is absorbed by the vegetable tissues, the amount found varying with the exposure to the fumes. A determination of the amount of sulfur present gives a measure of the injury done, which finally results in the death of the plant.

Walter A. Schmidt presented a paper on "The Electrical Precipitation Method" in which he described a number of recent installations of the Cottrell process which successfully precipitated fumes differing widely in character and chemical content.

Professor Edward Bartow read a paper on "The Purification of Sewage by Aeration in the Presence of Activated Sludge." A high state of purity and stability of the effluent from this process is obtained while the sludge contains about 6 per cent of nitrogen as well as phosphates and was shown by pot experiments to have a high fertilizing value.

After taking luncheon as the guests of Professor and Mrs. Stillman, the members and their guests inspected the laboratories and beautiful grounds and buildings of the Stanford University.

On Saturday the vineyard and wineries at Winehaven were visited.

THE RETURN TRIP

After visiting the Fair and other points of interest in San Francisco, the party proceeded to Portland where one day was spent and thence to Seattle, where the meeting of the American Chemical Society was attended for two days.

On Thursday, September 2nd, the party proceeded to Butte, Montana, where, on Saturday morning, one of the numerous mines in this district was visited and the party descended to the 2000-ft. level. The methods employed in running shafts, blocking out ore, blasting, firing and hoisting were inspected with great interest. The installation for pumping the water from the mine was also examined as well as the extraction of the copper from this water by means of scrap iron. At the surface the air compressors and hoisting machinery were examined, the latter with great interest on account of the use of compressed air in the engines which operated the hoist.

During the afternoon the Concentrator of the Timber Butte Milling Company was visited under the guidance of Professor Theo. Simons, Professor of Mining Engineering at the Montana State School of Mines. The ore carries zinc and lead in sphalerite and galena; copper in various sulfide ores. The ore is crushed in Farrel jaw breakers, then further reduced in Garfield rolling mills and finally powdered to pass 200 mesh in ball mills. The concentration is carried out on Wilfley and James tables which produce a lead-iron concentrate, a copper-iron concentrate, a copper-iron-zinc concentrate and tailings. The final separation is made by the oil flotation process, sulfuric acid and oil being added to the finely powdered ore suspended in warm water; after violent agitation, the sulfide minerals rise to the surface and are skimmed off by revolving paddles. The gangue which settles to the bottom is re-treated several times to remove the last trace of the ore. Treatment costs have averaged between $2.00 and $2.25 per ton of ore passed through the mill. This covers all expense except interest on investment and depreciation. About 96 per cent of the zinc is extracted and about 92.6 per cent of the sulfide contents of the original ore. A complete description of this very efficient concentrator, by Professor Theo. Simons, will be found in the *Transactions of the American Institute of Mining Engineers*.

The laboratories of the Montana State School of Mines were visited under the guidance of Professors Bowman and Simons. Great interest was shown in the very excellent installations of mining machinery where ore in ton lots could be crushed and concentrated, and smelting operations carried out so as to obtain information as to the commercial value of the ores. The museum of ores and minerals which had been collected from the local mines was also greatly admired.

The smelter at Anaconda was also visited under the guidance of L. V. Bender, Superintendent, and Professor C. H. Bowman, of the Montana State School of Mining. The concentration of the ore at this plant is carried out by a process very similar to that used at the Butte Concentrator. Coarse and fine concentrates are reduced in blast furnaces and also in open hearth furnaces, 300 to 325 tons of copper per 24 hours being produced at this plant. A portion of the smelter fumes is converted into sulfuric acid in a large chamber plant recently erected. A large portion of this acid is used to recover the copper from tailings which were discarded several years ago but which contain 0.6 per cent copper: after roasting, the copper is leached out by means of sulfuric acid until 0.09 per cent copper remains: the copper in the sulfuric acid solution is precipitated by means of scrap iron.

After visiting Yellowstone National Park the party proceeded East by rail, or, to Duluth and then by Anchor Line through the great Lakes.

JOHN C. OLSEN, *Secretary*

# JOINT COMMITTEE ON STANDARDS FOR GRAPHIC PRESENTATION

PRELIMINARY REPORT PUBLISHED FOR THE PURPOSE OF INVITING SUGGESTIONS FOR THE BENEFIT OF THE COMMITTEE[1]

As a result of invitations extended by The American Society of Mechanical Engineers, a number of associations of national scope have appointed representatives on a Joint Committee on Standards for Graphic Presentation. Below are the names of the members of the committee and of the associations which have coöperated in its formation.

WILLARD C. BRINTON, *Chairman*, American Society of Mechanical Engineers. [7 East 42nd Street, New York City.]
LEONARD P. AYRES, *Secretary*, American Statistical Association. [130 East 22nd Street, New York City.]
N. A. CARLE, American Institute of Electrical Engineers.
ROBERT E. CHADDOCK, American Association for the Advancement of Science.
FREDERICK A. CLEVELAND, American Academy of Political and Social Science.
H. E. CRAMPTON, American Genetic Association.
WALTER S. GIFFORD, American Economic Association.
J. ARTHUR HARRIS, American Society of Naturalists.
H. E. HAWKES, American Mathematical Society.
JOSEPH A. HILL, United States Census Bureau.
HENRY D. HUBBARD, United States Bureau of Standards.
ROBERT H. MONTGOMERY, American Association of Public Accountants.
HENRY H. NORRIS, Society for the Promotion of Engineering Education.
ALEXANDER SMITH, American Chemical Society.
JUDD STEWART, American Institute of Mining Engineers.
WENDALL M. STRONG, Actuarial Society of America.
EDWARD L. THORNDIKE, American Psychological Association.

The committee is making a study of the methods used in different fields of endeavor for presenting statistical and quantitative data in graphic form. As civilization advances there is being brought to the attention of the average individual a constantly increasing volume of comparative figures and general data of a scientific, technical and statistical nature. The graphic method permits the presentation of such figures and data with a great saving of time and also with more clearness than would otherwise be obtained. If simple and convenient standards can be found and made generally known, there will be possible a more universal use of graphic methods with a consequent gain to mankind because of the greater speed and accuracy with which complex information may be imparted and interpreted.

THE FOLLOWING ARE SUGGESTIONS WHICH THE COMMITTEE HAS THUS FAR CONSIDERED AS REPRESENTING THE MORE GENERALLY APPLICABLE PRINCIPLES OF ELEMENTARY GRAPHIC PRESENTATION

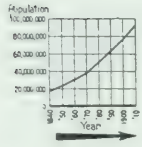



FIG. 1

1. The general arrangement of a diagram should proceed from left to right.

[1] Copies may be had from THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS, 29 West 39th St., New York: 5 cents to members; 10 cents to non-members. Discount in quantities.

FIG. 2

2. Where possible represent quantities by linear magnitudes as areas or volumes are more likely to be misinterpreted.

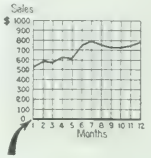



FIG. 3

3. For a curve the vertical scale, whenever practicable, should be so selected that the zero line will appear on the diagram.

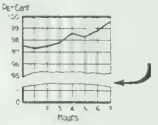



FIG. 4

4. If the zero line of the vertical scale will not normally appear on the curve diagram, the zero line should be shown by the use of a horizontal break in the diagram.

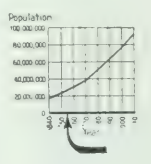



FIG. 5A

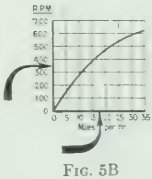



FIG. 5B

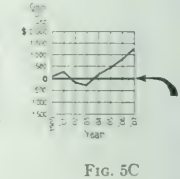



FIG. 5C

5. The zero lines of the scales for a curve should be sharply distinguished from the other coördinate lines.

FIG. 6A

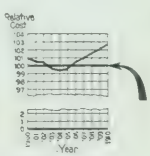



FIG. 6B

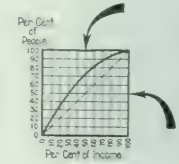



FIG. 6C

6. For curves having a scale representing percentages, it is usually desirable to emphasize in some distinctive way the 100 per cent line or other line used as a basis of comparison.

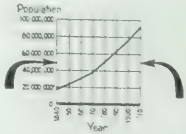



FIG. 7

7. When the scale of a diagram refers to dates, and the period represented is not a complete unit, it is better not to emphasize the first and last ordinates, since such a diagram does not represent the beginning or end of time.

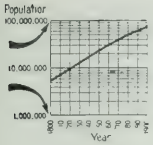



FIG. 8

8. When curves are drawn on logarithmic coördinates, the limiting lines of the diagram should each be at some power of ten on the logarithmic scales.

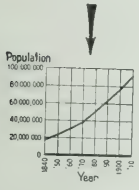



FIG. 9A

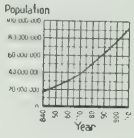



FIG. 9B

9. It is advisable not to show any more coördinate lines than necessary to guide the eye in reading the diagram.

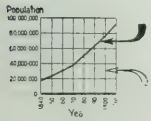



FIG. 10

10. The curve lines of a diagram should be sharply distinguished from the ruling.

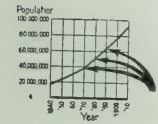



FIG. 11A

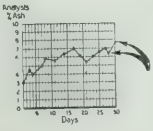



FIG. 11B

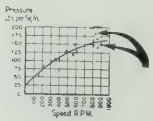



FIG. 11C

11. In curves representing a series of observations, it is advisable, whenever possible, to indicate clearly on the diagram all the points representing the separate observations.

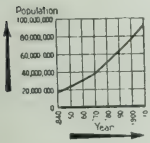



FIG. 12

12. The horizontal scale for curves should usually read from left to right and the vertical scale from bottom to top.

FIG. 13A

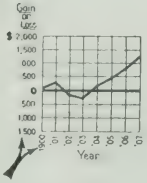



FIG. 13B

FIG. 13C

13. Figures for the scales of a diagram should be placed at the left and at the bottom or along the respective axes.

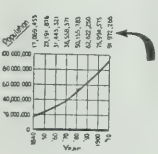



FIG. 14A

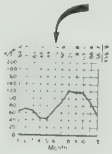



FIG. 14B

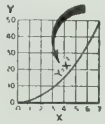



FIG. 14C

14. It is often desirable to include in the diagram the numerical data or formulae represented.

| Year | Population |
|---|---|
| 1840 | 17,069,453 |
| 1850 | 23,191,876 |
| 1860 | 31,443,321 |
| 1870 | 38,558,371 |
| 1880 | 50,155,783 |
| 1890 | 62,622,250 |
| 1900 | 75,994,575 |
| 1910 | 91,972,266 |

FIG. 15

15. If numerical data are not included in the diagram it is desirable to give the data in tabular form accompanying the diagram.

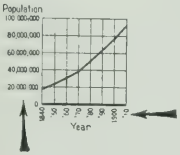
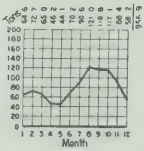



FIG. 16

16. All lettering and all figures on a diagram should be placed so as to be easily read from the base at the bottom, or from the right-hand edge of the diagram as the bottom.




ALUMINUM CASTINGS OUTPUT OF PLANT NO. 2, BY MONTHS, 1914
OUTPUT IS GIVEN IN SHORT TONS
SALES OF SCRAP ALUMINUM ARE NOT INCLUDED

FIG. 17

17. The title of a diagram should be made as clear and complete as possible. Sub-titles or descriptions should be added if necessary to insure clearness.

# THE NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

The first National Exposition of Chemical Industries held at the New Grand Central Palace, New York City, September 20th to 25th, was a notable success and an event of great importance to the evolution of chemical industries in America. The gate records show a total attendance of 63,377.

Expositions of this kind held in other countries have been of the greatest value in standardizing the processes and products of chemical manufacture, improving the relations between the manufacturers and producers of raw materials and developing coöperation between the designers and users of chemical engineering equipment.

The visitors at the show could not help but be impressed with the wonderful advances which have been made in developing the appliances and products shut off by the European war. The achievements of the chemical manufacturers in some lines indicate the possibilities to be attained in other equally important fields which have not received so much attention. The more complete and efficient utilization of many of our natural raw materials for the production of products heretofore manufactured and refined abroad will doubtless be one of the direct results of this Exposition.

Public interest in the industrial achievements of the chemist is a necessary prelude to the more complete development of chemical industries. Financial support cannot be obtained for enterprises which are not understood by the public because, after all, such financial support must be obtained from the investing public. Familiarity with the fields of activity and an understanding knowledge of the possibilities of profits to be made in industrial developments will be a natural sequence of such expositions as this, with the result that financial support will be obtainable for legitimate and deserving enterprises. Furthermore, public knowledge will help to remove the too frequently existing opinion that enterprises involving the use of chemistry are based upon some vague form of black art, and that chemists as a group are in possession of facts and practices unintelligible to the layman. The dissipation of these views is an essential step in the development of chemical industries. Public knowledge alone will solve the problem of obtaining financial support and reduce the dangers of imposition in these enterprises by unscrupulous fakirs. As soon as the public understand the real force and significance of legitimate processes and products of chemical manufacture and learn that the legitimate chemical industries are directed by technical men with high ethical standards, it will become increasingly difficult for the self-styled chemist or chemical engineer to hoodwink investors with questionable enterprises, processes or products of manufacture.

Such expositions will be of inestimable benefit to the chemical manufacturers themselves and to the engineers and chemists engaged in this field of industry. They cannot help but serve a useful purpose in the interchange of knowledge and ideas. The standardization of products, processes and appliances for use in this trade will be a natural result of such expositions, while professional development and manufacturing efficiency will result by natural selection of the best practices shown at such conventions. Progress in chemical engineering will then be built upon the mutual coöperation of many minds, as it is in other branches of engineering, rather than upon the achievements of individuals working alone, as has too often been the case in the past.

Great credit is due to Mr. Chas. F. Roth and Mr. Adriaan Nagelvoort, the managers of this Exposition, for their foresight in selecting this most auspicious time for such an undertaking, and for their great success in the launching of a new enterprise of such immense importance to American chemical industries. Mr. Roth and Mr. Nagelvoort were greatly assisted in their work by Mr. F. W. Payne, manager of the International Exposition Company, under whose auspices the expositions in the New Grand Central Palace are conducted.

### LECTURES AND FILM SHOWS

The lectures and scientific society meetings, as listed in our last issue, were well attended and many of them called forth considerable discussion.

The moving pictures and lantern slides proved interesting and of high educative value.

### GOVERNMENT EXHIBITS

Among the important exhibitors at the Exposition may be included the **United States Geological Survey,** showing charts, transparencies, minerals and a variety of the available raw materials of interest to the chemical industries. Many of these natural products have not been utilized in American factories but were sent abroad to be refined and returned to us in the form of commercial products. The **Bureau of Mines** exhibit included the equipment employed to insure the safety of miners, a demonstration of their process for the production of benzol and toluol from petroleum residues, the manufacture of radium from carnotite and other interesting items. The **Forest Service** exhibit showed many of the results obtained from the Pulp and Paper Laboratory at Madison, recent developments in the manufacture of vegetable colors, etc. The **Bureau of Chemistry** exhibited some of the results of a process recently devised for concentrating fruit juices by freezing, standards for the inspection of naval stores, the utilization of waste products, tanning materials, recovery of tanning waste, etc.

The **Bureau of Soils** exhibit included the method for extracting potash from the Pacific coast kelps; the **Bureau of the Census,** a complete set of the publications and statistics showing the conditions of the various chemical industries; and the **Bureau of Standards,** their work in the standardization of products of chemical industry. The **Bureau of Foreign and Domestic Commerce** showed their methods of collecting and distributing information in regard to foreign trade conditions, and distributed their pamphlets on The Utilization of Atmospheric Nitrogen; The Chemical Industries of Belgium, Holland, Norway and Sweden; Cottonseed Products; Dyestuffs for American Textiles and Other Industries; Foreign Trade in Denatured Alcohol; Foreign Trade in Paints and Varnishes; Foreign Salt Market and Industry; South American Market for Soap; Some Aspects of the Iron and Steel Industry in Europe; The Sugar Industry; The Pottery Industry; Etc.

### TECHNICAL ORGANIZATIONS

Besides the regular exhibits, many of the technical organizations such as the American Chemical Society, American Electrochemical Society, New York Section of the American Chemical Society, Technical Section of the American Pulp and Paper Association, The Chemists' Club, American Institute of Chemical Engineers, American Institute of Mining Engineers, Metallurgical and Chemical Engineering and the Chemical Engineering Catalogue Co., maintained booths for the entertainment and convenience of visitors.

### EXHIBITS OF APPARATUS, CHEMICALS, ETC.

**Abbé Engineering Co. and Beach-Russ Co.**—Full size laboratory Ball Mills, Laboratory Grinder, and a Continuous Grinder.

**American Bitumastic Enamels Co.** and **Cinnakol Chemical Sales Co.**—A disinfectant.

**American Hard Rubber Co.**—Acid Pumps, Piping and Utensils made of special acid-resisting hard rubber.

**Ault & Wiborg Co.**—A business card.

**Automatic Weighing Machine Co.**—Photographs and Catalogs of various machines, all of which were too large for booth display.

**J. T. Baker Chemical Co.**—A full line of analyzed chemicals.

**C. Becker, Inc. and Torsion Balance Co.**—A full line of Torsion Balances, including the new Chain Balance, in which an easily adjusted chain and vernier attachment, reading Mgs. and tenths of Mgs. takes the place of the customary rider.

**Brown Instrument Co.**—A full line of Pyrometers.

**Buffalo Foundry & Machine Co.**—A working model of a compound high-efficiency Vacuum Pump, full-sized improved Aniline Pot, Caustic Pot, Crystallizing Pan, Shelf Dryer, Condensing Body for Nitric Acid, Small Laboratory Vacuum Dryer, a specially designed model of a rotary Drum Dryer, castings of acid-resisting metal, etc.

**Bethlehem Foundry & Machine Co.**—Standard models of acid-proof castings.

**W. Beckers Aniline & Chemical Works**—A line of American coal-tar products including raw materials, reagents, intermediates, finished dyes, and large dyed samples.

**Benzol Products Co.**—Aniline Oil and other simple derivatives of American benzol.

**Condensite Company of America**—Applications of phenol condensation products, such as, in electrical machinery, musical records, valve discs, sporting goods, etc.

**Celluloid-Zapon Co.**—Lacquers for split leather products, glass, wood and metals, and several leather cloths and artificial leathers.

**Duriron Castings Co.**—Full size Acid Pump, acid proof Pans, Pipes, Valves, Centrifugal Pump, and a new Nitric Acid Condenser.

**J. P. Devine Co.**—Full size compound high-efficiency Vacuum Pump, laboratory Shelf Dryer and Condenser, Copper Vacuum Pan, Pressure Autoclave with Agitator, Nitrating Kettle, and a full equipment of recording and direct reading Gauges.

**Dorr-Cyanide Machinery Co.**—Working model of a continuous Causticizor and exhibition models of Dorr Classifiers, Agitators and Thickeners.

**Detroit Range Boiler Co.**—Line of Metal Bilge Barrels.

**E. I. duPont DeNemours Powder Co.**—A full line of explosives, artificial leather, pyroxylin solvents, Waterproof Cements, Wood and Metal Lacquers, Sodium Acetate, etc.

**Driver-Harris Wire Co.**—Resistance wire from Nichrome, Nichrome heating apparatus, and an acid-proof Nichrome dipping basket which had been in daily use for 8 months in fused potassium cyanide.

**Eimer & Amend.**—A full line of Laboratory Apparatus and Supplies.

**Elyria Enameled Products Co.**—Full size enameled Pots and Kettles.

**Chas. Engelhard and Hanovia Chemical Manufacturing Co.**—Full line of Heraeus Platinum, Palladium and Quartz glass apparatus, including Pyrometers, Thermometers, Resistance Thermometers, Multiple Recording Instruments, and the largest display of pure quartz glassware ever put on exhibit.

**Thomas A. Edison**—Benzol derivatives, dye intermediates, Thorium Nitrate, Lithium Compounds, Vanillin, and the Nickel Storage Battery.

**Fairview Fluorspar & Lead Co.**—Fluorspar and related minerals.

**Foote Mineral Co.**—Zirconium ores and Zirconia refractories.

**Geissinger Regulator Co.**—Various types of Industrial Temperature Control Systems.

**General Bakelite Co.**—Phenol condensation products: electrical insulations, sporting goods and novelties, lacquers, etc.

**Gerdes & Co.**—A line of Gears and Dies, Electric Valves, Thermostats, Grates, etc.

**Glens Falls Machine Works**—A full size Sulfur Burner

**Emil Greiner & Co.**—A full line of specially blown laboratory glassware, automatic Respirator, Gas-tight Rubber Goggles, etc.

**General Chemical Co.**—A baking powder.

**F. C. Huych & Sons**—A full line of woolen Filter Cloths.

**Huff Electrostatic Separator Co.**—Electrostatic Separator for Zinc ores.

**Heller & Merz Co.**—An exhibit of Ultramarine and other paint pigments, together with a line of coal-tar intermediates and finished dyes made from American materials.

**Hardinge-Conical Mill Co.**—A working model of a Conical Mill.

**International Filtration Corporation**—Two models of continuous Rotary Vacuum Filters and a demonstration model of a Vacuum Leaf Filter.

**International Instrument Co.**—Laboratory and plant Centrifugals and shakers of all types.

**Kelly Filter Press Co.**—A model of the Kelly Filter Press (E. E. Lungwitz, representative).

**Kieselguhr Company of America**—Models and demonstrations of insulation, filtering and refractory products made from American kieselguhr.

**L. O. Koven & Bro.**—Full size Fractionating Still and Water Still.

**Lenz & Naumann**—A line of chemical and laboratory apparatus.

**Lead Lined Iron Pipe Co.**—Display of lead-lined pipe, fittings, and chemical apparatus.

**Mogul Factors**—A line of acid-, alkali- and water-resisting paints and special materials.

**Monsanto Chemical Works**—Exhibit of Acetphenetidin, Caffeine, Chloral Hydrate, Coumarin, Phenolphthalein, Saccharin, Vanillin, and Sodium, Potassium and Calcium Glycerophosphates (made by this company only).

**J. L. Mott Iron Works**—Full size enameled Iron Kettles, laboratory Sinks, etc.

**Macbeth-Evans Glass Co.**—A full line of laboratory heat-resisting chemical glassware now being made to supply the lack of such ware from Bohemia and Germany.

**Merck & Co.**—An exhibit of Blue-Label Reagents and chemicals and a display of American Benzol and its simple derivatives.

**National Aniline & Chemical Co.**—An exhibit of American coal-tar intermediates and dyed products, including Yarns, Paper, Cotton, Wool, Silk, Leather, Hats, etc.

**Norton Company**—A full line of laboratory apparatus and refractories made from alundum, with demonstrations of their use.

**Pfaudler Co.**—Full size glass-enameled steel tanks, etc.

**Raritan Copper Co.**—Exhibit illustrating extraction of Copper, with the intermediates and by-products of its preparation from the ore: including, Silver, Nickel Sulfate, Copper Sulfate, Tellurium and the various forms of Selenium.

**Research Corporation**—A working model showing the Cottrell process for the precipitation of smoke and fumes, with samples of the products collected in actual installations. (American Transformer Co. apparatus used.)

**Swenson Evaporator Co.**—Full size Vacuum Pans, rectangular and cylindrical, with Jet Condenser Pump.

**Sweetland Filter Press Co.**—Working model of Sweetland Filter Press, with necessary vacuum pump, receivers, etc. Also a second model for exhibition purposes.

**Schaum & Uhlinger, Inc.**—Full size Centrifugals.

**Ernest Scott & Co.**—Plans and photographs of chemical plants for solving problems of Drying, Distilling, Solvent Extractions, Trade Waste Recoveries, etc.

**Sharples Specialty Co.**—Full size models of high-speed Centrifugals.

**Standard Aniline Products, Inc.**—Exhibit of special aniline products: Beta naphthol, Paranitraniline, Mono-sulfonic acid, etc.

**Schaeffer & Budenberg Mfg. Co.**—A full line of Measuring and Recording Instruments.

**Stamford Mfg. Co.**—A full line of fast vegetable dyes for blacks and the paler shades.

**Sowers Mfg. Co.**—Full size Seamless Steam-jacketed Kettles, Vacuum Pans, etc.

**Schutte & Koerting Co.**—A working model of the Bihn-Jones automatic apparatus for elevating liquids and a line of siphons, valves and chemical fittings.

**Tennessee Power Co.**—Lantern slides, pictures and maps illustrating their power production and distribution in the South.

**Tolhurst Machine Works.**—An operating model of a large-size overhead-drive Centrifugal and a smaller exhibition model of a bottom-drive Centrifugal.

**Thwing Instrument Co.**—A full line of Pyrometers and Pyrods.

**Troegerlith Tile Co.**—Fireproof composition flooring, and a special cork composition flooring.

**Toch Bros.**—A line of special paints, acid-proof paints, chemical driers, pigments, cement fillers, and a set of samples of the Barium compounds now being made at their Tennessee plant.

**Union Sulphur Co.**—Samples of the commercial forms of American Sulfur.

**U. S. Smelting, Refining & Mining Co.**—Samples showing the complete metallurgy of Copper, its mining, smelting and refining together with the by-products: Silver, Gold, Arsenic, Platinum, Palladium, Bismuth, Cadmium (from lead smelting), Hydrofluoric Acid, Antimonial Lead, Brass and special spelters.

**United Gas Improvement Co.**—Line of samples of coal-tar products and intermediates prepared therefrom.

**United Lead Co.**—Lead-lined brass and copper covered and lined Pipe, acid-proof Valves and Fittings, Lead Wool, Sheet and similar products.

**Valley Iron Works**—A full size improved Sulfur Burner.

**Wilson-Maeulen Co.**—A line of Recording, Direct-reading Pyrometers, Thermocouples, etc.

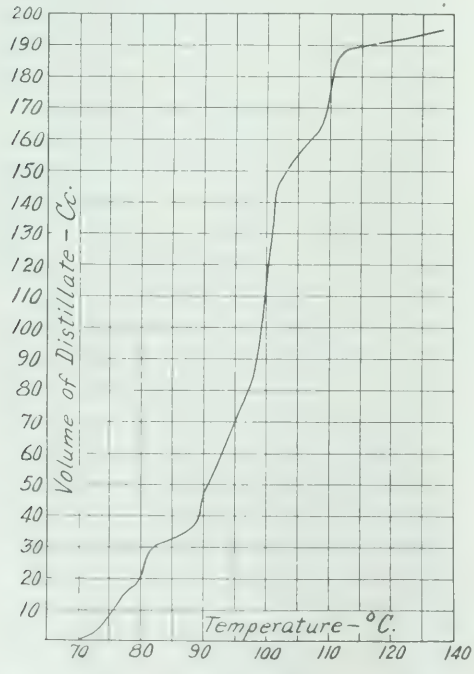
**Werner & Pfleiderer Co.**—Full size models of Mixing, Kneading and Incorporating machinery for the Celluloid, Carbon and Rubber industries.

**Zaremba Co.**—Exhibit lost, presumably on account of recent New Jersey strikes.

# NOTES AND CORRESPONDENCE

## EXAMINATION OF A CONDENSATE FROM CARBURETTED WATER GAS

A sample of a condensate which was formed during a very cold winter several years ago in the service pipes of the local gas works has been examined by us. The liquid was of a pale amber color, with rather a sharp odor and a specific gravity of 0.740. The plant manufactures carburetted water gas, using anthracite coal in the generator, and Pennsylvania crude petroleum in the carburetor.




The liquid proved to be composed of low boiling point compounds, 95 per cent distilling below 120° C. and 99 per cent below 130° C. The sample was fractionated carefully in order to locate individual compounds in substantial amounts, which would make their presence known by irregularities in a curve plotted from the results.

The fractionation was made using a 12-pear still head, and collecting the distillate in 2° fractions. The accompanying curve shows the boiling point to rise very regularly with the exception of breaks at 80 to 82°, 98 to 100° and 110 to 112°. In order to obtain an idea of the relative amount of unsaturated hydrocarbons in the different fractions the bromine absorption was determined in the combined distillate for each 10°. Excess of a $N/10$ solution of bromine in carbon bisulfide was allowed to react in the dark on 1 cc. of each of the undermentioned fractions for 15 minutes. The excess of bromine was titrated with $N/10$ sodium thiosulfate.

| Fractions | G Br absorbed by 1 cc. | Fractions | G Br absorbed by 1 cc. |
|---|---|---|---|
| 70–80° | 0.00950 | 110–120° | 0.00820 |
| 80–90° | 0.00930 | 120–130° | 0.01580 |
| 90–100° | 0.00875 | | |
| 100–108° | 0.00827 | Original | 0.0114 |

If we assume that the unsaturated is due to dodecylene boiling at 96° the percentage of unsaturation is

$$11.4 = 168.160 \times 1/740 = 1.62 \text{ per cent.}$$

The fraction boiling at 108–112° was redistilled and 1 cc. of that which came over at 111° was nitrated and toluene identified. The whole fraction 108–112 compared very well with commercial toluene.

The paraffins and olefins were estimated by use of dimethyl sulfate, which gave 77.5 per cent paraffins and olefins undissolved.

The composition of the sample thus works out as follows:

| Paraffins | Olefins | Aromatic | Total per cent |
|---|---|---|---|
| 75–88 | 1.62 | 22.5 | 99.90 |

The percentage distilling at 78 to 82° was about 12 per cent, corresponding to benzene mainly; that at 108 to 112, corresponding to commercial toluene, being about 10 per cent.

The above results lead the author to conclude that the possibility of producing toluene on a commercial scale during the manufacture of caburetted water gas may be not unreasonable. It would probably involve some method of condensing or ab-

sorbing the toluene along with the benzene and other compounds, and the subsequent separation of these compounds, retaining the toluene and returning the others for illuminating and heating purposes.

GORDON HALL OF CHEMISTRY
KINGSTON, ONTARIO, May 10, 1915 E. T. STERNE

## THE REMOVAL OF PHOTOGRAPHIC DEVELOPING AND FIXING AGENTS FROM FILMS AND PRINTS

The removal of developing, fixing and other reagents used in photography from films and prints by washing has been, as usually performed, very unscientific. It has been a "hit or miss" method, or wasteful of time and water. Examination of the films and prints of professionals, amateurs and novices very often shows products, which in the course of time, have become stained, discolored or otherwise changed by chemicals left in them as a result of incomplete washing. Books on photography, photographic journals, chemical journals and patent literature contain many references to developing and fixing agents, intensifiers, etc., but little has been printed concerning tests for detecting impurities during or after washing.

Directions for washing usually contain statements that the films and prints should be washed in a certain number of changes of clear, distilled or hydrant water, or that they should be immersed in running water for a certain period of time, the prints to be separated when they become matted together. Often much time is wasted, and when the wash water is warm and the time of washing long the films or prints are frilled or otherwise injured.

Insufficient washing becomes evident after the work is done, and sometimes years elapse before it becomes apparent by discolorations, stains and other less common phenomena. Occasionally the trouble is not due to incomplete washing, but such cases are comparatively rare.

C. Hauberrisser[1] published an article concerning the removal of hypo by washing at ordinary and elevated temperatures. Starch iodide was the indicator, and 1 cc. of wash water was used to 5 sq. cm. of print surface. Hauberrisser found that 3 successive washings of 5 minutes each in water at 50–60° C. or 6 washings in cold water eliminated practically all hypo that could be washed out except by prolonged immersion, in either warm or cold water. He also states that whether this residue is injurious can be determined only by experiments of long duration. To save time, therefore, warm water is sometimes used, with the addition of formalin as a hardening agent.

H. Lüppo-Cramer,[2] concerning "Time Required for Hypo Removal," states that while 10 minutes' washing eliminated the hypo from gelatin films fixed in a 10 per cent hypo bath, 20 to 25 minutes were required when an acid hypo bath was used. Cramer considered the difference due not so much to diffusion processes as to an adsorption by the gelatin of acid bath compounds which acted as tanning agents.

A number of experiments made by the writer, using different common reagents, showed that a 5 per cent silver nitrate solution was a satisfactory and generally available indicator to detect the presence of the common ingredients of developing and fixing solutions. Black, brown or flesh-colored precipitates are or can be formed by the action of silver nitrate solution upon these solutions, either alone or combined. Some hardening reagents, such as citric acid and alum, and a few other compounds used in photography do not yield precipitates or colored solutions under practical working conditions. The test was usually made by adding a few drops of silver nitrate solution to the wash water from which the films, plates or prints were last removed. Washing that was considered thorough in running water in enameled steel pans or in porcelain or glass trays in a sink often gave positive tests when the objects washed were transferred to a porcelain dish, washed once more, and the wash water tested.

The procedure in washing finally adopted by the writer, which has always produced unchanging films and prints, even when examined after several years, is as follows: Plates, films, filmrolls or prints, when removed from the fixing bath, are placed in running hydrant water in trays or dishes in the sink. They are then completely separated and transferred every 2 or 3 minutes to another clean tray of running water, and the water in the tray from the last washing is tested with a few drops of 5 per cent silver nitrate solution. The washing is thus continued until the last wash water yields no pale or yellowish brown coloration, which can readily be seen in white light in a white tray. This wash should undergo no visible change when tested, but should remain perfectly clear. The silver nitrate, of course, must never be added to the wash water containing the films or prints.

Where no running water is available, changes of water may be employed, and where the running water is too impure, successive changes of distilled or rain water may be used. The time of washing required in this procedure, even in warm parts of the country using hydrant water, does not cause troublesome softening of hardened films or prints.

The writer finds it convenient to dry prints by spreading them upon sheet filter paper and then smoothing them, when thoroughly dry, in packs of the same size, by pressing them in a letter-copying press.

It is hoped that, by following the procedure outlined above, better and more certain results can be secured, water and time can be saved, and thus the common directions for washing negatives and prints will be made more definite and also more satisfactory and scientific.

CHEMICAL LABORATORY
FLORIDA STATE COLLEGE FOR WOMEN
TALLAHASSEE, JULY 15, 1915 C. A. BRAUTLECHT

## THE HARDWOOD DISTILLATION INDUSTRY IN AMERICA

*Editor of the Journal of Industrial and Engineering Chemistry:*

It was not noticed that Mr. Chute had communicated his remarks (THIS JOURNAL, **1915,** p. 55) read by him in the discussion of our paper before the American Institute of Chemical Engineers at Philadelphia, for publication simultaneously with our paper [THIS JOURNAL, **7** (1915), 47]. We had asked him to send us a copy of his remarks for reply, if necessary, but received none. In due time we received a copy from the Secretary of the Institute and replied to the same for publication in the, as yet unissued, Transactions of the Institute.

Mr. Chute in his discussion of our paper has added some interesting facts and details, with most of which our experience is in perfect agreement, and in fact many more interesting details could be readily given.

Mr. Chute refers to the isolated American case which we cited, of the Vertical Removable Retort-Crane system of Wood Distillation, as being a system in extended use in France. This we understood to be true. It has been used in other countries also, but not as extensively as in France. The experience of most men, as well as ourselves, who have been connected with this industry, seems to indicate that the one cited by us was the sole installation of this type in this country, and we so stated. Since writing the paper it has come to our attention, however, that in the days of the early charcoal burning for iron production in New Jersey and Maryland, a French company near Havre de Grace, Maryland, installed a by-product charcoal plant which is said to have been of this French type. The remains of the plant are said to be in existence but we have not yet been able to verify these statements concerning this plant.

[1] *Phot Rundschau*, **24**, 91; *Chem Abs*, **4**, 1718
[2] *Brit. J Photo*, **59**, 638; *Chem Abs*, **6**, 3371.

If it did exist it was probably built in the early part of the last century, and may antedate all the plants which we have cited.

Mr. Chute is correct, in the main, when he states that it is the gas *from* the wood which burns in the charcoal kiln for the production of the carbonizing temperature, but it certainly is not erroneous to consider that this gas was a *part* of the weight of the original wood.

The statement by Mr. Chute with reference to the returns from kiln-plant investment is evidently merely intended to call attention to the low initial cost of kiln-plant erection, for it must not be forgotten that the kiln gives but scanty returns —figured on the basis of the operating capital in the shape of the wood consumed. This so far overcomes the advantage of low initial cost in the kiln plant that many kilns are gradually being replaced by the more modern and expensive oven plants to secure this increased by-product recovery, and these oven plants are not only more profitable but they are more in the interests of conservation.

The explanation that western plants do not recover distillates as efficiently as eastern plants is not an adequate explanation of the lower western yields to which we called attention, for inefficiency in operation is not characteristic of any one district, as a number of such plants in New York and Pennsylvania will testify. Our comparison was between well operated plants, western as well as eastern. On the whole, there is ground for believing that there are more skilled operators in the east than in the west, but the plants in the west being newer are of better design.

Our own experience makes us more optimistic than Mr. Chute in the matter of future improvement in yields though we agree that the industry is reasonably efficient. This same experience also makes us differ in the matter of acetic acid production for the reasons already given in the original article.

Regarding the tar mentioned by Mr. Chute it should be stated that the output from a single plant is quite small and the material would have to be stored for some time to accumulate sufficient to make shipment feasible in the great majority of plants. Those familiar with the coal-tar industry know the bother which small coal-tar producing plants are to the coal-tar industry. It is the large tar producers which have assisted in making this coal-tar industry grow as it has done. It should be remembered also that this tar from wood is an *acid* tar while coal tar is an ammoniacal material. The wood tar can scarcely ever be made to cease being acid or developing acid properties. It is very soluble in any alkali and this seriously affects it as a water-proofing material for many purposes. It is not nearly so insoluble in water itself as coal tar and the American coal-tar industry is essentially a water-proofing industry. Upon distilling or heating it develops quite different odors from coal tar and odors which are unpleasant and of a choking character. One becomes accustomed to coal tar but wood tar would be quite different in this respect. Wood creosote oil, while it is actually used as a wood preservative, is again an entirely different substance from coal-tar creosote, some portions of it being entirely miscible with water which makes it much inferior to the coal-tar product. In spite of this difficulty, however, much more has actually been done with the tar than would appear from discussion and *much* money has been lost, too, in experimental tar utilization plants. There can be no question, however, but that more use will be found for this product in the future as the prices of various well known materials now used in the arts increase. Some of the oils from this tar have been used for a great while in shingle-stains and paints though the odor mentioned is against them. The creosote could, undoubtedly, be used for preserving such things as meat if it were permissible. Rope is actually not preserved with this *hardwood creosote* at all, as claimed in the discussion, but with the *tar* from *pine wood* which is a different kind of material entirely. This brings out another matter of considerable practical importance, *i. e.*, that the nature of the tar varies enormously with the kind of wood. This gives us the difficulty, though to a greatly exaggerated extent in the case of wood tar, which the coal-tar distiller finds when he is bothered with tar from varying kinds of coal.

E. H. FRENCH
JAMES R. WITHROW
OHIO STATE UNIVERSITY
COLUMBUS, July 16, 1915

## THE CHEMICAL SOCIETIES IN NEW YORK CITY 1915-1916 SEASON—RUMFORD HALL, THE CHEMISTS' CLUB

American Chemical Society—October 8th.

Society of Chemical Industry—October 22nd.

American Chemical Society—November 12th.

Society of Chemical Industry—November 19th.

JOINT MEETING—American Chemical Society, Society of Chemical Industry and American Electrochemical Society—December 10th.

Society of Chemical Industry: Perkin Medal Award—January 21st.

JOINT MEETING—American Electrochemical Society, American Chemical Society and Society of Chemical Industry—February 21st.

American Chemical Society: Nichols Medal Award—March 10th.

Society of Chemical Industry—March 24th.

Society of Chemical Industry—April 21st.

JOINT MEETING—Society of Chemical Industry, American Chemical Society and American Electrochemical Society—May 19th.

American Chemical Society—June 9th.

## PLATINUM THEFT

*Editor of the Journal of Industrial and Engineering Chemistry:*

Between the 19th and 21st of June there were stolen from our laboratory ten platinum dishes about three inches in diameter and weighing around fifty grams each.

I shall greatly appreciate any help that may be given in locating these.

B. W. KILGORE
DEPARTMENT OF AGRICULTURE
RALEIGH, N. C., July 17, 1915

## THE MANUFACTURE OF GASOLINE AS A BY-PRODUCT FROM HIGH BOILING PETROLEUM OILS, ETC.—A CORRECTION

In my article under the above general title, THIS JOURNAL, **7** (1915), 737, the following corrections should be made:

P. 739, col. 2, line 24—"Dry test" should be "Dr. test;"
lines 29 and 33—"Above" should be "Over;"
line 32—"64.2" should be "52.2."

P. 740, col. 2, line 22—"Primary distillate" should be "Primary residual oil;"
line 41—"Dry test" should be "Dr. test;"
lines 45 and 48—"Above" should be "Over."

P. 741, col. 1, line 35—"Primary distillate" should be "Primary residual oil;"
line 52—"Dry test" should be "Dr. test."

A. M. MCAFEE
BAYONNE, NEW JERSEY
September 10, 1915

# PERSONAL NOTES

Edward B. Moore, former United States Commissioner of Patents, died at his home in Washington, D. C., on September 6th, in his sixty-fourth year. From the time when he became a page in the United States Senate in 1866, his whole life was spent in Government employ. He was with the Patent Office for thirty years and was Commissioner from 1907 until 1913, when he left to become a member of the patent law firm of Moore and Clark, of Washington. In addition to his routine connection with the Patent Office, Mr. Moore succeeded in a number of delicate diplomatic missions to other countries, during which he made permanent arrangements for safeguarding American patents.

Mr. Moore was a former President of the District of Columbia Society of the Sons of the American Revolution, a member of the Taft Chapter of the fraternity of Phi Alpha Delta, and a member of the Cosmos and Washington Country Clubs.

The following is the program of papers for the 28th General Meeting of the American Electrochemical Society, held in San Francisco, Sept. 16 to 18, 1915:

"Treatment of Silver Furnace Fumes by the Cottrell Process"—Chas. H. Aldrich.
"Collection and Therapeutic Use of Radium Emanation"—R. S. Bosworth.
"Electrolytic Precipitation of Gold, Silver and Copper from Cyanide Solutions"—G. H. Clevenger.
"Solution Stratification as an Aid to the Purification of Electrolytes"—F. R. Pyne.
"Electrolysis of Copper Sulfate Liquors Using Carbon Anodes"—Lawrence Addicks.
"Use of the Flaming Arc in Paint and Dye Testing"—W. R. Mott.
"Radiography of Metals"—W. P. Davey.
"Electrolytic Antimony Refining"—Anson G. Betts.
"Electrodeposition of Nickel"—C. W. Bennett, C. C. Rose and L. G. Tinkler.
"Power for Electrochemical Industries"—D. R. Lyon and R. M. Keeney.
"Peptonization of Chromium Oxide"—W. D. Bancroft.
"Synthesis of Phenylhydroxylamine"—F. M. Frederiksen.
"Electric Steel Costs"—F. T. Snyder.
"Electric Furnace Melting of Ferro-Alloys"—R. S. Wile.
"Heat Losses from an Electric Steel Furnace"—W. H. Wills, Jr., and A. H. Schuyler.
"Electrochemical Possibilities on the Pacific Coast"—J. W. Beckman.
"Electromotive Forces"—W. D. Bancroft.
"Single Potentials in the Silver Cyanide Plating Bath, as Affected by Its Composition and Concentration"—F. C. Frary and R. E. Porter.
"The Thermal Insulation of High Temperature Equipment"—P. A. Boeck.
"Roasting and Leaching Concentrator Slimes Tailings"—L. Addicks.
"Overhead Electrolysis and Porcelain Strain Insulators"—S. L. Foster.

The Secretary of the Navy has announced the membership of the Naval Advisory Board of Inventions which consists of twenty-three members, including Mr. Thomas A. Edison, who was selected by Mr. Daniels to serve as the presiding officer of the Board. The other twenty-two members of the Board, who were chosen by the eleven scientific societies invited by the Secretary, are:

*American Chemical Society*—Willis R. Whitney and Leo H. Baekeland.
*American Electrochemical Society*—Joseph W. Richards and Lawrence Addicks.
*American Institute of Electrical Engineers*—Frank J. Sprague and B. G. Lamme.
*American Mathematical Society*—Robert S. Woodward and Arthur G. Webster.
*American Society of Civil Engineers*—Andrew M. Hunt and Alfred Craven.
*American Aeronautical Society*—Matthew B. Sellers and Hudson Maxim.
*The Inventor's Guild*—Peter C. Hewitt and Thomas Robbins
*American Society of Automobile Engineers*—Andrew L. Riker and Howard E. Coffin.
*American Institute of Mining Engineers*—William L. Saunders and Benjamin B. Thayer.
*American Society of Mechanical Engineers*—William L. Emmet and Spencer Miller.
*American Society of Aeronautic Engineers*—Henry A. W. Wood and Elmer A. Sperry.

Van. H. Manning, of Holly Springs, Mississippi, has been appointed by President Wilson to be Director of the Bureau of Mines. The appointment fills the vacancy caused by the death of Dr. J. A. Holmes. Mr. Manning was appointed to the Bureau of Mines when it was created in 1910, and was made Assistant Director in the following year. Since June 1st, when Dr. Holmes was forced by failing health to suspend work, he has been in charge of the bureau.

Thomas A. Edison was the guest of honor at a dinner given at the Chemists' Club in New York City by William F. Hoffmann, sales agent for the new Edison aniline dye products. A number of chemists interested in the American production of dye products from coal tar were present, and the new processes for manufacturing dyestuffs were discussed. After the dinner the guests went to the National Exposition of Chemical Industries at the Grand Central Palace. Among those at the dinner were Charles H. Herty, M. C. Whitaker, Charles Baskerville, Major Allegart, J. W. Aylesworth, Mr. Meadowcroft, Hugo Schweitzer, T. J. Parker, E. G. Love and F. S. Low.

The program of lectures of the Franklin Institute for 1915–1916, is as follows:

*Oct. 7, 1915*—B. T. Brooks, Mellon Institute of Industrial Research: "The Decomposition of Petroleum Hydrocarbons by Heat and Its Application to the Motor Fuel Problem."
*Oct. 14, 1915*—Ulric Dahlgren, Princeton University: "Production of Electricity by Animals."
*Oct. 20, 1915*—H. O. Hofman, Massachusetts Institute of Technology: "Recent Progress in the Metallurgy of Copper."
*Oct. 28, 1915*—F. K. Cameron, U. S. Department of Agriculture: "The Development of a Dynamic Theory of Soil Fertility."
*Nov. 4, 1915*—C. H. Herty, University of North Carolina: "Turpentine Industry in the Southern States."
*Nov. 11, 1915*—J. C. McLennan, University of Toronto: "Spectra, Their Origin and Some of Their Characteristics."
*Nov. 17, 1915*.—A. A. Michelson, University of Chicago: "On the Ruling of Diffraction Gratings."
*Dec. 2, 1915*—J. D. Ball, General Electric Company: "Magnetic Investigations of Iron and Steel."
*Dec. 9, 1915*—W. F. M. Goss, University of Illinois: "Smoke as a Source of Atmospheric Pollution."
*Dec. 15, 1915*—A. C. Abbott, University of Pennsylvania: "The Transmissibility of Diseases, and the Public Health."
*Jan. 6, 1916*—F. H. Wagner, The Bartlett Hayward Company, Baltimore: "Coal Gas Residuals."
*Jan. 13, 1916*—H. C. Sherman, Columbia University: "Some Problems in the Chemistry of Nutrition."
*Jan. 19, 1916*—M. E. Stone, The Associated Press: "Supplying the World with News."
*Jan. 27, 1916*—Lt.-Col. J. E. Hoffer, U. S. War Department: "Modern Ordnance."
*Feb. 3, 1916*—A. M. Greene, Rensselaer Polytechnic Institute: "The Development of the Pumping Engine."
*Feb. 10, 1916*—Charles Baskerville, College of the City of New York: "Refining of Animal and Vegetable Oils."
*Feb. 16, 1916*—G. E. de Schweinitz, Philadelphia: "Drug and Occulation Amblyopias."
*Feb. 24, 1916*—W. D. Uhler, State Highway Department, Pennsylvania: "Highway Problems of the State of Pennsylvania."
*Mar. 2, 1916*—G. A. Rankin, Carnegie Institution of Washington: "Portland Cement."
*Mar. 9, 1916*—G. C. Whipple, Harvard University: "The Element of Chance in Sanitation."
*Mar. 15, 1916*—A. L. Day, Carnegie Institution of Washington: "Volcanic Eruptions."
*Mar. 23, 1916*—Harold Pender, University of Pennsylvania: "Recent Developments in Electrical Apparatus."
*Mar. 30, 1916*—G. K. Burgess, U. S. Bureau of Standards: "Some Problems in Physical Metallurgy at the Bureau of Standards."
*Apr. 6, 1916*—C. J. Gadd, American Iron and Steel Company, Lebanon, Pa.: "Use of Powdered Coal in Metallurgical Processes."
*Apr. 13, 1916*—C. W. Waidner, U. S. Bureau of Standards: "Heat Measurement as Related to the Industries."
*Apr. 19, 1916*—C. P. Steinmetz, General Electric Company: "Scientific Research in Relation to the Industries."
*Apr. 27, 1916*—W. V. Turner, Westinghouse Air Brake Company: "The Vital Relation of Train Control to the Value of Steam and Electric Railway Properties."
*May 17, 1916*—Conferring of the Franklin Medal. Address by the President of the Institute.

The first regular monthly meeting of the Detroit Chemists for the season of 1915–1916 was held on September 16th. Mr. C. A. Jennings, of Chicago, presented a paper on "Disinfection of Public Water Supplies," illustrated with lantern slides. The October meeting, which is to be "Ladies' Night," will be held on the 21st; Dean Coulter, of Purdue University will speak. The November meeting will be held on the 18th with Dr. Burrage,

of the Biological Department of Eli Lilly & Company, as speaker. The new President of the Detroit Section is Mr. C. T. Bragg, a graduate of Purdue University in 1906 and the Technical Director of Berry Bros., Inc., Detroit, Mich. He is a member of the American Society for Testing Materials, the American Institute of Chemical Engineers, the American Institute of Metals and the American Chemical Society.

The British Minister of Munitions has constituted a Munitions Inventions Branch of the Ministry, with Mr. E. W. Moir as Comptroller. For the present the branch is located in Armaments Building, Whitehall Place and will have the duty of considering projects for inventions relating to munitions for warfare on land or matters appertaining thereto. The Comptroller and staff of the branch will be assisted in their work of examination, and, if thought necessary, in the investigation and development of any projects that may be considered worthy of being developed, by a panel of honorary scientific and other experts. The following gentlemen have accepted Mr. Lloyd George's invitation to act on this panel: Colonel Goold Adams, Mr. Horace Darwin, Mr. Macdougal Duckham, Mr. W. Duddell, Mr. Sebastian Z. de Ferranti, Professor Glazebrook, Sir Robert Hadfield, Professor J. S. Haldane, Colonel N. B. Heffernan, Sir Alexander Kennedy, Mr. F. W. Lanchester, Professor A. P. Laurie, Professor Vivian Lewes, Mr. Michael Longridge, Mr. W. H. Maw, Sir Hiram Maxim, Captain Moore, Sir Henry Norman, Mr. F. G. Ogilvie, Major-General G. K. Scott-Moncrieff, Mr. Wilfrid Stokes, Mr. James Swinburne, Sir Joseph John Thomson, Mr. A. J. Walter, Mr. C. J. Wilson.

Mr. F. W. Harbord has been appointed honorary adviser in metallurgy to the British Munitions Committee, and is now devoting his whole time to the work.

The Gold Medal ofthe Company of Dyers, London, has been awarded to Professor Arthur G. Green, University of Leeds, and Mr. W. Johnson, a research student of the University of Leeds, for an investigation into the constitution of aniline black. The medal is awarded annually on the recommendation of the Society of Dyers and Colourists.

A special joint committee of the London Chemical Society and the Society of Chemical Industry has been nominated to consider and advise with regard to the technical aspect of any inventions and problems which may be submitted to these Societies.

Dr. L. Chas. Raiford, of the department of chemistry of the University of Chicago, has been elected professor of chemistry in the Oklahoma Agricultural and Mechanical College.

The Braun Laboratory Appliances, consisting of crushers, pulverizers, samplers, furnaces, burners and other equipment, have been awarded a Gold Medal at the Panama-Pacific International Exposition at San Francisco. The exhibit was in conjunction with the Bureau of Mines who have maintained a working laboratory for research work that has proven extremely valuable and interesting to the many visitors at the Exposition. In addition to the Gold Medal, The Braun Corporation of Los Angeles and the Braun-Knecht-Heimann Co., of San Francisco, have been awarded Silver Medals as collaborators. The above awards are not the first ones received by the Braun Appliances, Gold Medals having been awarded at the Expositions at St. Louis, Jamestown, Portland and Bendigo, Australia.

Dr. Frederick L. Dunlap, formerly a member of the Board of Food and Drug Inspection of the Department of Agriculture at Washington, D. C., has opened up an office as a Consulting Chemist, in the Monadnock Block, Chicago.

The second meeting of the Missouri Valley Public Health Association was held in Kansas City, Mo., at the Coates House on the 28th and 29th of September.

Dr. Frederick H. Getfman, associate professor of chemistry in Bryn Mawr College, has resigned, and Dr. James Llewellyn Crenshaw of the Geophysical Laboratory, Washington, has been appointed associate in physical chemistry.

Dr. E. K. Bolton, formerly Sheldon Fellow from Harvard University to the Kaiser Wilhelm Institute at the University of Berlin, has accepted a position in the Research Laboratory at the Experimental Station of the du Pont de Nemours Powder Company, Wilmington, Del.

The Joseph A. Holmes Chair of Safety and Efficiency Engineering has been established in the Colorado School of Mines as a memorial to the late Dr. Joseph A. Holmes, Director of the United States Bureau of Mines.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### BUREAU OF CORPORATIONS

**Conditions in the Healdton Oil Field.** 116 pp. Paper, 15 cents. This report is made on an investigation required by the United States Senate in order to determine the cause of reduction in price of crude oil in the "Ardmore" oil field, and in particular to determine "whether corresponding changes had been made in the prices of the finished products manufactured from such oil, and whether discriminations were practiced on the part of the company as between different producers of oil in the field, especially against the oil on Indian allotments."

Among other matters information is given as to the properties of the oil and the fractions obtainable on distillation. Sections are devoted to the specific gravity, the products obtainable, the manufacture of lubricants, the quantity of sulfur, and the comparative value of the products of this and other Oklahoma crude oils. A large amount of data is given of crude-oil prices and prices of the refined products

### BUREAU OF LABOR STATISTICS

**Wages and Hours of Labor in the Iron and Steel Industry, 1907 1913.** Bulletin 168 328 pp Paper, 35 cents

### UNITED STATES GEOLOGICAL SURVEY

**The Production of Fuller's Earth in 1914.** Jefferson Middleton. Separate from Mineral Resources of the U. S. 1914. Part II, pp. 35–40. "The fuller's earth industry showed considerable progress in 1914, the marketed production increasing in both quantity and value, the former from 38,594 short tons in 1913 to 40,981 short tons in 1914, and the latter from $360,750 in 1913 to $403,646 in 1914, an increase of 2,387 tons in quantity and of $33,896 in value."

The imports during the same period showed even a larger increase, the total amounting to 25,000 short tons, 94 per cent of which was wrought or manufactured earth. The following summary of the uses of fuller's earth is of particular interest:

"Fuller's earth obtains its name from its original use in fulling cloth. Little is now used in this country for this purpose, it being used principally in bleaching, clarifying, or filtering fats, greases, and oils. It is also used in the manufacture of pigments for printing wall papers, for detecting certain coloring matters in some food products, and as a substitute for talcum powder. The common practice in filtering mineral oils is to dry the earth carefully and then to grind it to suitable sizes and run it into long cylinders, through which the crude, dark mineral oils are allowed to percolate slowly. As a result, the oil that comes out first is perfectly water-white and much thinner than that which follows. The oil is allowed to percolate through the earth until its color reaches a certain maximum shade.

"The process of filtering vegetable oils is radically different. The oil is heated in large tanks beyond the boiling point of water, from 5 to 10 per cent of its weight of fuller's earth is added, and the mixture is vigorously stirred and then filtered off through bag filters. The coloring matter remains with the earth, the filtered oil being of a pale straw color, provided the operation has been performed with sufficient care."

**Fuel Briquetting in 1914.** EDWARD W. PARKER. Separate from Mineral Resources of U. S., 1914. Part II, pp. 57–60. There were produced in the United States in 1914, 250,000 short tons of briquets valued at $1,500,000. This was an increase of nearly 40 per cent in quantity and 15 per cent in value as compared with 1913. The raw materials and binders employed are discussed. The following two statements are of particular interest: "The failure to make more substantial progress in the production of briquets from anthracite is probably due to the fact that an absolutely smokeless product has not been obtained, and consumers accustomed to smokeless anthracite object even to the small amount of smoke emitted from the briquets.". . . . . "The chief objection to the use of pitch binders is the emission of smoke when first fired, which results in the deposition in the flues and on other surfaces of a tarry soot, which is difficult to remove."

**The Production of Mica in 1914.** DOUGLAS B. STERRETT. Separate from Mineral Resources of the U. S., 1914. Part II, pp. 67–77. The discussion of the occurrence of mica and of the mica industry shows that this ore finds very little application in the chemical industries.

### BUREAU OF STANDARDS

**An Aneroid Calorimeter.** H. C. DICKINSON AND N. S. OSBORNE. Scientific Paper 247. 26 pp. This includes a description and discussion of the principles in design of an aneroid calorimeter which differs from instruments of this general class in the fact that both a thermometric element and the heating element are embedded in the mass of metal itself. The method of calibration is described in detail and data are given on determinations of the specific heat of water.

**Interference Measurements of Wave Lengths in the Iron Spectrum (λ = 2851 3701).** KELVIN BURNS. With Notes on: **Comparison of Lengths of Light Waves by Interference Methods and Some Wave Lengths in the Spectrum of Neon Gas.** W. F. MEGGERS. Scientific Paper 251. 27 pp.

**The Relation of the Horsepower to the Kilowatt.** Circular No. 34, 3rd Edition. 16 pp. "It is considered desirable that the watt and kilowatt be used as the units of power, whenever possible, for all kinds of scientific, engineering, and other work. It is not unlikely that the unit of horsepower will ultimately go out of use. In the meantime, however, it is desirable that its definition be uniform. This circular has been written to point out that if the horsepower is to represent *the same amount of power at different places* its relation to the watt must be a constant number, and the number of local foot-pounds or kilogram-meters per second which it represents must vary from place to place. Table 2 and others of this circular show clearly this variation with locality. (This variation is 0.6 per cent.)

"It is recommended that engineering societies and other interests concerned recognize the value of the 'English and American horsepower' as 746 watts (or 550 foot-pounds per second at 50° latitude and sea level, approximately the latitude of London), employing Table 2 to obtain the value in foot-pounds per second at other places. It is likewise recommended that the value of the continental horsepower be taken uniformly as 736 watts (or 75 kilogram-meters per second at latitude 52° 30', the latitude of Berlin), and that the value in kilogram-meters per second at other places be obtained from such a table as Table 5 of this circular.

"The same value, 746 watts, is used by the Bureau of Standards as the exact equivalent of the English and American horsepower. The Bureau recommends the use, whenever possible, of the kilowatt instead of the horsepower."

**Measurements of Length and Area, Including Thermal Expansion.** Circular No. 2, 5th Edition. 21 pp. This Circular gives regulations under which tests of standards of length and area are made including comparison of yard and meter standards, machine shop gauges, engineers' tapes, and precision screws and calipers. Some information as to the interrelation of secondary and special units of length and area are given with tables of equivalents and there is included a discussion of the conditions influencing the dimensions of bodies.

### DEPARTMENT OF AGRICULTURE

**Methods of Bacterial Analysis of Air.** G. L. A. RUEHLE. *Journal of Agricultural Research*, **4** (1915), 343–68. This reviews the various methods and proposes a new apparatus as an aeroscope for taking bacterial samples from air. A large number of test results and a brief bibliography are included.

### COMMERCE REPORTS—AUGUST, 1915

An important industry of Marseilles is the **seed-oil** industry, producing oil for edible purposes and for **soap.** The principal materials crushed are sesame, peanut, flaxseed, rape, ravison seed, cottonseed, poppy seed, castor seed, pulgheri, kapok, mafouraire, copra, palm kernels, morvrali, and illipe. (Supplement 5*d*.)

The world's production of **nickel** in 1913 was 34,000 tons, of which 24,838 tons was obtained from Canadian ore. The latter was reduced to matte which was either refined in the United States by the "salt cake process," or in England by the Mond process. (Pp. 548–9.)

The first metallic **nickel** produced in Canada has been made by the Canadian Smelting and Refining Company at Orillia, Ontario. (P. 731.)

A commission has been appointed in Ontario to consider the local refining of the **nickel** ore and matte. (P. 671.)

The consumption of Chilean **sodium nitrate** for agricultural and military purposes has increased, so that the price has become normal. (Pp. 553 and 1002.)

Since the Russian supply has been cut off, the manufacture of **"liquid petroleum"** or white medicinal oil, used as a laxative, has been started in the United States. (P. 553.)

Extensive deposits of **molybdenite** have been discovered near State Lake, British Columbia. (P. 565.)

Efforts are being made in Germany to extract the **fats** from solids obtained in **sewage purification.** (P. 587.)

An export tax on **minerals** from Peru is being considered. (P. 600.)

The consumption of **pulp-wood** in Canada is increasing. (P. 607.)

An embargo has been placed by Greece upon the export of **magnesite,** crude or calcined. (P. 609.)

A marked increase in the use of **fuel oil** in Brazil is noted. (P. 638.)

Owing to the increased price of **zinc,** zinc ore mining in Canada has been stimulated. (P. 666.)

The scarcity of **thymol** has caused the price in the United States to increase from $2.25 to $12 per lb. Thymol is manufactured most easily from the oil of **ajowan seed,** raised in Egypt and India, and formerly exported to Germany. The oil is distilled with steam, and the thymol separated from the distillate by treatment with NaOH, in which the thymol dissolves. It is then precipitated with HCl, and recrystallized from alcohol or glacial acetic acid. While thymol may be obtained from **horsemint,** indigenous to the United States, it is probable that to establish the industry here, a supply of **ajowan seed** will have to be imported. (Pp. 674–5.)

Exports of **rubber** from the Amazon Valley to the United States in June, 1915, show a marked increase over June, 1914. (P. 710.)

The **sugar** industry of Swatow, China, has declined steadily, due to lack of modern methods of agriculture and manufacture. (P. 727.)

Regulations for the operation of the newly discovered **potash** deposits of Spain, require uninterrupted working of the mines. (P. 739.)

A company has been organized in California to manufacture lemon by-products, such as **citrate of lime, lemon oil, lemon emulsion,** etc. (P. 755.)

Both **semi-anthracite** and **bituminous coal** are mined in the Kwangtung province, China. (Pp. 766–7.)

The **pitch** and **tar** industry of Russia has greatly increased in recent years, although primitive methods are still in general use. (P. 803.)

Among the important mineral products of Portugal are ores of **tungsten, copper, tin, iron** and **uranium.** (P. 836.)

Among the principal commodities carried through the Panama Canal during last year are, **nitrates, sugar, coal, refined petroleum, iron and steel,** and **iron ore.** (P. 843.)

Great difficulty is being experienced in obtaining any supply of **indigo** for the American **dye** industry. Logwood is being used, but only to a limited extent. The production of natural indigo in China is now sufficient to permit some exportation. The Chinese indigo, however, contains only about 1 per cent of the pure dye as compared with 40 to 70 per cent in other commercial natural indigoes or 20 per cent in the artificial paste. The Chinese product cannot, therefore, compete at present prices. (P. 855.)

Examination of the **rock asphalt** discovered in Leyte, P. I., has shown that it is suitable for paving. (P. 856.)

The **iron ore** deposits of Surigao, P. I., are estimated to contain 500,000,000 tons of ore consisting of hydrated oxides. After drying and sintering, the ore contains about 54 per cent of iron. It is exceptionally free from phosphorus and sulfur. (P. 873.)

Considerable **alum** is being manufactured from alunite near Newcastle, Australia. (P. 991.)

In Germany, a substitute for **hemp** and **jute** has been found in the fiber of a native wild plant, the rough haired willow rose (*Epilobium hirsutus*). (P. 999.)

**Coal** is now being exported from Norfolk to Greece. (P. 1015.)

STATISTICS OF EXPORTS TO THE UNITED STATES

LONDON, ENGLAND—875
Rubber
Tin
Paper stock
Natural indigo
Glycerine
Hides
Plumbago
Leather
Creosote oil
Chemicals

SPAIN—901
Iron pyrites
Copper iron pyrites
Copper
Cork

VENICE, ITALY—914
Dried beet pulp
Glassware
Glycerine
Hides
Jute
Talc

COLOMBIA—Sup. 42*b*
Balsam
Divi-divi
Gold
Platinum
Silver
Hides
Ipecac
Rubber
Tagua nuts
Tannic extract

BELGIUM—Sup. 2*a*
Acids
Aluminum
Aniline dyes
Antimony
Asbestos
Barytes
Basic slag
Beeswax
Bone meal
Chemicals
Clay
Copper
Diamonds
Fertilizers
Fire brick
Glass
Glue
Glycerine
Gum copal
Hides
Iron
Lithopone
Matches
Naphthalene
Nickel
Oils—Cocoanut, creosote, lubricating, sod, vegetable
Paper
Paraffin
Phosphates
Potash
Quebracho
Rubber
Artificial silk
Stearin
Wool grease
Zinc dust
Zinc oxide

ITALY—Sup. 8*b*
Citrate of lime
Essential oils
Pumice stone
Sulfur
Tartar
Citric acid
Sumac
Aluminum
Hides
Sienna

HOLLAND—Sup. 9*b*
Aluminum
Beeswax
Acids—Acetic, carbolic, formic, phosphoric, tartaric
Albumen
Tartar
Dextrine
Fusel oil
Glycerine
Gum copal
Gum damar
Madder
Magnesite
Prussiate of potash
Prussiate of soda
Paraffin
Earthenware
Electric lamps
Glass
Glue
Hides
Rubber
Manganese ore
Matches
Citronella oil
Creosote oil
Oleostearin
Lithopone
Paper stock
Tin
Peanut oil

RUSSIA—Sup. 13*a*–13*b*–13*c*
Blood albumen
Potassium carbonate
Licorice root
Lycopodium
Fusel oil
Glue stock
Glycerine
Hides
Asbestos
Manganese ore
Reclaimed rubber
Turpentine
Wood pulp
Asbestos
Safety matches

SWEDEN—Sup. 16*b*
Casein
Cocoa butter
Enameled iron
Ferrosilicon
Fusel oil
Hides
Iron and steel
Iron ore
Matches
Milk powder
Paper
Potash
Soda
Paper pulp

SAXONY—1084
Chinaware
Enameled iron
Artificial silk
Tungsten

FRANCE—Sup. 5*a*
Fusel oil
Lubricating oil
Paper stock
Tanning extract
Chemicals
Filter paper
Vanilla

SWITZERLAND—Sup. 15*a*
Aluminum
Chemicals
Ferrosilicon
Gelatin
Glass
Hides
Artificial silk
Coal tar dyes
Artificial indigo
Artificial abrasives
Synthetic perfumes

BRAZIL—Sup. 40*b*
Hides
Rubber
Ipecac
Carnauba wax

CHILE—Sup. 41*a*
Beeswax
Copper
Copper ore
Glue
Gold
Silver
Hides
Iron ore
Sodium nitrate
Quillaja bark
Iodine
Tin

CANADA—966
Coal
Coke
Drugs, etc.
Hides
Gold ore
Silver ore
Nickel ore
Asbestos
Paper

PARAGUAY—Sup. 45*a*
Hides
Oil of petitgrain

CHINA—Sup. 52*g*
Antimony
Beeswax
Egg albumen
Camphor
Gall nuts
Musk
Turmeric
Hides
Gold
Grease
Vegetable tallow
Soya bean oil
Cottonseed oil
Chinese wood oil
Zinc ore

Borings for **petroleum** are being made near Kingston, South Australia. P. 1031.

A deposit of **bitumen** or **asphalt** has been discovered in Honduras. (P. 1074.)

The **dyestuff** situation in England is not much improved, the British Dyes Company not yet having established a plant. The Bradford Dyers' Association has announced that all orders are accepted dependent upon the necessary dyes being obtainable and no guarantee of quality is given. (P. 1081.)

The **platinum** production of Colombia has increased to 9,382 ozs. in 1914. (Supplement 42 *b*.)

The following Special Supplements were issued during the month. In general they contain discussions of the manufacturing and trade conditions, and in most cases import and export statistics.

Belgium—2*a*
France—5*a*
Italy—8*a*
Netherlands—9*d*
Russia, Moscow—13*a*
Petrograd—13*b*, Finland—13
Switzerland—15*a*
Brazil—40*b*
Chile—41*b*
Colombia—42*b*
Paraguay—45*a*
China, Shanghai—52*g*
Manchuria—52*e*
Sweden—16*b*
French Indo China—54*a*
New Zealand—67*a*
British East Africa—65*a*
British South Africa—66*a*

# BOOK REVIEWS

**Chemical Technology and Analysis of Oils, Fats and Waxes.** Fifth Edition. Vol. III. By J. LEWKOWITSCH; edited by GEORGE H. WARBURTON. London: Macmillan & Co., 1915. Price, $6.50.

This new edition of Vol. III follows the well-known fourth edition so closely as not to require a detailed description. The total number of pages is increased from 407 to 483, the new matter consisting chiefly of details added to the various sections of the fourth edition to bring them up to date. An exception may be noted in the case of the new section of seven pages devoted to the hydrogenated oils and fats. In general more space and attention are devoted to the descriptive chemistry of the materials and products of the oil, fat, and wax industries than to the engineering of factory processes. The tabulations of statistical data, which in the fourth edition ended with those of the year 1907, have in the present volume been brought down to 1912 (inclusive) and in some cases to 1913.

A general subject index of 29 pages covers the three volumes of the present edition and, in conjunction with the index of botanical and zoölogical names appended to Vol. II, will suffice to make easily accessible the vast amount of reference material contained in the completed work.

H. C. SHERMAN

**The Rare Earths—Their Occurrence, Chemistry and Technology.** By S. I. LEVY, B.A., B.Sc., A.I.C. Price, $3.00 net. Longmans, Green & Co., 1915.

This work aims, as is well expressed in the preface, "to give a general but fairly comprehensive account of the Rare Earth group." The author has treated his subject principally from a chemical point of view, and has followed the usual custom of including Thorium and Zirconium in his classification. No one will take exception to this, but many will consider it superfluous to include Titanium among the Rare Earths, as is done in this work. The book, which is attractively edited, has a very gracious and complimentary introduction by Sir William Crookes.

The author has divided his work into three parts: I, Occurrence of the Rare Earths (111 pp.); II, The Chemistry of the Elements (154 pp.); and III, The Technology of the Elements (77 pp.).

In the first part of the book credit is given to Dr. Carl Auer von Welsbach for inspiring much of the research work that has been done in this branch of chemistry during the past thirty years. The list of minerals given is complete and well arranged, and the classification very logical, special importance being placed upon those minerals that possess a commercial interest. The treatment is first general and then specific, making this a valuable feature of the work. An entire chapter is devoted to Monazite Sand, the American and the Brazilian deposits receiving particular attention, and the methods of mining and concentration being described at considerable length. This part of the work closes with a well written chapter on Radioactivity, which is exceedingly clear and very appropriate in a book of this character.

In the second division of his work, the author has treated the chemistry of the Rare Earths in a very comprehensive manner. The elements are classified under the Cerium, Terbium, Erbium and Ytterbium groups, and the chemical data of both of the groups in general, and the specific elements themselves is very attractively arranged, special emphasis being wisely placed upon Titanium, Zirconium and Thorium. An extremely valuable chapter is devoted to the methods of separating the various elements of these groups.

Part III is introduced by a chapter on the incandescent mantle industry. In the historical treatment of this subject, no reference is made to the pioneer work of Prof. Robert Hare of Penna., U. S. A., who in 1801 produced the oxy-hydrogen blowpipe or "lime-light," thus antedating by just twenty-five years the work of Drummond, to whom the credit is given for this invention. This priority, which is well authenticated, has evidently escaped the author's notice. There are a few other minor omissions mainly of American inventions.

The work of Dr. Auer in developing the Welsbach system of illumination is treated in considerable detail, and is very logically followed by a chapter on the chemical treatment of Monazite, in which the author has assembled a great deal of information relative to the technical manufacture of thorium and cerium nitrates, including a digest of the methods of analysis of this, the only commercial thoria mineral. Two chapters are devoted to the manufacture of incandescent gas mantles. The artificial silk industry is also reviewed, and its application to the mantle industry is treated both historically and technically. The work concludes with two chapters on the various uses of the Rare Earth group, both suggestive and practical, in which the subject of pyrophoric alloys is treated quite fully.

The book is profuse in references to the chemical and patent literature of the world, making the work so complete that it should be in the library of every rare earth chemist. The author has succeeded in presenting this subject in a very attractive manner, and such a comprehensive and reliable work in the English language should be welcomed by all, especially those who are unfamiliar with the German and French languages.

H. S. MINER

**A Manual of Oils, Resins and Paints.** By HARRY INGLE, D.Sc., PH.D., F.I.C. Vol. I, 129 pp., 6 illustrations. London: Chas. Griffin & Co.; Philadelphia: J. P. Lippincott Co., 1915. Price, $1.25.

This volume is devoted to the analysis and valuation of the materials treated of. In it an attempt is made to give in a very brief form the whole subject of the analysis of oils, resins, paints, varnishes, fats, and waxes. The introduction states that the book is designed to provide students and analysts who have had little or no experience with oils with a short account of the methods used in the analysis of this class of substances. It is natural that in so brief a review of the subject, the details of the analytical methods and of the apparatus used should be very largely omitted so that the reader can hardly hope by following the text to find enough information to enable him to carry out any method without reference to larger works, but there is, however, a brief reference to most of the important methods of analysis, so that the reader who has little or no knowledge of the subject whatever will find the most important methods and principles set forth in a concise form. That part of the work devoted to the analysis of oils is much more full and satisfactory than the parts devoted to paint, resins, and soap.

In some cases the abbreviation has been carried farther than is perhaps wise. For example, in describing the method for determining the combined insoluble fatty acids and unsaponifiable matter on page 40, the step which consists in removing the alcohol by evaporation has been omitted, and in the determination of glycerin by the acetin method, no instructions are given for obtaining from the fat or oil the crude glycerin which is to be examined. Although the permanganate method of determining glycerin has considerable space devoted to it, the dichromate method, which is much more frequently used, is not mentioned.

This book gives general information concerning operations which require skill and experience, but does not pretend to take the place of larger and more elaborate treatises which are now available.

PARKER C. MCILHINEY

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Analysis: Aids to the Analysis and Assay of Ores, Metals, Fuels, Etc** By J. J. MORGAN. 2nd Ed. 18mo. Price, $0.75. Baillière, Tindall and Cox, London.

**Boiler Room Practice and Smoke Abatement.** By J. T. HODGSON. 8vo. 321 pp. Price, $1.00. "Railway Engineer," London.

**Cement: Schwellung und Schwindung von Zement und Zementmoertein in Wasser und Luft.** By M. GARY. 8vo. Price, $0.75. W. Ernst & Sohn, Berlin.

**Chemists' Year Book. 1915.** 2 Vol. By F. W. ATACK. 18mo. Price, $2.75. Sherratt and Hughes, London.

**Coal-Gas: The By-Products of Coal-Gas Manufacture.** By K. R. LANGE. 12mo. 155 pp. Price, $2.00. D. Van Nostrand Co., New York.

**Colloids: Introduction à la connaissance des solutions colloidales.** By G. REBIÈRE. 8vo. 72 pp. Gounouilhou, Bordeaux.

**Concrete: Versuche zur Ermittlung des Rostschutzes der Eiseneinlagen im Beton.** By H. SCHEIT AND O. WAWRINIOK. 8vo. Price, $2.00. W. Ernst & Sohn, Berlin.

**Electric Wiring Specifications.** By J. H. MONTGOMERY. 8vo. 139 pp. Price, $1.00. D. Van Nostrand Co., New York.

**Internal Combustion Engine.** By H. E. WIMPERIS. New and revised Ed. 8vo. 319 pp. Price, $3.00. D. Van Nostrand Co., New York.

**Internal Combustion Engines.** By R. L. STREETER. 8vo. 418 pp. Price, $4.00. McGraw-Hill Book Co., New York.

**Iron and Steel: The Sampling and Chemical Analysis of Iron and Steel.** By O. BAUER AND E. DEISS. 8vo. 373 pp. Price, $3.00. McGraw-Hill Book Co., New York.

**Irrigation Practice and Engineering.** Vol. I. By B. A. ETCHEVERRY. 8vo. 213 pp. Price, $200. McGraw-Hill Book Co., New York.

**Machines: The Theory of Machines.** By R. F. MCKAY. 8vo. Price, $3.75. E. Arnold, London.

**Masonry: Stability of Masonry.** By E. H. SPRAGUE. 8vo. 258 pp. Price, $1.35. D. Van Nostrand Co., New York.

**Mining and Mine Ventilation; a Practical Handbook on the Physics and Chemistry of Mining.** By J. J. WALSH. 12mo. 180 pp. Price, $2.00. D. Van Nostrand Co., New York.

**Ore Dressing: The Theory and Practice of Ore Dressing.** By E. S. WIARD. 8vo. 426 pp. Price, $4.00. McGraw-Hill Book Co., New York.

**Physical Chemistry: Elements of Physical Chemistry.** By H. C. JONES. 4th Ed. 8vo. Price, $4.00. Macmillan & Co., New York.

**Porcelain: Die technischen Eigenschaften des Porzellans.** By ERNST ROSENTHAL. 8vo. Price, $0.75. G. Stalling, Oldenburg.

**Sewage: Guide to the Reports, Evidence and Appendices of the Royal Commission on Sewage Disposal.** By G. B. KERSHAW. 8vo. 178 pp. Price, $2.00. D. Van Nostrand Co., New York.

**Soil: Die Raumwirkung im Erdreich.** By K. ZIMMERMANN. 8vo. 96 pp. Price, $1.50. W. Ernst & Sohn, Berlin.

**Steam: The Callendar Steam Tables.** By H. L. CALLENDAR. 8vo. Price, $0.75. E. Arnold, London.

**Steam: Properties of Steam and Ammonia.** By G. A. GOODENOUGH. 4to. 108 pp. Price, $1.25. John Wiley & Sons, New York.

**Steam Power.** By W. E. DALBY. 760 pp. Price, $6.00. Longmans, Green & Co., New York.

**Valves and Valve Gears.** Vol. 2. By F. D. FURMAN. 190 pp. Price, $2.00. John Wiley & Sons, New York.

## RECENT JOURNAL ARTICLES

**Air Extractor.** By J. D. SAVERY. *Ice and Refrigeration*, Vol. 49 (1915), No. 3, p. 113.

**Air Moistening: Ueber Luftbefeuchtung.** By KARL KAYSER. *Rauch und Staub*, Vol. 5 (1915), No. 9, pp. 137–141.

**Alloys: L'Influence de la coalescence sur les propriétés mécaniques des alliages.** By A. PORTEVIN AND V. BERNARD. *Revue de métallurgie*, Vol. 12 (1915), No. 3, pp. 147–154.

**Balances: Heusser Multiple Weight Attachment for Chemical Balances.** By WILFRED HEUSSER. *Engineering and Mining Journal*, Vol. 100 (1915), No. 8, p. 314.

**Benzol: Etude sur la vitesse de nitration de benzène et de quelques-uns de ses dérivés.** By J. P. WIBAUT. *Recueil des travaux chimiques des Pays-Bas et de la Belgique*, Vol. 34 (1915), No. 4/5, pp. 241–258.

**Boiler-House Design.** By R. D. DEWOLF. *Engineering Magazine*, Vol. 49 (1915), No. 6, pp. 837–842.

**Corean Beeswax.** By SÉICHI UENO. *The Analyst*, Vol. 40 (1915), No. 473, pp. 343–344.

**Crystalline Growth in Strained Ferrite.** By K. B. LEWIS. *Steel and Iron*, Vol. 19 (1915), No. 24, pp. 823–824.

**Electrolytic Bleach Plants for Paper Mills.** By F. G. WHEELER. *Paper*, Vol. 16 (1915), No. 26, pp. 11–12.

**Explosives: Miscugli di esplosivi nitrati e nitrazione del toluene.** By M. GIUA. *Gazzetta chimica italiana*, Vol. 45 (1915), Pt. 2, No. 1, pp. 32–44.

**Flotation Testing Machine.** By R. W. SMITH. *Engineering and Mining Journal*, Vol. 100 (1915), No. 10, pp. 395–396.

**Formic Acid: Bestimmung von Ameisensaeure neben Essigsaeure.** By R. LAUFFMAN. *Chemiker-Zeitung*, Vol. 39 (1915), No. 91-92, p. 575.

**Glassware: To Cut Glassware Easily.** By E. J. HALL. *Engineering and Mining Journal*, Vol. 100 (1915), No. 8, p. 315.

**Grinding: Practical Details about Grinding.** By C. G. SMITH. *Iron Trade Review*, Vol. 58 (1915), No. 10, pp. 443–444.

**Heat Emitting Capacity of Radiation.** By C. D. ALLAN. *The Heating and Ventilating Magazine*, Vol. 12 (1915), No. 8, pp. 32–34.

**Hydrogen-Phosphide: Quantitative Bestimmung des Phosphorwasserstoffs.** By H. RECKLEBEN. *Zeitschrift fuer analytische Chemie*, Vol. 54 (1915), No. 5, pp. 241–252.

**Hydrogenation: L'Hydrogénation des huiles et corps gras.** By G. F. JAUBERT. *Memoirs de la société des ingénieurs civils de France*, Vol. 67 (1915), No. 7–12, pp. 305–353.

**Iron-Cobalt Alloy, $Fe_2Co$, and its Magnetic Properties.** By T. D. YENSEN. *General Electric Review*, Vol. 18 (1915), No. 9, pp. 881–887.

**Leather Waste: Verwertung der Lederabfaelle.** By KARL MICKSCH. *Kunststoffe*, Vol. 5 (1915), No. 14, pp. 161–163.

**Metal: Protective Coatings for Metal.** By H. B. C. ALLISON. *General Electric Review*, Vol. 18 (1915), No. 9, pp. 878–880.

**Oil Engines: Weight and Power of Oil Engines.** By C. S. SALFELD. *The Gas Engine*, Vol. 17 (1915), No. 9, pp. 463–468.

**Ore: Zur Anwendung metallographischer Methoden auf die mikroskopische Untersuchung von Erzlageraetten.** By B. GRANIGG. *Metall und Erz*, Vol. 12 (1915), No. 10, pp. 190–200.

**Petroleum: Die festen Bestandteile des Erdoels.** By J. MARCUSSON. *Chemiker-Zeitung*, Vol. 39 (1915), No. 93, pp. 581–582.

**Platinum: Die Abscheidung des Platins aus Erzaufschluessen fuer die massanalytische Eisenbestimmung.** By L. BRANNT. *Chemiker-Zeitung*, Vol. 39 (1915), No. 88/89, pp. 553–555.

**Pumps: Unity Cylinder Ratio for Dry-Vacuum Pumps.** By R. S. HOWARD. *Power*, Vol. 42 (1915), No. 10, pp. 327–328.

**Radioactivity: Neure Forschungen auf dem Gebiet der Radioaktivitaet in den Jahren 1913 und 1914.** By F. HENRICH. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 28 (1915), No. 52, pp. 297–303.

**Recorders in the Power Plant.** By J. C. SMALLWOOD. *Engineering Magazine*, Vol. 49 (1915), No. 6, pp. 818–836.

**Refrigeration: Operating a Refrigerating Plant.** By T. G. THURSTON. *Power*, Vol. 42 (1915), No. 6, pp. 185–186.

**Rosin: Microscopical Characteristics of Rosin.** *Paper*, Vol. 16 (1915), No. 18, pp. 13–14.

**Scheelite: Sur la phosphorescence cathodique des scheelite et des alumines.** By CH. DEROHDEN. *Annales de Chimie*, Vol. 3 (1915), pp. 338–366.

**Silica Brick: Making Silica Brick for High Heat Service.** By C. C. LYNDE. *Steel and Iron*, Vol. 19 (1915), No. 24, pp. 831–833.

**Soap: Der Nachweis von Galle in Seifen.** By F. STEINITZER. *Chemische Revue ueber die Fett- und Harz-Industrie*, Vol. 22 (1915), No. 8, pp. 69–70.

**Steam: How to Increase Steam Production.** By H. R. CALLAWAY. *Engineering Magazine*, Vol. 49 (1915), No. 6, pp. 843–849.

**Steam: The Heating Value of Exhaust Steam.** By D. M. MYERS. *Engineering Magazine*, Vol. 49 (1915), No. 5, pp. 712–717.

**Steam: A Pressure Survey Study Constituting a Report on the Comparative Use of Exhaust and Live Steam for Heating.** By C. C. WILCOX. *The Heating and Ventilating Magazine*, Vol. 12 (1915), No. 8, pp. 23–32.

**Tannery: Gerbereichemie 1914.** By W. FAHRION. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 28 (1915), No. 44, pp. 257–258.

**Ultra-Violet Rays for Water Purification.** By M. VON RECKLINGHAUSEN. *Journal of the New England Water Works Association*, Vol. 20 (1915), No. 2, pp. 202–213.

**Wastes in the Power Plant.** By C. I. HUBBARD. *Engineering Magazine*, Vol. 49 (1915), No. 6, pp. 809–817.

**Welding: Modern Practice in Electric Arc Welding.** By J. A. RANDOLPH. *The Foundry*, Vol. 43 (1915), No. 276, pp. 316–317.

**Welding: Modern Electrical Welding Practice.** By J. A. RANDOLPH. *Iron Trade Review*, Vol. 42 (1915), No. 11, pp. 490–491.

**Welding: A Power-Driven Spot Welding Machine.** *The Iron Age*, Vol. 96 (1915), No. 2, p. 85.

**Zinc: The Refining of Zinc Waste.** By L. J. KROM. *The Metal Industry*, Vol. 13 (1915), No. 7, pp. 281–283.

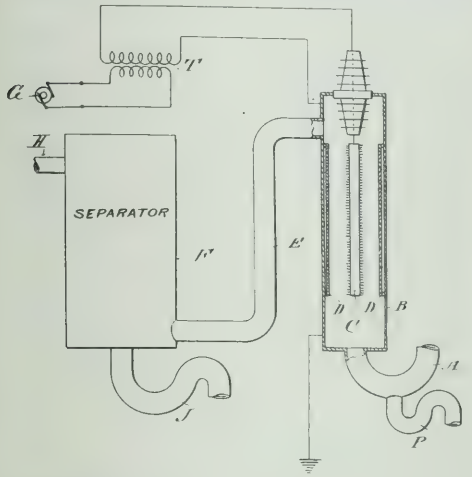
# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. Parker

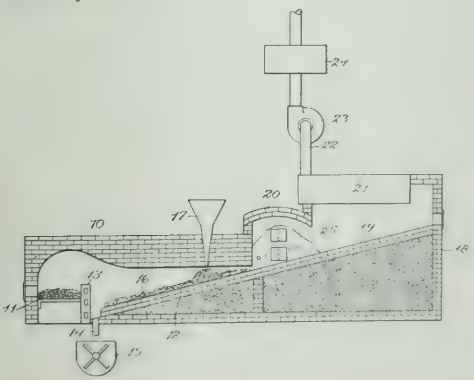
Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Removing Tar from Gas. F. W. Steere, March 2, 1915. U. S. Pat. 1,130,213.** Tar and similar suspended particles are removed from gas by passing the gas through an electric field




of alternating polarity thereby producing an agglomeration of the particles. The gas is removed from the electric field while holding the agglomerated particles in suspension and the particles are afterward separated from the gas.

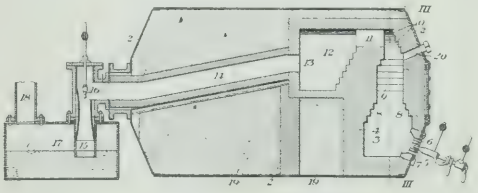
**Sodium Sulfid. H. K. Moore, March 2, 1915. U. S. Pat. 1,130,317.** Lignin liquor resulting from the manufacture of sulfate pulp is sprayed into a smelting chamber where the inorganic content of the liquor is smelted for the formation of sodium carbonate. The resulting carbonate is caused to flow downwardly in a molten condition into the furnace and sodium




sulfate is continuously added to the flowing carbonate in the presence of a reducing agent. Heat is supplied for the reduction of the sulfate and fusion of the sodium sulfid formed by such reaction. The resulting mass is withdrawn in a molten condition and the products of sublimation are reclaimed by passing them through a spray of lignin liquor.

**Artificially Maturing or Aging Wines, Spirits, or other Potable Liquors. V. Henri, A. Helbronner and M. von Recklinghausen, March 2, 1915. U. S. Pat. 1,130,400.** The liquor to be aged is subjected to the direct action of concentrated ultra-violet rays produced by a vapor electric lamp in close proximity to the liquor under treatment.

**Manufacture of Producer-Gas. L. E. Hirt, March 2, 1915. U. S. Pat. 1,130,512.** Comminuted fuel is injected by means of steam into a combustion chamber and burned, the products of




combustion passing through a contracted passage into an expansion chamber, the expanded products next passing into a reduction tube in contact with incandescent carbon carried on the tube walls. Steam is then injected into the treated gases.

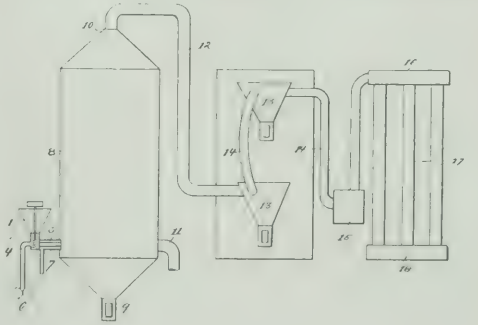
**Manufacture of Furnace Tubes or Chambers. R. P. Pictet, March 2, 1915. U. S. Pat. 1,130,533.** Powdered refractory material is mixed with finely divided carbon produced by the dissociation of a hydrocarbon. A paste of such mixture is formed and subsequently fired in a non-oxidizing atmosphere.

**Refining Animal and Vegetable Oils. C. Baskerville, March 9, 1915. U. S. Pat. 1,130,698.** Cottonseed or similar oils are treated with caustic alkali and a saline electrolyte. A hydrating agent is then added and the oil heated until coagulation occurs. The coagulum is then separated from the oil.

**Treating Masses of Concrete. C. Ellis, March 9, 1915. U. S. Pat. 1,130,717.** The surface of the concrete is roughened and the roughened surface impregnated with a water-resistant binding material. The depressions of the concrete surface are then filled substantially to a level with the peaks with a waterproofing material, whereby the wear is taken substantially by the peaks.

**Vulcanized Synthetic Caoutchouc. F. Hofmann and K. Gottlob, March 9, 1915. U. S. Pat. 1,130,903.** A vulcanizing agent and a small amount of a piperidin base are incorporated with $\beta$-$\gamma$-dimethylbutadiene caoutchouc. The resulting product is heated to effect vulcanization.

**White Pigment. H. W. Kessler, March 9, 1915. U. S. Pat. 1,131,144.** An ignited combustible mixture of powdered metallic

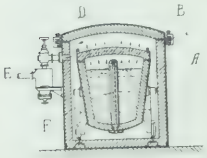


lead, air, and gaseous hydrocarbon fuel is discharged into a chamber containing carbon dioxid and admixed steam and the carbon produced separated from the gases in the chamber.

**Decolorizing Liquids. F. R. Bachler, March 9, 1915. U. S. Pat. 1,131,308.** Liquids containing oxidizable coloring matters are treated with a composition comprising hydrogen dioxid absorbed in kieselguhr.

**Granular Nitrate of Ammonia. F. L. Gallup, March 9, 1915. U. S. Pat. 1,131,361.** Ammonium nitrate liquor having a definite degree of concentration according to the size of grains desired, is crystallized and stirred.

**Vacuum Process for Production of Steel. E. Dolensky, March 9, 1915. U. S. Pat. 1,131,488.** A clearing vessel, heated approximately to the temperature of the molten metal to be purified and containing the molten metal, is placed within a second container. The second container is then exhausted whereby the molten metal is cleared.




**Varnishes, Etc. A. B. Walker and F. P. Walker, March 9, 1915. U. S. Pat. 1,131,578.** The varnish comprises a liquid solution of metallic soap of aluminum and an oxid of an alkaline earth metal, characterized by an absence of an organic resin or gums.

**Desulfurizing Ores. G. Fusina, March 16, 1915. U. S. Pat. 1,131,691.** The ores are desulfurized by passing a quantity of air through the material in one direction and then passing a a quantity of air and steam through the material in the opposite direction.

**Compound for Treating Road-Surfaces. W. J. Reynolds, March 16, 1915. U. S. Pat. 1,131,793.** This is a normally liquid compound consisting solely of crude petroleum and rosin dissolved therein, the petroleum largely predominating and the amount of rosin being sufficient to make the compound sticky and resistant to weather conditions.

**Pure Resin-Oil. M. Melamid, March 16, 1915. U. S. Pat. 1,131,939.** Phosphoric acid is added to resin and the mixture heated to about 300° C. whereby phosphoric acid is converted into pyro-phosphoric acid and meta-phosphoric acid which compounds are then allowed to act upon the resin.

**Explosive Containing Liquid Air or Oxygen and Lampblack. G. Claude, March 16, 1915. U. S. Pat. 1,131,994.** This is an explosive cartridge comprising a mixture of lampblack, naphthalene and liquid air or oxygen permeating the mixture.

**Satinizing Cotton Fabrics. H. Dutschke, March 16, 1915. U. S. Pat. 1,132,001.** The fabric is impregnated with a solution of a crystallizable salt which will not act injuriously on the fabric and the thus treated fabric is repeatedly passed through a calendar heated from about 100 to 200° C.

**Chemically-Pure Soluble Silicic Acid. B. Schwerin, March 16, 1915. U. S. Pat. 1,132,394.** An alkaline silicate solution is subjected to the action of an electric current in the anode compartment of a shell provided with a diaphragm of such potential as will allow the migration of alkali through it but prevents the migration of silicic acid. The silicic acid so obtained is subjected to the action of an electric current in a cathode compartment of a shell provided with a diaphragm of such potential that it will admit of the migration of acid residues through it, but prevent migration of the soluble silicic acid.

**Treating Clay and Like Materials. F. Thompson, March 16, 1915. U. S. Pat. 1,131,537.** Iron is removed from clay by subjecting the clay to the action of dilute hydrochloric acid under the influence of heat and pressure and dissolving out the resulting iron compound or compounds produced.

**Clarifying Liquid Silicate of Soda, Etc. J. G. Vail, March 23, 1915. U. S. Pat. 1,132,640.** The liquid silicate of soda is clarified by heating in a closed container without agitation.

**Detoxicating Oil, Etc. C. Ellis, March 23, 1915. U. S. Pat. 1,132,710.** The oil, fat or the like under treatment is exposed to the action of a spent catalyzer previously employed in hydrogenation to combine with or absorb catalyzer poisons. The spent catalyzer is then separated from the treated material and such material subjected to the action of an active catalyzer in the presence of hydrogen.

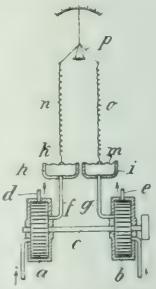
**Aluminum Oxid from Sulfate of Alumina. G. Schwahn, March 23, 1915. U. S. Pat. 1,132,736.** Aluminum oxid is produced by subjecting porous aluminum sulfate in the presence of aqueous vapor to about an orange-red or orange heat.

**Purification of Hydrogen. C. Bosch and W. Wild, March 23, 1915. U. S. Pat. 1,133,087.** Hydrogen is freed from sulfur by treating hydrogen containing sulfur under a pressure exceeding that of five atmospheres with a hot solution of fixed caustic alkali.

**Lubricant. A. Warrell, March 23, 1915. U. S. Pat. 1,133,204.** The lubricant is a permanent putty-like magma of a soapstone mineral and lubricating oil.

**Primer and Varnish. A. Eichler, March 30, 1915. U. S. Pat. 1,133,432.** The composition is composed of polymerization products of cumarone and liquid hydrocarbon solvents.

**Method of Quantitatively Analyzing Gas Mixtures of Known Constituents and Apparatus Therefor. H. Gerdien, March 30, 1915. U. S. Pat. 1,133,556.** Gas mixtures having known constituents are quantitatively analyzed by imparting a rotary motion through the gas mixture and rotating a test or standard gas in unison therewith to generate differences in pressure in said gas thereby. Uniformity of the rotation is maintained and the molecular weight of the gas mixture is indicated as a multiple of that of the test or standard gas.




**Carburizing Iron or Steel. S. S. Eveland, March 30, 1915. U. S. Pat. 1,133,626.** The iron or steel is heated in a closed chamber in proximity to the fibrous refuse from the manufacture of sugar.

**Chicle Substitute. G. B. Bradshaw and W. H. Bradshaw, March 30, 1915. U. S. Pat. 1,134,073.** Resin is treated with a purifying agent and to the resin is added gutta after having been subjected to a purifying agent.

**Preventing Decomposition of Hydrogen-Peroxid Solutions. A. Faragó, April 6, 1915. U. S. Pat. 1,134,323.** The hydrogen peroxid solution is saturated with oxygen and subjected to high gaseous pressure in hermetically closed receptacles.

**Decomposing Alkali-Metal Silicates. S. Peacock, April 6, 1915. U. S. Pat. 1,134,413.** This is a process of simultaneously producing volatile carbo-nitrids of an alkali metal and by mixing carbon with a mineral containing the alkali metal, heating the mixture in an atmosphere of nitrogen to a temperature sufficient to produce carbo-nitrids and recovering such nitrids.

**Boron Nitrid. G. Weintraub, April 13, 1915. U. S. Pat. 1,135,232.** A mixture of boron-containing material and potassium cyanid are heated to a temperature at which reaction occurs and products other than boron nitrid are volatilized.

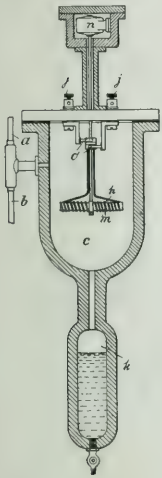
## BRITISH PATENTS

By D. Geddes Anderson
Chemical Engineer and Patent Chemist, Glasgow, Scotland

The following abstracts are taken direct from the patent specifications as soon as these are published by the British Patent Office. The date given at the end of the abstract is the date of acceptance.

**Manufacture of Solid Peroxides and Perborates. H. Wade, Feb. 2, 1915. Brit. Pat. 1,687.** 20 parts borax, 4.2 parts sodium hydrate and 22 parts sodium sulfate are dissolved in 1000 parts water. The solution is electrolyzed with a cathode of amalgamated silver and with an anode of platinum or lead, and separated from the cathode space by a diaphragm tube. Oxygen is continuously introduced. Pure sodium perborate containing 10.3 per cent of active oxygen is obtained.—July 8, 1915.

**Manufacture of Ammonia. G. Calvert, April 29, 1914. Brit. Pat. 10,612.** Action between the nitrogen and hydrogen is promoted by using a moving catalyst. In figures shown hydrogen and nitrogen are passed into the reaction chamber *c* by pipes *a* and *b*. The catalyst is carried by the rotatable arm in which are the heating coils *h*.—May 20, 1915.




**Metal Polishing Composition. H. Levin, Application, Feb. 9, 1914. Brit. Pat. 3,367.** The chief ingredient in the composition is the insoluble basic sulfate of iron which is thrown down on treating iron solutions with an oxidizing agent in the presence of alkali sulfate; 20 parts of this material are mixed with 32 of petrol, 7 of fat and 1 of oleic acid.—May 20, 1915.

**Perborate of Zinc. Henkel and Cie, Feb. 10, 1914. Brit. Pat. 3,477.** Zinc sulfate is intimately mixed with perborate of sodium and the mixture kept at 70° C. for some time.—June 24, 1915.

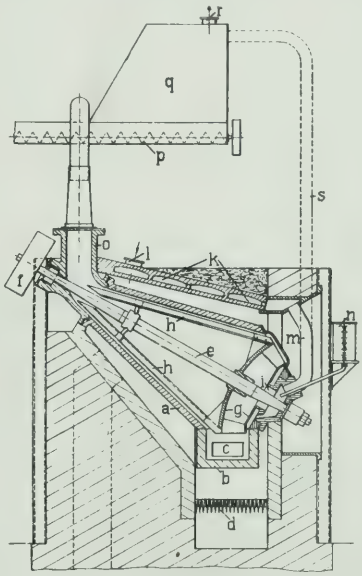
**An Improved Fuel. F. M. Hickman, Feb. 18, 1914. Brit. Pat. 4,214.** A dense hard coke is obtained from inferior coal having no coking properties, by the addition, before distillation, of a small percentage of mineral matter of such a nature as will form a fusible compound with the ash of the coal.—May 18, 1915.

**Artificial Mother of Pearl. C. Claessen, March 18, 1914. Brit. Pat. 6,893.** An artificial product which is quite similar to real mother of pearl is obtained when materials producing luster, such as fish-scale tincture, are added to solutions of cellulose esters, and the mixture formed into films. The films are then placed in presses and formed into blocks by heat.—June 17, 1915.

**Manufacture of Aluminous Compounds. H. Spence, W. B. Llewellyn and P. Spence and Sons, April 11, 1914. Brit. Pat. 9,148.** This invention relates to a process of purifying impure solutions of aluminum sulfate from compounds of iron. The impure aluminum sulfate is agitated at 50° C. and a solution of potassium sulfate added. Ferric oxide compounds precipitate out and are separated in any usual manner.—June 11, 1915.

**Coating Iron Surfaces. A. Samuel, May 15, 1914. Brit. Pat. 12,045.** Iron is covered with a thin coating of linseed oil, then an intimate mixture of red lead and powdered aluminum in the proportion of 10 red lead to 5 aluminum is laid on, and the flame of a blow-lamp passed over the part covered.—May 17, 1915.

**Apparatus for Producing Lead Oxide. E. Barthelmess, April 15, 1914. Brit. Pat. 9,333.** The metallic lead is heated in pot *b*, which is in direct connection with the oxidation chamber *a*. The latter is fitted with a spindle, *e*, carrying a stirring device consisting of a centrifugal wheel, *g*, and a series of conically




disposed blades *h*. The wheel *g* sucks in a stream of heated air or gas through *i* and the measuring vessel *n* delivers the water necessary for the oxidation of the lead.—June 17, 1915.

**Solutions of Cellulose Xanthogenate. L. Lilienfeld, June 15, 1914. Brit. Pat. 14,339.** Raw viscose, preferably in a diluted condition containing not more than 5 per cent of cellulose or cellulose hydrate, is subjected to a temperature of 60° C. to 80° C., and maintained at this temperature until the polymerized xanthogenate is precipitated. The precipitate is thoroughly washed with water and dissolved in alkali.—June 15, 1915.

**Composition for the Manufacture of Rubber Thread. W. P. Bradley, June 15, 1914. Brit. Pat. 14,355.** Lampblack 2 to 7 per cent, ceresin wax 2 to 7 per cent are added to high-grade rubber stock.—June 15, 1915.

**Refining Fats and Oils. S. Morgenstern, June 17, 1914. Brit. Pat. 14,571.** The fat is mixed with slaked lime and the mixture heated in a closed autoclave for six hours at a temperature of 200° C. The special feature of the process is that the mass is heated for a period of time after complete saponification has taken place.—June 17, 1915.

**White Cement. B. Hannen, June 20, 1914. Brit. Pat. 14,865.** This invention relates to a method for preparing a white cement from materials containing a small proportion of iron: 2 to 3 per cent of common salt is added to the lime and clay mixture which is then burned at a temperature of 1100 to 1200° C.—June 21, 1915.

**Manufacture of Hydrous Alkali Silicates. E. A. Paterson, Dec. 13, 1914. Brit. Pat. 24,099.** Sodium silicate glass is partially dried at 60° C. under reduced pressure until the water content is 30 per cent. The material is then solid, and is ground to a fine powder, and further dried to a water content of 12 per cent. In this condition it forms a dry powder easily soluble in cold water.—June 17, 1915.

# MARKET REPORT—SEPTEMBER, 1915

AVERAGE WHOLESALE PRICES IN THE NEW YORK MARKET FOR LARGE QUANTITIES OF STANDARD CHEMICALS

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lime, gray | 100 Lbs. | 4.00 | @ | 4.05 |
| Alum, lump | 100 Lbs. | 3.75 | @ | 5.50 |
| Aluminum Sulfate, high-grade | 100 Lbs. | 1.75 | @ | 2.00 |
| Ammonium Carbonate, domestic | Lb. | 8½ | @ | 9½ |
| Ammonium Chloride, gray | Lb. | 6¼ | @ | 6½ |
| Ammonium Phosphate, commercial, 98–100% | Lb. | 10 | @ | 10½ |
| Aqua Ammonium, 16°, drums | Lb | 2¼ | @ | 2½ |
| Arsenic, white | Lb. | 3½ | @ | 4 |
| Barium Chloride | Ton | | @ | 100.00 |
| Barium Nitrate | Lb. | 15 | @ | 16 |
| Barytes, prime white, foreign | Ton | 19.00 | @ | 23.00 |
| Bleaching Powder, 35 per cent | 100 Lbs. | 2.25 | @ | 2.50 |
| Blue Vitriol | Lb. | 7¼ | @ | 7½ |
| Borax, crystals, in bags | Lb. | 5¼ | @ | 5¾ |
| Boric Acid, powdered crystals | Lb. | 9 | @ | 9¼ |
| Brimstone, crude, domestic | Long Ton | 22.00 | @ | 22.50 |
| Bromine, technical, bulk | Lb. | 1.25 | @ | 1.60 |
| Calcium Chloride, lump | Ton | — | @ | 11.78 |
| Calcium Chloride, granulated | Ton | — | @ | 14.78 |
| Caustic Soda, 70 @ 76 per cent | 100 Lbs. | 5.00 | @ | 5.25 |
| Caustic Soda, powdered or granulated, 76 per cent | 100 Lbs. | 5.25 | @ | 5.75 |
| Chalk, light precipitated | Lb. | 5 | @ | 5¼ |
| China Clay, imported | Ton | 20.00 | @ | 30.00 |
| Feldspar | Ton | 8.00 | @ | 12.00 |
| Fuller's Earth, foreign, powdered | 100 Lbs. | 80 | @ | 1.00 |
| Glauber's Salt, in bbls. | 100 Lbs. | 60 | @ | 75 |
| Green Vitriol, bulk | 100 Lbs. | 70 | @ | 80 |
| Hydrochloric Acid, commercial, 18° | 100 Lbs. | 1.50 | @ | 1.75 |
| Hydrochloric Acid, C. P., conc., 22° | 100 Lbs. | 2.00 | @ | 2.25 |
| Iodine, resublimed | Lb. | 4.00 | @ | 4.25 |
| Lead Acetate, white crystals | Lb. | 11 6/8 | @ | 12⅛ |
| Lead Nitrate | Lb. | 11½ | @ | 12 |
| Litharge, American | Lb. | 6½ | @ | — |
| Lithium Carbonate | Lb. | 90 | @ | 1.00 |
| Magnesium Carbonate | Lb. | 5½ | @ | — |
| Magnesite, "Calcined" | Ton | 30.00 | @ | 32.00 |
| Mercuric Chloride, commercial | Lb. | 1.40 | @ | 1.50 |
| Nitric Acid, 68 per cent, sp. gr. 1.42 | Lb. | 5⅞ | @ | 6¼ |
| Nitric Acid, fuming | Lb. | 7⅞ | @ | 8¼ |
| Phosphoric Acid, sp. gr. 1.750 | Lb. | 28 | @ | 31 |
| Phosphorus | Lb. | 35 | @ | 75 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate, casks | Lb. | 20 | @ | 21 |
| Potassium Bromide | Lb. | 23 | @ | 23½ |
| Potassium Carbonate, calcined, 80 @ 85% | 100 Lbs. | 25 | @ | 27 |
| Potassium Chlorate, crystals, spot | Lb. | 31 | @ | 32 |
| Potassium Cyanide, bulk, 98–99 per cent | Lb. | 25 | @ | 29 |
| Potassium Hydroxide | Lb. | 23 | @ | 25 |
| Potassium Iodide, bulk | Lb. | 3.70 | @ | 3.75 |
| Potassium Nitrate | Lb. | 18 | @ | 19 |
| Potassium Permanganate, bulk | Lb. | 1.25 | @ | — |
| Quicksilver, flask, 75 lbs. | | 88.00 | @ | 90.00 |
| Red Lead, American, dry | Lb. | 6½ | @ | — |
| Salt Cake, glass makers' | 100 Lbs. | 55 | @ | 65 |
| Silver Nitrate | Oz. | 31¼ | @ | 33¼ |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash, 48 per cent | 100 Lbs. | 75 | @ | 80 |
| Sodium Acetate | Lb. | 4½ | @ | 4¾ |
| Sodium Bicarbonate, domestic | 100 Lbs. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate, English | Lb. | 3½ | @ | 3⅝ |
| Sodium Bichromate | Lb. | 14 | @ | — |
| Sodium Carbonate, dry | 100 Lbs. | 1.10 | @ | — |
| Sodium Chlorate | Lb. | 14 | @ | 16 |
| Sodium Fluoride, commercial | Lb. | 12 | @ | — |
| Sodium Hydroxide, 60 per cent | 100 Lbs. | | 2.25 | |
| Sodium Hyposulfite | 100 Lbs. | 1.80 | @ | 2.00 |
| Sodium Nitrate, 95 per cent, spot | 100 Lbs. | 2.40 | @ | 2.50 |
| Sodium Silicate, liquid | 100 Lbs. | 85 | @ | 1.10 |
| Sodium Sulfide, 30%, crystals, in bbls. | Lb. | 1¾ | @ | 2¼ |
| Sodium Sulfite, crystals | Lb. | 2½ | @ | 2⅝ |
| Strontium Nitrate | Lb. | 16 | @ | 18 |
| Sulfur, flowers, sublimed | 100 Lbs. | 2.20 | @ | 2.60 |
| Sulfur, roll | 100 Lbs. | 1.80 | @ | 2.15 |
| Sulfuric Acid, chamber, 60° | 100 Lbs. | 1.00 | @ | 1.75 |
| Sulfuric Acid, conc., sp. gr. 1.842 | 100 Lbs. | 1.50 | @ | 2.00 |
| Sulfuric Acid, oleum (fuming) | 100 Lbs. | 1.75 | @ | 2.00 |
| Talc, American | Ton | 9.00 | @ | 13.00 |
| Terra Alba, American, No. 1 | 100 Lbs. | 75 | @ | 80 |
| Tin Bichloride, 50° | Lb. | 11¾ | @ | 12 |
| Tin Oxide | Lb. | 39 | @ | 41 |
| White Lead, American, dry | Lb. | 5½ | @ | |
| Zinc Carbonate | Lb. | 12 | @ | 13 |
| Zinc Chloride, commercial | Lb. | 10 | @ | — |
| Zinc Oxide, American process | Lb. | 8 | @ | 10 |
| Zinc Sulfate | Lb. | 6½ | @ | 7 |

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid, C. P., in bbls. | Lb. | 1.10 | @ | 1.15 |
| Acetic Acid, 28 per cent, in bbls. | 100 Lbs. | 2.75 | @ | 3.25 |
| Acetic Acid, glacial, 99½%, in carboys | Lb. | 15 | @ | — |
| Acetone, drums | Lb. | 27 | @ | 29 |
| Alcohol, denatured, 180 proof | Gal. | 38 | @ | 39 |
| Alcohol, grain, 188 proof | Gal. | 2.60 | @ | — |
| Alcohol, wood, 95 per cent, refined | Gal. | 50 | @ | 51 |
| Amyl Acetate | Gal. | 2.90 | @ | 3.00 |
| Aniline Oil | Lb. | 1.35 | @ | 1.50 |
| Benzoic Acid, ex-toluol | Lb. | 3.00 | @ | — |
| Benzol, 90 per cent | Gal. | 90 | @ | 1.00 |
| Camphor, refined in bulk, bbls. | Lb. | 43 | @ | — |
| Carbolic Acid, U. S. P., crystals, drums | Lb. | 1.40 | @ | 1.50 |
| Carbon Bisulfide | Lb. | 7 | @ | 7½ |
| Carbon Tetrachloride, drums, 100 gals. | Lb. | 16 | @ | 17 |
| Chloroform | Lb. | 35 | @ | — |
| Citric Acid, domestic, crystals | Lb. | 55 | @ | 55½ |
| Cresol, U. S. P. | Gal. | 1.15 | @ | 1.25 |
| Dextrine, corn (carloads, bags) | 100 Lbs. | 3.00 | @ | — |
| Dextrine, imported potato | Lb. | 10 | @ | 12 |
| Ether, U. S. P., 1900 | Lb. | 15 | @ | 20 |
| Formaldehyde, 40 per cent | Lb. | 8½ | @ | 9½ |
| Glycerine, dynamite, drums included | Lb. | 24 | @ | 25 |
| Oxalic Acid, in casks | Lb. | 39 | @ | 40 |
| Pyrogallic Acid, resublimed bulk | Lb. | 1.35 | @ | 1.55 |
| Salicylic Acid | Lb. | 2.75 | @ | 2.90 |
| Starch, cassava | Lb. | 3½ | @ | 4½ |
| Starch, corn (carloads, bags) | 100 Lbs. | 2.25 | @ | — |
| Starch, potato | Lb. | 6½ | @ | 7 |
| Starch, rice | Lb. | 7 | @ | [illegible] |
| Starch, sago | Lb. | 3¾ | @ | 4 |
| Starch, wheat | Lb. | 6½ | @ | 7 |
| Tannic Acid, commercial | Lb. | 70 | @ | 71 |
| Tartaric Acid, crystals | Lb. | 46½ | @ | 47 |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax, pure, white | Lb. | 42 | @ | 45 |
| Black Mineral Oil, 29 gravity | Gal. | 12½ | @ | 13 |
| Castor Oil, No. 3 | Lb. | 10½ | @ | 11 |
| Ceresin, yellow | Lb. | 10 | @ | 14 |
| Corn Oil | 100 Lbs. | 6.00 | @ | — |
| Cottonseed Oil, crude, f. o. b. mill | Gal. | 37½ | @ | 38½ |
| Cottonseed Oil, p. s. y. | Lb. | 6 | @ | 6¼ |
| Creosote, beechwood | Lb. | 3.00 | @ | 4.00 |
| Cylinder Oil, light, filtered | Gal. | 20 | @ | 25 |
| Fusel Oil, crude | Lb. | 2.40 | @ | 2.50 |
| Japan Wax | Lb. | 13 | @ | 14 |
| Lard Oil, prime winter | Gal. | 84 | @ | 88 |
| Linseed Oil, raw (car lots) | Gal. | 51 | @ | — |
| Menhaden Oil, crude | Gal. | 35 | @ | 36 |
| Naphtha, 68 @ 72° | Gal. | 12 | @ | 13 |
| Neat's-foot Oil, 20° | Gal. | 93 | @ | 94 |
| Paraffine, crude, 120 & 122 m. p. | Lb. | 2½ | @ | 3 |
| Paraffine Oil, high viscosity | Gal. | 22 | @ | 23 |
| Rosin, "F" Grade, 280 lbs. | Bbl. | | 3.65 | |
| Rosin Oil, first run | Gal. | — | @ | 25 |
| Shellac, T. N. | Lb. | 14¼ | @ | 14¾ |
| Spermaceti, cake | Lb. | | 25 | |
| Sperm Oil, bleached winter, 38° | Gal. | 70 | @ | — |
| Spindle Oil, No. 200 | Gal. | 17 | @ | 18 |
| Stearic Acid, double-pressed | Lb. | 11 | @ | 11½ |
| Tallow, acidless | Gal. | 62 | @ | 63 |
| Tar Oil, distilled | Gal. | 30 | @ | 31 |
| Turpentine, spirits of | Gal. | 41 | @ | 41½ |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum, No. 1, ingots | Lb. | 32 | @ | 34 |
| Antimony, Hallets' | Lb. | 39 | @ | 42 |
| Bismuth, New York | Lb. | | 3.00 | |
| Copper, electrolytic | Lb. | 17⅞ | @ | 18 |
| Copper, lake | Lb. | 18 | @ | 18½ |
| Lead, N. Y. | 100 Lbs. | | 4.45 | |
| Nickel, electrolytic | Lb. | 50 | @ | — |
| Nickel, shot and ingots | Lb. | 45 | @ | — |
| Platinum, refined | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | | 48¾ | |
| Tin | 100 Lbs. | 33.00 | @ | — |
| Zinc, N. Y. | Lb. | | 13½ | |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | 100 Lbs. | | 3.40 | |
| Blood, dried | Unit | | 2.45 | |
| Bone, 4½ and 50, ground, raw | Ton | | 30.00 | |
| Calcium Cyanamid | Unit of Ammonia | | 2.30 | |
| Calcium Nitrate, Norwegian | 100 Lbs. | | — | |
| Castor Meal | Unit | | — | |
| Fish Scrap, domestic, dried, f. o. b. works | Unit | 2.65 | & | 10 |
| Phosphate, acid, 16 per cent, bulk | Ton | 8.00 | @ | 9.00 |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble, 68 per cent | Ton | | 2.25 | |
| Tennessee, 70–80 per cent | Ton | 5.00 | @ | 5.50 |
| Potassium "muriate," basis 80 per cent | Ton | 220.00 | @ | 250.00 |
| Pyrites, furnace size, imported | Unit | 10½ | @ | 11 |
| Tankage, high-grade | Unit | 2.50 | & | 10 |

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# FOREST PRODUCTS SYMPOSIUM

Papers presented at the 51st Meeting of the AMERICAN CHEMICAL SOCIETY, Seattle, August 31 to September 3, 1915

## THE CHEMICAL ENGINEERING OF THE HARDWOOD DISTILLATION INDUSTRY

By JAMES R. WITHROW

It would require more time than we have at our disposal to go into the details of the chemical engineering of the hardwood distillation industry. They will be apparent to a certain extent in the accompanying lantern slides, though many interesting points must not even be mentioned. General features will be pointed out sufficiently to give a broad survey of the problems involved in plant operation.

The industrial demand which the hardwood distillation industry meets is sufficiently indicated by the mere mention of acetic acid, methyl alcohol, acetone, chloroform, and formaldehyde, without burdening you with statistics of their production, consumption, exportation and importation. The number of industries and objectives in the arts which benefit by the availability of these substances is surprisingly great, though not all of them are exclusively the products of this industry.

### DEVELOPMENT

The development of the industry appears to have been very simple. From the earliest times charcoal appears to have been used in the arts and especially in metallurgy. That liquid products could be formed, during the charcoal production, was very early observed. Uses were gradually found for these products and in course of time a demand was created for them with the result that wood carbonization was largely changed in method, so as to improve the yield of the desired by-products. The historical development of this industry is one of the most interesting in the annals of Industrial Chemistry, because it illustrates so well the battledore and shuttlecock fortune of so many of these industries. So often the by-product of to-day becomes the main product of to-morrow; and the new industry, which appears the worst competitive enemy of one industry, becomes the greatest blessing of the old industry in the next decade. The liquid products accompanying charcoal production are said to have been recovered by the ancient Egyptians and utilized by them in embalming the dead. Pliny mentions their recovery in Syria and Theophrastus in Macedonia. As chemical knowledge in those days appears to have been very limited and engineering skill as much so, the recovery of liquid products must have been trifling and it was many centuries before chemical knowledge made possible and the arts demanded intelligent development. Notwithstanding the later development of the engineering as well as chemical side of the industry, the essential features of primitive wood carbonization have come down practically unaltered to the present day. This primitive charcoal burning is still practiced wherever wood is plentiful in Russia, Scandinavia, Austria-Hungary, Germany (Westphalia and the Harz), New Jersey, Maryland, etc.

In spite of various uses to which they were put in early times no real appreciation of the value of the liquid substances known to be formed during carbonization of wood came until the dawn of modern chemical investigation. Lack of sufficient fundamental chemical knowledge was largely responsible for this. For instance as early as 1658 Glauber identified the so-called "burnt-wood acid" with acetic acid, yet not until 1802 was it identified with the acetic acid of fermentation, by Thenard. In 1661 Robert Boyle discovered wood-spirit in wood distillate, yet not until 1812 did Taylor notice its analogy to grain alcohol. The true character of this "spirit" was established only after a series of investigations by Colin, Dobereiner, Gmelin, Liebig, Sweitzer and especially Dumas and Pèligot, ending about 1835. As a result of these investigations together with those on the composition of the wood-tar and wood gas, there came an increased effort to recover such of these by-products as were suitable for use in the arts in general, as well as in the organic chemical industries that were at this time struggling for a footing upon the investigations of the great masters of our science. The first step in this revolution was the use of by-product kilns and retorts, in place of the old sod covered pits or heaps, for carbonization. It would seem that from this point, at least, the development of the industry should have been consistent and perhaps rapid but this was not the case.

Apparently the first product to have been systematically recovered was the wood-gas. This was first used in England for illuminating purposes somewhat prior to the chemical developments just mentioned. The honor, however, for the exhaustive investigation of the illuminating, heating and power value of this gas, belongs to the Frenchman, Phillip Lebon.

The weakly illuminating wood gas was soon outclassed, however, by the development of coal gas production and the whole hardwood distillation industry had a precarious existence during a large part of the last century even in spite of the fact that a satisfactory method of purifying the crude acetic acid had been devised as early as 1824 by Mollerat and Jasmeyer. The products of the destructive distillation of coal, such as coke, illuminating gas, tar and tar-distillates were sharp competitors of the wood products. Yet when the wood industry seemed about to be relegated to the primitive woods, the sudden development of the coal-tar color industry started a demand for acetic acid, methyl alcohol and acetone which has since been augmented by the demand for the same products in the production of celluloid and smokeless powder as well as many synthetic organic substances used in pharmacy and the arts. The demand for methyl alcohol within a few years after Perkins' discovery of aniline dyes became so great that the price was enormous. It is not surprising, therefore, that at that time in England wood was distilled with the sole object of getting wood alcohol. A like situation is said to have arisen at one time in benzol manufacture, coal having been for a while distilled with the sole object of obtaining benzol for aniline production.

These general statements regarding the development of the industry bring us to the present situation where we recover mainly the primary products wood gas, raw liquor (pyroligneous acid), tars and oils, and charcoal. It should be noticed in passing that while most engineering skill is a matter of quite recent development and chemical engineering is perhaps the most recently developed phase of engineering, yet it has been able reasonably to keep pace with chemical development in this industry at least, and this may be due largely to the fact that the development of engineering methods and the understanding and fabrication of engineering materials of construction developed along with the science of chemistry and are somewhat dependent upon it.

### THE PROBLEM OF THE INDUSTRY

Broadly speaking, the problem of the hardwood distillation industry is the complete utilization of the weight of the original wood as far as this is possible by economical chemical engineering manipulation, for the production of the products which it will yield of main industrial use or value, *i. e.*, charcoal, acetic acid and methyl alcohol.

Economical chemical engineering involves the use and sequence of such operations as will give the maximum financial return, per unit of raw material consumed, consistent with a proper balance between low cost of operation, low initial cost of plant and highest speed of turn over (processing raw material).

When wood is heated sufficiently in the atmosphere it tends to burn of course to residual ash, steam and carbon dioxide, for the most part. If the air is partially excluded we obtain residual charcoal and volatile products varying widely in composition, depending upon the extent of air exclusion, from the condition of almost complete combustion of volatile products, to practically entire elimination of combustion or atmospheric oxidation when air is excluded as completely as possible. The problem of the industry may be met therefore by heating the wood sufficiently to carbonize it and in such a way as to eliminate as far as possible any atmospheric oxidation of the volatile products, and at the same time handle the distillates in such a way as to minimize refining or purification difficulties.

Modern chemical engineering skill has met the conditions of reasonably efficient solution of the problem with fair success as is shown by the extent of the industry[1] and without doubt it will advance still further.

Every problem, however large, is merely a series of smaller sub-problems and each of these in turn is often resolvable into still other problems. In studying the problem of any chemical industry it is natural to divide it as far as possible into:

1—The nature of the demand or market for the products, or objectives of the industry;

2—The chemistry involved;

3—The operations or engineering involved.

The chemistry of the hardwood distillation industry finds its basis in the phenomena attending destructive distillation. Much more should be known about destructive distillation than *is* known. Our concern at this time, however, is with the engineering problems involved in the utilization of this chemistry. Suffice it to say in the matter of the chemistry involved, that the products of heating the wood, as is usually the case in destructive distillation, are gaseous, liquid (condensate) and solid (residual charcoal). The gas as a whole is combustible. The liquid is acid and in two (or three) nearly non-miscible phases—tar (and oil) and dilute alcoholic acetic acid, with dissolved tar and other substances.

### CHEMICAL ENGINEERING OPERATIONS

The engineering operations of the industry group themselves mainly into four divisions as follows:

I—Preliminary handling of raw material.

II—Destructive distillation proper or so-called primary distillation.

III—Treatment of the liquid distillate or secondary distillation.

IV—Refining operations and derived product production.

The latter is not generally connected with what is known as the Crude Hardwood Industry and will, therefore, be indicated with great brevity.

The engineering operations themselves are as follows:

I—Preliminary Handling of Wood
- 1—Harvesting the timber { Cutting / Splitting
- 2—Seasoning, transportation and storage

II—Primary Distillation (*Destructive distillation, proper*)
- 1—Loading oven cars
- 2—Charging and sealing ovens
- 3—Firing ovens (*Distillation*)
- 4—Condensation and fuel gas recovery
- 5—Pulling ovens (*Discharging hot charcoal cars*)
- 6—Cooling charcoal
- 7—Pulling charcoal coolers
- 8—Ageing charcoal
- 9—Screening charcoal

*Final Product:* Charcoal for the Market

III—Secondary Distillation (*of condensate obtained in II, 4*)
- 1—Settling "Raw Liquor" (*condensate II, 4*)
- 2—Separation of tar (and oil) from "Raw Liquor" (*continuous decantation*)
- 3—Redistillation of settled tar (*for further recovery of "Raw Liquor"*) from copper or wooden stills.
- 4—Condensation of acid distillate [*Oil added to "Boiled Tar," water added to original "Raw Liquor"* (*condensate II, 4*)]
- 5—Redistillation of settled "Raw Liquor" (*for further tarry bodies elimination*) from continuous copper stills
- 6—Condensation of "boiled liquor"
- 7—"Mixing" "boiled liquor" with lime (*Neutralization*)
- 8—Distillation of neutralized "boiled liquor" in lime-lee still (iron)
- 9—Condensation of weak alcohol-acetone
- 10—Settling or filtering lime-lee still residue (*aqueous calcium acetate*)
- 11—Evaporation and crystallization of lime-lee residues
- 12—Drying (sacking, weighing, analysis) crystallized acetate of lime

*Product:* Gray Acetate of Lime (80 Per Cent) for the Market
- 13—Redistillation of weak alcohol-acetone for oil separation and concentration (*Burcey pans, fractionation*)
- 14—Condensation of alcohol-acetone in fractions

*Product:* Crude 82 Per Cent Alcohol-Acetone for Market or Refinery

IV—Refining and Derived Product Manufacture

(*a*) *Alcohol:*
- 1—Chemical treatment of crude alcohol ($NaOH$ or $H_2SO_4$)
- 2—Distillation and condensation for elimination of chemicals, etc.
- 3—Fractional distillation in column still
- 4—Condensation with "heads and tails" elimination

*Product:* Refined Methyl Alcohol and Acetone-Alcohol for Market

(*b*) *Gray Acetate:*
- 1—Distillation with sulfuric acid (or HCl)
- 2—Dust elimination from vapors
- 3—Condensation of acetic acid (*Commercial*)
- 4—Refining by redistillation and fractionation after chemical or electrical treatment

*Product:* Refined and Concentrated Acetic Acid for Market

(*c*) *Gray Acetate:*
- 1—Destructive distillation
- 2—Dust elimination from vapors
- 3—Condensation of crude acetone and oils
- 4—Separation of oils from acetone
- 5—Chemical treatment for acid elimination
- 6—Redistillation for "white oil" elimination
- 7—Fractional distillation of acetone
- 8—Condensation

*Product:* Acetone for the Market

Each and every one of these operations calls for its own special form of apparatus or construction and modifies to a varying extent the design and operation of the plant. They are the essential operations or chemical engineering proper which must be carried out to secure the results obtained in first-class practice. There has been indicated also, in a limited way, how some of these operations must be carried out. Sufficient preliminary discussion of the development of the industry has been given to illustrate the connection which appears to have existed between the development of both chemical knowledge and engineering skill, and the growth and development of this industry.

In concluding I must express my indebtedness to Mr. Edward H. French, to whom I owe my first opportunity (a number of years ago) of working upon the problems of this industry, upon which he was himself engaged, and who has been of much assistance in securing plant photographs from which slides have been prepared.

Ohio State University, Columbus

[1] This Journal, 7 (1915), 47.

## WHAT CHEMISTRY HAS DONE TO AID THE UTILIZATION OF WOOD

By S. F. Acree

An attempt to discuss fully the influence of chemistry on the utilization of waste wood leads so deeply into practically all fields of chemistry that a paper of this kind must necessarily be limited to a small number of topics. Attention is given, therefore, to those phases of this subject which are of most importance commercially and which seem to show greatest promise for the future. The number of eminent chemists who have contributed to the few subjects to be discussed is so large that it is impossible to treat their individual researches as they deserve. Such being the case, a brief mention here and there of a few investigations by the Forest Service, with which the writer

is personally familiar, will not be understood as a failure to appreciate the work of others.

The technical processes involved in the apparently simple distillation and extraction of woods lead both into the abstruse problems of thermodynamics and into the most refined technique of organic chemistry, and advances in these investigations have been described by Klason, Wislicenus, Klar, Withrow, Palmer, and others. The distillation of waste hardwoods is now one of the most important industries in this country and has reached a high state of efficiency in the hands of Messrs. Stevens, Quinn Brothers, Troy, Gaffney, Clawson and the Cleveland Cliffs Chemical Company. There are over 100 plants in operation, in which about 1,200,000 cords of wood are distilled annually. The chief products obtained are charcoal, acetic acid, methyl alcohol, wood oils, and wood tars, and these are so valuable that extended researches have been made by the Forest Products Laboratory to increase the yields. The quantitative studies on the regulation of the reactions have resulted in improved processes and increased earnings. Charcoal is the least valuable by-product of the wood distillation industry, but is used in large quantities as a household fuel, in decolorizing grain alcohol and other liquids, in the manufacture of gunpowder and lubricants, and in the manufacture of fine charcoal steel. The acetic acid is utilized for the production of such substances as mordants for dyes, acetanilide, and sugar of lead. Acetone is produced by the distillation of calcium acetate and is used to the extent of 3,000,000 gallons annually in the manufacture of denatured alcohol, chloroform, photographic films, celluloid, and, especially, explosives.

Wood alcohol is one of the most striking illustrations which we have today of the value of chemistry and chemical methods in the purification and utilization of a waste product. When Mr. E. B. Stevens, President of the Wood Products Company of Buffalo, N. Y., constructed his first still out of a tin can and attempted to purify the evil-smelling distillate from a near-by wood distillation plant, he little realized what a tremendous future awaited his efforts as an enthusiastic boy of seventeen. Today, crude 82 per cent wood alcohol is changed by simple chemical and physical methods into a product which has a purity of 99.95 per cent. This substance is used all over the world and new fields are being discovered for its utilization. The 10,000,000 gallons produced in this country are used for making celluloid and similar products, dyestuffs, denatured alcohol, photographic films, formaldehyde, artificial leather, varnishes, shellacs, artificial rubber, and other substances too numerous to mention, in whose manufacture and use hundreds of millions of dollars and large numbers of men are employed. European countries use nearly as much wood alcohol as the United States but chiefly for denaturing ethyl alcohol, for the manufacture of formaldehyde, for the methyl group of aniline colors, and for other purely chemical purposes. There is at present no substitute for wood alcohol in the preparation of the methyl groups of various dyes, especially the violets and blues, and hundreds of millions of dollars are invested in the dyestuff business and in the wool, cotton, linen, and silk cloth industries and others using these colors. These dyes are used today in many cases of disease in staining tissues and bacteria, thus allowing medical men to make a proper diagnosis.

Wood alcohol acts as a poison when taken internally, or when its concentrated vapors are inhaled in enclosed spaces, and sometimes produces blindness and death under these conditions. The wood alcohol manufacturers themselves condemn its use as such in any article of food, drink, or medicinal or toilet preparation. When, on the other hand, these objectionable properties are destroyed by chemical changes, it becomes one of the substances necessary for the production of other products for the protection of the health of the community. Pure methyl (wood) alcohol is the only substance which can be converted on a commercial scale into formaldehyde, which is used universally for disinfection against such contagious diseases as smallpox, scarlet fever, diphtheria, tuberculosis, infantile paralysis, and spinal meningitis in its epidemic form. It should, furthermore, be pointed out that many native and alien crop diseases are becoming epidemics in this country and destroying yearly from ten to twenty million dollars worth of foodstuffs, besides infecting the farming lands and rendering them far less valuable for the production of certain crops. The United States and State Governments prescribe formaldehyde as the disinfectant for the seeds, which are sterilized before planting. By this disinfection crop losses, due to certain fungi, can be greatly reduced. Formaldehyde is practically the only efficient disinfectant which can be legally employed in embalming the dead and preventing the spread of contagious diseases causing their deaths. Formaldehyde and phenol are the basis of the manufacture of bakelite which is now used in tremendous quantities in large chemical apparatus in certain industries, and is finding wide use as insulating material in the electrical world. Formaldehyde is, furthermore, used in large quantities in the preparation of various dyes discussed above.

Another by-product from wood distillation, which has received little consideration up to this time, is the hardwood tar. This substance has a large percentage of derivatives which should find wide use in chemical industries. Already we find small quantities of these tars in use as wood tar creosotes for the preservation of wood, and the insufficient production of coal-tar creosote in this country will, without doubt, enable wood tar creosote to come into its own, especially as it has been found to have a high toxicity toward certain fungi.

In the field of distillation of softwoods, we find that some of our most important commercial products are obtained by this combination of physical and chemical methods. The chief products are turpentine, pine oils, tar oils, rosin and charcoal. The turpentine is used chiefly in the production of paints, varnishes, and shellac. The pine oils are used to a large extent as solvents and as medicine. The tar oils are used for treating such things as rope and fish nets in order to preserve them in salt water. The rosin is used in making soaps, paper sizing, varnishes, and shellacs. Charcoal is used chiefly for fuel.

The value of the paper and pulp industry in this country is apparent immediately when we think of the benefit derived from the tremendous number of books, periodicals and of newspapers. Wood pulp is used for making men's summer clothes, papers of all kinds, binder twine to replace sisal, sacks, filter papers, and rugs. It is used for making fiber vessels, vulcanized fiber for electrical insulation, and is now the basis of viscose which is finding a wide field of application. Viscose is colloidal cellulose which can be made into "fiber silk" thread and sausage coverings. The thread can be woven alone, or in combination with cotton or silk, into all kinds of fabrics, such as artificial silk socks, neckties, and cloth, all of which can be dyed beautifully in any color. Surgeons' thread, and erasers of this material are cheap and efficient.

Cellulose can be made in a very pure form from certain woods and has been used extensively in explosives. Not only is it converted directly into nitrocellulose but we find that wood flour is used very extensively as an absorbent in the manufacture of dynamite. The very finely divided wood flour absorbs 60 per cent of nitroglycerine and is more efficient than kieselguhr. This wood flour is also used in making certain grades of linoleum and is much cheaper than cork.

Turning now to the dyestuffs, we find that the aniline industry of Germany has not entirely driven vegetable colors from the market. A number of West Indian and South American woods, such as the fustic, logwood, Brazil wood, and peach wood, are imported into this country and the Forest Products Laboratory

has recently been instrumental in calling the attention of manufacturers to the fact that Oklahoma and Texas contain large quantities of osage orange[1] which can be used very cheaply as a source of a valuable yellow dye for textiles and leather. The enormous leather industry is dependent not only upon the use of vegetable dyestuffs but especially upon the tannins obtained from hemlock, oak, chestnut and other materials. Certainly the preparation of tanning material involves the most delicate physical and chemical, as well as biological, operations, as has been shown by the work of Proctor, Stiasny, Levi, Balderston and others.

That the production and consumption of ethyl alcohol in the United States is an important activity is emphasized by the fact that the taxes on distilled spirits and fermented liquors amounted in 1913 to $223,000,000, which was over 65 per cent of the entire internal revenue of the country. It will be recalled that over 100 years ago Braconnot carried out an investigation in which wood was hydrolyzed by acids into glucose, which was then fermented into ethyl alcohol. In recent years, this problem has been studied energetically by Simondson, Classen, Cohoe, Ewen and Tomlinson and others, and four plants were erected in the United States. Three of these failed but the experience gained thereby and the research work on this problem by the Du Pont de Nemours Powder Company and the Forest Products Laboratory have now made the outlook for this industry very bright. It is believed that a plant could now be constructed under proper conditions of location, transportation, and other such factors, which would make possible the manufacture of ethyl alcohol from sawdust at a price which would allow it to compete with the production of ethyl alcohol from molasses. Especially important in this connection is the discovery by the Forest Products Laboratory that western larch contains about 10 per cent of a galactan yielding only galactose. If fermentation methods can be devised for the commercial conversion of galactose into ethyl alcohol, the western larch butts, which are at present waste material, will become a very cheap source of alcohol. The increased efficiency of alcohol at high pressures in internal combustion engines may thus place this material in a position where it can compete with gasoline when this becomes scarcer.

The preservation of woods in railroad ties, telegraph poles, heavy bridge timbers, structural timbers, and in houses, is one of the most important phases of forest conservation before the public today. In this preservation over 100,000,000 gallons of coal-tar creosote, water-gas-tar creosote, and mixtures of these chemicals with petroleum residues are used. Aqueous solutions of zinc chloride, sodium fluoride, copper sulfate, and many other inorganic chemicals are also used very widely. Millions of dollars are thus involved in an industry whose business it is primarily to preserve this investment. It follows then that chemical methods must be developed for the analysis of the creosotes, and that chemical studies should lead to the manufacture of better materials at lower cost. The Forest Products Laboratory has made investigations on the analysis of creosotes and the isolation of their many constituents, together with tests of the toxicity of these compounds toward wood-destroying fungi, and these researches have shown that great improvements could easily be made in the preservation of wood by the use of better specifications for the materials and methods of treatment.

In the above paragraphs, only a few of the industries involving the utilization of chemical methods in the use of waste wood have been discussed. But daily the problems along these lines are being extended and the future will probably show that the application of chemistry to the utilization of forest products extends into nearly every field of human endeavor.

FOREST PRODUCTS LABORATORY AND UNIVERSITY OF WISCONSIN
MADISON

[1] THIS JOURNAL, 6 (1914), 462

## THE TANNIN CONTENT OF PACIFIC COAST CONIFERS

By H. K. BENSON AND THOS. G. THOMPSON

The tannin extract industry of the United States utilizes for its raw material chestnut wood and the bark of the Eastern hemlock and the chestnut oak. From these species a standard extract containing 25 per cent tannin is manufactured, annually amounting to over 200,000,000 lbs. An equal or greater quantity of extract is either imported, or made from materials imported, of which quebracho is of chief importance. In view of the large sources of available supply of tannin-containing materials on the Pacific Coast, a study was made of the tannin content of Western hemlock, Douglas fir and Western spruce.

### WESTERN HEMLOCK

The Western hemlock extends from Alaska to Marin County, California, and eastward, in some places, as far as Montana, thriving in the cool, moist climate characteristic of western Washington and Oregon. It grows along with spruce, cedar and fir, often being left as useless by the timber cutters. An excellent example of the distribution of these trees is found in a recent survey of the merchantable timber of the Olympic National Forest. It was found that out of this forest, containing 25,500,000,000 ft. of timber, 35 per cent was Western hemlock, 37 per cent Douglas fir, and the remainder spruce and cedar.

The bark of the Western hemlock is thinner than that of the Eastern hemlock, but, as is commonly known, it contains a higher tannin content. This fact was first brought to the attention of the Washington public in 1893 when several samples of the bark were submitted to Dr. H. W. Wiley, who reported the following analyses:

| SAMPLE: | Ashford | Enumclaw |
|---|---|---|
| Moisture | 10.55 | 10.01 |
| Total solids | 24.03 | 22.16 |
| Soluble solids | 22.59 | 20.58 |
| Reds | 1.44 | 1.58 |
| Non-tannins | 6.59 | 5.76 |
| Available tannins | 16.00 | 14.86 |
| Woody fiber | 65.42 | 67.83 |

The first results that were published[1] calling attention to the differences in percentage of the tannin content of the Western and Eastern hemlock were the following analyses made by H. G. Tabor of hemlock bark from trees in Washington, Pennsylvania and Quebec:

| SOURCE: | Washington | Pennsylvania | Quebec |
|---|---|---|---|
| Tannin | 17.04 | 13.28 | 10.16 |
| Non-tannin | 6.40 | 7.52 | 4.56 |
| Reds | 1.56 | 3.48 | 1.92 |
| Woody fiber | 75.00 | 75.72 | 83.36 |

Western hemlock bark has been used as the exclusive tanning agent in at least one tannery in Washington for a number of years. This concern manufactures chiefly skirting leather for saddles. Its larger use has been prevented by the lack of tanneries, due to economic reasons, rather than unsuitableness. The prevailing cost of hemlock bark f. o. b. tannery has been $11.50 per cord.

### EXPERIMENTAL

Inasmuch as few references to the tannin content of Douglas fir and Western spruce could be found, and as far as is known no effort has ever been made to demonstrate the tannin content of sawmill waste from these species, an experimental study was undertaken.

PREPARATION OF SAMPLE—The sawmill waste taken for analysis consisted of bark, slabs, and sawdust from the crosscut saws. Samples of 100 lbs. were taken for the bark, from 100 to 150 lbs. for slabs, and about 25 lbs. for the sawdust. The bark and the slabs were each reduced in a Mitts and Merrill chipper and the chips quartered to obtain an average sample. Before subjecting the sample to analysis it was further reduced to a fine powder in a Grumbaugh mill.

[1] *Hide and Leather*, June 24, 1893

EXTRACTION OF SAMPLE—The apparatus used for extraction is shown in Fig. I. From 50 to 75 grams of the sample were placed in the percolator A. The flask B contains the water for extraction. On boiling, the steam flowed through the tube C, and entered the percolator where partial condensation occurred in D. Boiling water continually drops upon the material in A until it reaches the height indicated by E, after which it is returned to the boiling vessel B. To prevent rifts or channels in the sample, the latter was mixed with broken glass before extraction, and to prevent particles of bark or wood from siphoning over with the liquid, a small perforated porcelain disk and glass wool were placed over the outlet tube. It was found advisable to use as large an outlet tube for the condenser as possible and to spread glass wool or wire gauze over the top of the sample in the percolator. Both the extraction and the analysis were made in accordance with the Official Method of the American Leather Chemists' Association.

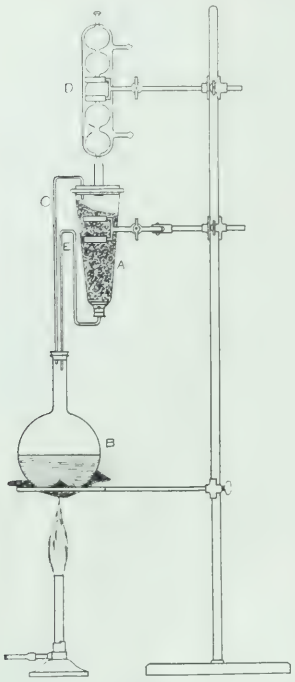

FIG. I

TANNIN CONTENT OF DOUGLAS FIR

The extract obtained from the Douglas fir was reddish brown in all cases except from the freshly cut bark which was yellow-brown and contained a yellow precipitate. The logs from which the samples were obtained had been cut for a period of eight months and during a portion of this time they were in water. However, the bark of the Douglas fir is so thick that there is probably very little loss of tannin by leaching in floating the logs to the sawmills. From the yields given in Table I, it is shown that the cambium layer, which is dark brown in seasoned wood and yellow-brown in freshly cut wood, contains most of the tannin. When a sample of bark is taken from a seasoned log not all of the cambium layer is taken. The slab, however, contains the cambium layer in its entirety with a relatively small quantity of wood in addition to the bark proper. The analyses of various samples appear in Table I, the results being reported on the dry material.

TABLE I—TANNIN CONTENT OF DOUGLAS FIR

| SAMPLE: | Sawmill bark | Sawmill slab | Fresh bark | Cambium layer | Sawdust |
|---|---|---|---|---|---|
| Total solids | 14.75 | 14.92 | 11.41 | 21.96 | 5.78 |
| Soluble solids | 13.36 | 13.02 | 9.36 | 19.28 | 4.40 |
| Reds | 1.39 | 1.90 | 1.95 | 2.68 | 1.38 |
| Non-tannins | 7.02 | 7.10 | 6.74 | 9.36 | 3.34 |
| Tannin | 6.34 | 5.92 | 2.62 | 9.92 | 1.06 |
| Moisture | 9.06 | 6.91 | 14.27 | 20.59 | 15.51 |

TANNIN CONTENT OF WESTERN SPRUCE

The extract from spruce was a clear brown in color. The bark is much thinner than in fir. On account of remoteness of the mill from which the samples were obtained no history of the logs is available but it is probable that they were floated in water a longer period than in the case of the fir logs. While check analyses were made, time did not permit as complete an examination as for fir. The results of the analysis, reported on a dry basis, are given in Table II.

TABLE II TANNIN CONTENT OF WESTERN SPRUCE

| SAMPLE | Sawmill bark | Sawmill slab |
|---|---|---|
| Total solids | 12.83 | 11.25 |
| Soluble solids | 12.30 | 10.38 |
| Reds | 0.53 | 0.87 |
| Non-tannins | 6.42 | 6.74 |
| Tannin | 5.88 | 3.69 |
| Moisture | 15.23 | 9.15 |

TANNING VALUE OF FIR EXTRACT

The fir chips from the bark and slabs not required for samples were extracted by the West Coast Tanning Company, Seattle, and several skins tanned in the resulting extract. A very desirable leather was produced, having a color similar to that obtained from oak tannin.

COMMERCIAL POSSIBILITIES FOR FIR EXTRACT

When it is remembered that the tannin content of chestnut wood is 6.62 per cent, it appears that the low cost of fir slabs containing an average of 5 per cent tannin should make the use of fir slabs a possible raw material for the tannin extract industry. It is known to the writers that fir slabs can be purchased from some of the mills at as low a cost as 75 cents per cord. In mills located in large cities, where they are sold for fuel, the cost is usually $1.50 to $2.00 per cord. Compared with Western hemlock bark at $11,50 per cord, it is found that three cords of fir slabs will yield as much as one cord of hemlock bark but at less than one-half the cost of the bark.

CONCLUSIONS

I—The tannin content of fir sawmill waste is above 5 per cent while that of spruce is above 4 per cent.

II—It is believed that fir waste is a suitable material for use in the tannin extract industry.

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## YIELD OF BY-PRODUCTS FROM DESTRUCTIVE DISTILLATION OF SOME WESTERN CONIFERS

BY H. K BENSON AND MARC DARRIN

The utilization of forest wood and mill waste by destructive distillation has been attempted in the Pacific Northwest on a commercial scale, but without success. It has accordingly been thought worth while to undertake a study of the yields obtained from various species and from various classes of waste wood from a given species. For this purpose an experimental plant for operation on a semi-commercial scale was erected, coöperatively, by the United States Forest Service and the University of Washington. The design of this plant has already been described.[1]

This plant was operated by chemists detailed by the United States Forest Service, in coöperation with the University of Washington. This paper presents a résumé of results obtained in a series of runs, part of which were made by G. M. Hunt, and part by Marc Darrin, chemists in Forest Products, United States Forest Service.

SPECIES AND CLASSES OF WOOD USED

For Douglas fir three classes of wood were distilled: (1) common run mill waste; (2) selected mill waste; (3) common run stump wood. In the case of the Western yellow pine both common run stumps and common run mill waste were distillled while for Western hemlock only the common run mill waste was used for distillation. Before final and conclusive results covering the Western conifers can be obtained, similar studies of selected Western yellow pine and of spruce should be made.

[1] THIS JOURNAL, 5 (1913), 935.

### METHOD OF OPERATION

The capacity of the retort is about one-half cord. For distillation, the wood is cut into 2 ft. lengths, measured, weighed, and loaded vertically into three retort buggies. These are run into the retort, which is fired with heat control for 12 hours. The temperature at various points of the retort is measured by four thermo-couples. Water manometers are used to ascertain pressure conditions. The rate of distillation is determined by measuring in a graduate the quantity of distillate per minute. The gross distillate from the retort is redistilled in a copper still heated with steam in coils at 125 lbs. pressure. The liquids and gases from distillation flow from the bottom of the retort into the tar separator, from which the retort tar is drawn. After passing through the cold water condenser the fixed gases pass through a rotary pump which maintains the proper pressure in the retort and also acts as a mechanical separator of the tar globules in the gas. This tar is removed by means of a trap attached to the pump. From the rotary pump the gas passes through a 60-light meter for measurement, and thence into a holder.

### PRODUCTS OF DESTRUCTIVE DISTILLATION

"TURPENTINE AND LIGHT OIL" are made to include all oils of a turpentine character. While much of this fraction is not pure turpentine, the general uses of this fraction in paints and for other technical purposes justify the grouping of these oils under one class.

"TAR" includes both the yields of the so-called retort tar and still tar, *i. e.*, residues from still. These tars in distillation yield about a third of their weight of tar oils, which consist principally of wood creosote, fir oil, some turpentine, and other wood oils. The residue, after removal of tar oil, is a heavy black pitch. The retort tar is heavier and darker than the still tar and contains a lower percentage of the tar oils. The gas tar from the rotary pump is included in the yields of still tar. It is very light and fluid and contains a high percentage of tar oils.

"WOOD ALCOHOL" was measured by means of a Westphal float attached to an analytical balance. This method computes the acetone as wood alcohol. In the case of the Douglas fir, the proportion of acetone in the wood alcohol is about 20 per cent.

"ACETATE OF LIME" was computed from a titration of the aqueous distillate with potassium hydroxide, with phenolphthalein as the indicator.

"CHARCOAL" contains from 80 to 90 per cent fixed carbon, and 1 to 2 per cent ash.

The "GAS" was measured from the time that a small pilot burner in the main caused continuous ignition. A uniform sample from this point in the run was obtained from the holder and its heating value determined in a Sargent calorimeter. The results of these determinations show its heating value to be a little below that of commercial illuminating gas.

### DOUGLAS FIR COMMON RUN MILL WASTE

Douglas fir common run mill waste consists chiefly of slabs, edgings, and some inside wood. This wood was taken just as it left the saws and was passing up the conveyor. It was in no way selected. In fact pitchy pieces were discarded as not of an average character, in order that the results obtained might be of a conservative nature. Altogether on this class of material, 21 runs were made. These consisted of four or five runs from four different sections of the state. There was found, however, so little difference in the yields from the various localities, that the tests on the remaining conifers were made only on species from one locality.

The average amount of common run Douglas fir mill waste for the four principal mills in Seattle is 32.2 cords per day per 100,000 feet cut.

### DOUGLAS FIR SELECTED MILL WASTE

Douglas fir selected mill waste consists chiefly of inside wood, more or less of a split and shaky nature around the pitch seams. The fact that the pitchy mill waste, in the case of Douglas fir, is of this split character, is the probable cause that this lumber is not suitable for any commercial use as lumber, whereas, in the case of Western yellow pine, it was found that most of the pitchy material occurred in hard inside material which is suitable for some commercial uses. The raw material was taken from the mill just as it came from the saws, but included only that portion which was especially suitable for distillation because of its resinous nature. In determining whether the material was of a resinous nature or not every stick passing up the conveyor which contained a single seam of pitch on the sides or ends, was taken, care being exercised to insure that an average sample of the selected mill waste was being obtained. The average amount of common run Douglas fir mill waste for the four principal mills, as previously stated, is 32.2 cords per day per 100,000 feet cut. Of this amount 13.3 per cent consisted of the selected material. This amounts to 4.3 cords per day per 100,000 cu. ft.

### DOUGLAS FIR COMMON RUN STUMP WOOD

Douglas fir common run stumps consist of large, solid pieces. There was little or no rotten material in connection with the stumps, although many of them had been in the ground for a long number of years after the trees were cut. The stumps were taken just as they occurred in the clearing of logged-off land, and were strictly unselected, being an average sample of the common run from the locality. Before the material was selected, the ground was gone over in order to determine if the stumps occurring in that logged-off district could be considered a fair average for the western part of the State. In the selection of the individual stumps none showed signs of pitch on the outside.

### WESTERN YELLOW PINE COMMON RUN MILL WASTE

Western yellow pine common run mill waste consists chiefly of small slabs and edgings and practically no inside wood. This material was taken from the mills just as it came from the saws and was strictly unselected, being an average sample of the common run of yellow pine mill waste. It should be especially noted in connection with this material that there is much less pitchy and inside wood than in the case of the mill waste from Douglas fir. This observation is apparently at variance with the well-known fact that yellow pine is especially pitchy, but may be explained as follows:

An examination of the logs as they are being first cut by the band saw shows, in many cases, considerable dark, pitchy wood, especially in the inside of the logs. Instead of cutting out this pitchy material, and making small lumber out of the remaining portion, as in the case of Douglas fir, the entire pitchy portion is cut into heavy planks which are suitable for use on roads, etc.

### WESTERN YELLOW PINE COMMON RUN STUMP WOOD

Western yellow pine common run stumps, before being cut up, varied in diameter from 11 to 32 in., and in height of the crown above the roots from 26 to 36 in. The stumps were from a few months' to six years' standing, and in several instances showed signs of decay. After the material was cut into two-foot lengths they could be roughly classified as follows: (1) top crown of stump; (2) lower body of stump; (3) roots. The top crowns of the stumps constitute about 40 per cent of the total, and are similar to ordinary forest cord wood, but are a little more resinous. The lower bodies of the stumps constitute nearly a similar portion, and are for the most part large, knotty pieces which are difficult to handle or split. Little difficulty was found later, however, in charring even these

TABLE I—AVERAGE RESULTS OF TESTS ON VARIOUS WASTE WOODS BY DESTRUCTIVE DISTILLATION

| WOOD MATERIAL TESTED | Av. wt. of measured cord Lbs. | Turpentine and light oil Gal. | Tar Gal | Wood alcohol Gal | Acetate of lime Lbs | Char coal Lbs. | Gas Cu. ft |
|---|---|---|---|---|---|---|---|
| Douglas fir common run mill waste | 3,340(a) | 3.40 | 27.80 | 3.90 | 75.6 | 657 | .... |
| Douglas fir selected mill waste | 4,250(b) | 10.86 | 46.37 | 3.71 | 74.3 | 900 | .... |
| Douglas fir common run stump wood | 3,260(b) | 5.59 | 19.88 | 2.60 | 55.8 | 675 | 6,270 |
| Western yellow pine common run mill waste | 2,840(b) | 4.91 | 24.80 | 3.25 | 73.4 | 478 | 6,120 |
| Western yellow pine common run stump wood | 2,620(b) | 6.06 | 23.05 | 1.83 | 60.8 | 520 | 3,950 |
| Western hemlock common run mill waste | 3,270(c) | 2.76 | 21.60 | 5.00 | 94.0 | 938 | .... |

(a) Based on 15 half-cords. (b) Based on 4 half-cords (c) Based on 5 half-cords.

larger pieces. The roots constitute 10 to 20 per cent of the total, and are for the most part rotten, except in the interior, which, in many cases, is hard and resinous. Only two of the stumps showed signs of pitch on the outside. The stumps were taken just as they occurred in the clearing of logged-off lands, and were strictly unselected, being an average sample of the common run of pine stumps for the Eastern part of the State of Washington.

### WESTERN HEMLOCK COMMON RUN MILL WASTE

This material consisted chiefly of slabs, and some edgings and inside wood. It was obtained in the same manner as the Douglas fir common run mill waste.

### DISCUSSION OF RESULTS

The results of the runs on the various woods are given in Table I; they show that the heaviest material is Douglas fir selected mill waste, and the lightest, Western yellow pine common run stumps. This difference is due chiefly to the fact that the former consists mostly of inside wood piled up closely with a small percentage of voids, whereas the stump wood can be piled, even after cutting into 2-ft. lengths, in a very irregular manner, with a large percentage of voids. The common run mill waste from the Douglas fir and the Western hemlock is several hundred pounds heavier than the similar material from Western yellow pine. Likewise the fir stumps are heavier than the pine stumps. In this connection it should be remembered that the yields given in Table I are based on the measured cord, as this is the method employed in the ordinary commercial handling of wood, and moreover, as it is this volume factor which limits the capacity of any distillation apparatus.

The yields of gas are available only in three cases, the greatest being for Douglas fir stumps. Although Douglas fir and hemlock mill waste were not tested for the yield of gas, it is possible that the yield may be higher in these cases than those recorded, as it is seen that the yield from the mill waste in the case of the pine is greater than that from the stumps.

### CONCLUSIONS

None of the classes of the materials tested gave a higher yield of *all* the by-products than any other class of raw material. The question of *which is the most suitable class of material for distillation*, therefore, limits itself to a function of the market values of the respective by-products, the cost of obtaining the raw material, and the operating expenses.

Although one set of conditions might favor the use of one class of material to the exclusion of all others, still, conditions, such as the cost of raw material, market for charcoal, etc., might be so changed as to reverse this.

Under the present conditions, unless other factors enter into the consideration, such as the increased value of the land, due to the removal of the stumps, the order of commercial suitability for distillation is somewhat as follows:

1—Douglas fir selected mill waste
2—Douglas fir common run mill waste
3—Western hemlock common run mill waste
4—Western yellow pine common run mill waste
5—Western yellow pine common run stump wood
6—Douglas fir common run stump wood

A change in the market conditions, especially for charcoal, or a possible sale of the gas, or a possible utilization of the pyroligneous acid for the production of acetone,[1] or a change in the cost of raw material, may greatly change the order of the commercial value. The value of the Douglas fir selected mill waste, however, is so far advanced over that for the other raw materials tested that there is little doubt it is the most suitable for distillation.

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## THE USE OF AMMONIUM HYDROXIDE FOR THE EXTRACTION OF ROSIN FROM WOOD

By H. K. BENSON AND HERBERT N. CRITES

The extraction of rosin from "light wood" in the Southern States is accomplished by first steaming the chips, next covering them with a petroleum distillate, reheating until the distillate begins to vaporize, and then withdrawing the solution of rosin. By subjecting this solution to re-distillation, the solvent is recovered first, and finally the turpentine and pine oil, leaving the rosin as a residue. The main difficulty with this method is the loss of solvent in the cycle, which, according to operators, is as high as 50 gallons per cord of wood extracted.

Various plans have been suggested to overcome this loss. Clopé proposes to use[2] the volatile distillate boiling between 170 and 185° C. obtained from the steaming of wood, as a solvent for rosin. The loss of this solvent is reported at less than 6 gallons per cord of wood extracted, and as it is being constantly produced in the process, no additions from external sources need be supplied This solvent is, however, a fraction of turpentine generally permissible in commercial grades. It consequently diminishes the yield of turpentine per cord of wood, incurring a financial loss equal to or greater than that prevailing with the petroleum solvent.

To a limited extent a hot bath of some non-volatile or high-boiling material, such as molten rosin, pine tar, pine oil, etc., has been employed but has been abandoned by the commercial plants in which it had been attempted. Recently the use of alkalies such as caustic soda or soda ash has been suggested[3] for the extraction of rosin. The alkali combines with the rosin acids and forms a soluble rosin soap while the turpentine and pine oil may be removed from the solution by distillation with steam. The difficulty in this method lies in the form in which rosin is finally recovered, *i. e.*, as a soap, for which apparently no great demand exists as obtained from wood by this process.

The present investigation was based upon two facts: (1) the instability of ammonium salts when heated, and (2) the completeness of recovery of ammonia as commercially carried on in the coal gas plants of this country.

### EXPERIMENTAL

Powdered rosin was added to a 25 per cent solution of warm ammonium hydroxide and formed a thick, light yellow, translucent solution which became quite firm on cooling It slowly decomposed while standing in the air and on adding heat, the ammonia was driven off, leaving rosin as a residue.

### GENERAL METHOD OF PROCEDURE

The next step consisted in the use of resinous fir wood containing from 20 to 30 per cent rosin. The wood was used in

[1] THIS JOURNAL, 7 (1915), 927.
[2] U. S. P. application, Serial No. 875,463.
[3] U. S. Department of Agriculture, Bureau of Chemistry, *Bull.* 169.

the form of chips (1 in. × 1/8 in. × 1/8 in.), shavings, and sawdust. The general method of procedure was to cover a weighed quantity of wood with a known quantity of ammonium hydroxide. This was heated in pressure bottles to various temperatures for several hours, and while still warm the brown syrupy liquor was poured off and the wood washed with very dilute ammonium hydroxide. The combined liquors were heated, the ammonia passing off and being regained in wash bottles containing cold water. After complete evaporation, a black, tarry mass remained, which was next treated with gasoline and filtered. The filtrate is a solution of rosin while the solid matter upon the filter paper consists of portions of the wood which are also soluble in ammonium hydroxide and which for convenience will be designated as "humus." Upon evaporation of the gasoline, a residue of rosin of fine golden color remains. To ascertain the efficiency of extraction, the extracted chips were dried, finely ground in a Grumbaugh mill and extracted with ether in a Soxhlet apparatus.

Table I—Preliminary Extraction Experiments

| Exp. No. | Conditions of Extraction: $NH_4OH$ used Per cent | Cc. | Time Hrs. | Temp. ° C. | Washing: Time | Hrs. | Wash Liquor: Vol. Cc. | Per cent $NH_4OH$ in | Per cent Rosin: Extracted | Not Extracted | Efficiency of rosin extraction Per cent |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 25 | 150 | 500 | 18 | 2 | 6 | 150 | 3 | 16 | 12 | 57 |
| 2 | 25 | 200 | 500 | 18 | 2 | 6 | 200 | 3 | 22.8 | 2 | 92 |
| 3 | 25 | 150 | 500 | 18 | 2 | 5 | 100 | 3 | 12 | 10 | 54.5 |
| 4 | 25 | 90 | 6 | 100 | 1 | 2 | 100 | 5 | 18 | 5.6 | 76 |
| 5 | 3 | 70 | 7 | 100 | 1 | 1 | 80 | 1 | 18 | 9.05 | 64.5 |
| 6 | 5 | 70 | 7 | 100 | 1 | 1 | 80 | 1 | 21.6 | 5.6 | 79.5 |
| 7 (NaOH) | 2.6 | 90 | 14 | 100 | 1 | 1 | 80 | 0 | 16 | 1 | 94 |

Table II—Extraction of Resinous Chips

| Exp. No. | Conditions of Extraction: Liquor used Cc. | Time Hrs. | Washing: Time | Hrs. | Wash Liquor: Vol. Cc. | Per cent $NH_4OH$ in | Per cent rosin extracted in liquor: 1st | Wash | Per cent humus extracted in liquor: 1st | Wash | Per cent rosin not extracted | Efficiency of rosin extraction Per cent |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 100 | 3 | 1 | 3 | 80 | 5 | 16.9 | 1.5 | 7.7 | 6.9 | 7.4 | 71 |
| 2 | 175 | 8 | 1 | 3 | 90 | 1 | 19.7 | | 21.0 | | 2.2 | 90 |
| 3 | 200 | 6 | 1 | 3 | 90 | 1 | 15.8 | | 14.9 | | 2.0 | 89 |
| 4 | 200 | 5 | 1 | 3 | 60 | 1 | 16.4 | 1.0 | 10.4 | 2.2 | 0.8 | 95.6 |

## PRELIMINARY EXPERIMENTS

In Table I are given the results obtained from the preliminary experiments. The efficiency of extraction is found by dividing the amount of rosin extracted by the sum of the quantity extracted plus that not extracted. Owing to the manner in which rosin is distributed in Douglas fir, it is difficult to get samples with uniform rosin content. This fact accounts in part for variations in total rosin content. Experiments 1, 4, 5, 6 and 7 were with chips, while in 2, sawdust, and in 3, shavings were used: 25-gram samples were used in each case.

Experiments 1 and 3 show that extraction of chips and shavings is impracticable at room temperatures while sawdust can be thus extracted. While extraction was not complete in Experiments 4, 5 and 6, the latter shows that a five per cent solution of ammonium hydroxide is equally efficient as concentrated ammonium hydroxide under the same conditions. Experiment 7 was made with sodium hydroxide for comparison. The quantity of rosin extracted in this experiment was obtained by acidifying the sodium resinate solution, drying and weighing the rosin thus obtained. Fineness of wood, higher temperatures (involving closed vessels under pressure), and sufficient volume of liquor are consequently necessary factors for efficient extraction.

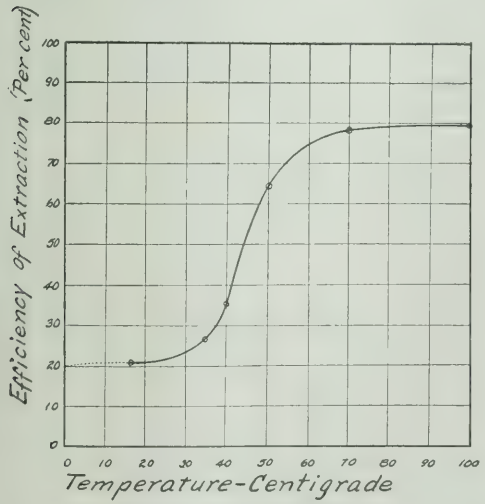


Fig. I—Effect of Temperature on Extraction

## EFFECT OF TEMPERATURE ON EXTRACTION

A series of seven extractions was undertaken and carried out under the same set of conditions with the exception of temperature. A concentration of 5 per cent ammonium hydroxide was used. The efficiency of extraction is shown in Fig. I., from which it is observed that rapid extraction begins at 40° to 50° C. and reaches its maximum at 70° C.

## EFFECT OF VOLUME OF LIQUOR AND TIME OF EXTRACTION

To ascertain the effect of the volume of ammonium hydroxide solution and the period of time of extraction, a number of extractions were made, the results of which are given in Table II. Twenty-five grams of chips, a 5 per cent solution of ammonium hydroxide and a temperature of 70° C. for extraction and washing were used in each case. In Experiments 2 and 3 the percentage of rosin and of humus in the wash liquor were not determined, but only the total quantity of each in the combined extraction and wash liquors.

In Experiment 1, with a short period of extraction and a small volume of extracting liquor, poor extraction was obtained. While only a small amount of rosin is obtained by washing, the quantity of humus is nearly as great as in extraction. In Experiments 2 and 3 the effect of 2 hours' heating is found to be very slight on the yield of rosin, but high on humus. Maximum rosin and minimum humus extraction are obtained in Experiment 4, in which the minimum period of heating and volume of wash liquor are employed.

## USE OF HUMUS

While this investigation did not include a study of the humus, the dry powdery form in which it is separated from the rosin makes it adaptable to such uses as have been suggested by Cram[1] for the humus obtained in the soda process for wood pulp.

## CONCLUSIONS

I—When resinous wood is treated with a five per cent solution of ammonium hydroxide equal to eight times the weight of the

[1] This Journal, 6 (1914), 896.

wood at 70° C. for five hours, nearly complete extraction of rosin occurs.

II—From the general properties of ammonia and its complete recovery in gas works, it is believed that nearly complete extraction of rosin from wood may be made and complete recovery of ammonia obtained.

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## DISCOLORATION OF MAPLE IN THE KILN

By Roy C. Judd

In kiln-drying green frozen maple lumber, a brown stain or discoloration occurs unless the most favorable conditions are maintained. An investigation of the causes and of the nature of the discoloration was made. Irving W. Bailey[1] states that some sap staining is due to an enzyme. To substantiate this view, Mr. Bailey states that the action can be arrested by simply dipping the lumber in hot water.

To study the possibility that this action is due to some enzyme, such as an oxydase, several small blocks of maple were given various preliminary treatments, and then placed in an oven where the humidity exceeded 90 per cent. The temperature was maintained at 90° C. for from one to three hours. The preliminary treatments were made as follows:

1—Dipping in water at 90° C.

2—Soaking in boiling water for 1, 2, 5, 60, and 200-minute periods.

3—Steaming at 100° C. for 5, 60, and 200-minute periods.

4—Heating in a drying oven at 105° C. for 10 min., 30 min., 1 hr., 2 hrs., 10 hrs., and 20 hours.

5—Previous treatment with solutions of germicides:

*a*—Zinc chloride
*b*—Mercuric chloride
*c*—Sodium fluoride
*d*—Phenol
*e*—Arsenious oxide
*f*—Hydrogen peroxide
*g*—Sodium carbonate

Discoloration appeared in every case when these samples were finally subjected to the unfavorable conditions of a warm humid atmosphere. The stain was formed on the surface first, but, on remaining for a longer period in the moist air, the stain appeared throughout the specimen. The possibility of the discoloration being caused by an enzyme was disproven because at least some of the above treatments would have destroyed the enzyme. If dipping maple in hot water prevents subsequent staining in the kiln, it is not because the enzymes are destroyed but because the heated wood dries more readily.

A series of experiments were carried on in an autoclave. Pieces of fresh green maple were given the following treatments:

1—Enough of a 3 per cent solution of hydrogen peroxide was added to cover the sample. The air was pumped out and the temperature of 75° C. maintained.

2—An atmosphere of sulfur dioxide was supplied and the temperature kept at 80° C.

3—An atmosphere of carbon dioxide was added and the temperature maintained at 80° C.

4—The air was removed and live steam passed through continuously.

5—An $NH_4OH$ solution was placed in the autoclave and the air exhausted. The temperature was kept at 75° C.

6—A little water was added and air was left in. A temperature of 80° C. was maintained.

The duration of the above experiments was from two to four hours. The results of these experiments showed that discoloration did not appear in the presence of hydrogen peroxide, carbon dioxide, sulfur dioxide, nor with steam in the absence of air. In an atmosphere of air saturated with moisture and also in the experiment with ammonium hydroxide, discoloration was very appreciable.

Three sets of experiments were carried on simultaneously. Pieces of maple were placed in flasks containing distilled water. Air was continuously bubbled through one and carbon dioxide and sulfur dioxide, respectively, through the other two. The initial temperature of 40° C. was maintained for one hour. Then the temperature was raised 10° at one-hour intervals till the temperature of boiling water was obtained. At the end of the process the pieces of maple in the flasks through which carbon dioxide or sulfur dioxide had been passed were even lighter colored than the original, while the maple in the flasks through which air had been passed was very badly discolored. The first evidence of discoloration appeared at about 60° C. and became more pronounced as the temperature was raised. Several experiments indicated that weak solutions of organic or mineral acids prevent discoloration. Some experiments were carried out on a small scale in laboratory drying ovens. It was found that no staining took place when the humidity of the air in immediate contact with the drying wood was kept low. The investigation seems to indicate that the staining is probably of a physical chemical nature and is independent of enzymes.

This paper is not intended to cover the subject of kiln-drying but is written for the purpose of showing that it is possible with conditions well under control to dry green maple lumber artificially and still retain its natural color. The conditions that prevail in a commercial kiln for drying lumber are not as easily controlled as those in a small laboratory apparatus. The section of timber physics in the Forest Products Laboratory has worked out its application in a dry kiln. The only available means of overcoming this difficulty in commercial practice is by the use of a low temperature (120° to 130° F.) and a low humidity (60 per cent or less) in the dry kilns. Fortunately, maple is a wood which does not check easily and hence these low humidities are quite practicable on a commercial scale.

I wish to express my appreciation of the suggestions and interest contributed by Mr. H. D. Tiemann, in Charge, Section of Timber Physics, and a specialist in kiln-drying, and Dr. S. F. Acree, Chief of the Section of Derived Products, who suggested the studies of the chemical and enzymic phases of this problem.

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[1] *Botanical Gazette*, **50**, 142–147, No. 2, August, 1910.

## MANUFACTURE OF ETHYL ALCOHOL FROM WOOD WASTE—II. THE HYDROLYSIS OF WHITE SPRUCE

By F. W. Kressmann

A paper[1] presented at the Forty-Ninth Meeting of this Society at Cincinnati, described (1) the scope of the work, (2) the apparatus used, (3) the method of procedure, and in addition gave the results obtained from a series of preliminary experiments on white spruce. Since the above work was done the yeasting operations and fermentation conditions have been standardized so that duplicate and comparable data have been made possible.

The yeast used is a pure culture strain of *Saccharomyces cerevisiae*, isolated from a yeast used in a Hungarian distillery, producing alcohol from beet sugar molasses. It is well adapted to the fermentation of sugar solutions obtained from the hydrolysis of wood, although the addition of nitrogenous food is necessary. This yeast nutrient is a mixture of ammonium sulfate and malt sprouts. The details of yeast propagation and the preparation of the mashes for fermentation along with other details of the present work will be given later in the form of a professional paper of the United States Department of Agriculture. In all cases, 7,500 cc. of a solution having a gravity

[1] THIS JOURNAL **6** (1914), 625.

around 12.5° Brix were used for fermentation. The fermentations were carried out in a constant temperature room, maintained at 30° C. ± 0.5°, which could be kept in a sterile condition. The beers were distilled after 96 hours (distilleries operating on this type of materials are classed as sour mash distilleries from four different cooks, give an indication of the method of fermentation, the average results and degree of accuracy that are being obtained at present.

In the former paper the influence of temperature and pressure and time of cooking were discussed. The ratio of water to dry

TABLE I FERMENTATION RECORD FOR WHITE SPRUCE

Fermenter set at 9.15 A.M. Distillations begun at 9.15 A.M. five days later. Fermentation continued during 128.5 hours, including the time of filling the fermenter, which took 32.5 hours

| | | YEAST | | | | MASH BEFORE FERMENTATION | | | | BRIX RECORD | | | | | BEER | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Seed yeast | 96 Hour yeast | | | | | | | | | | | | | | | | | |
| Fermentation No. | Cook No. | Brix. | Acidity. | Sp. gr. at 15° C. | Alcohol % by weight | Acidity | Sp. gr. at 15° C. | Reducing sugar Grams per liter | Acidity | Total solids Per cent | Brix | 1st day | 2d day | 3d day | 4th day | 5th day | Attenuation Degrees | Brix 4th day | Reducing sugar G. per liter | Sp. gr. at 15° C. | Acidity | Total solids % by weight | Alcohol % by weight |
| 17 | 55 | 11.4 | | 1.0216 | 5.922 | 18.7 | 1.0470 | 64.48 | 3.2 | 9.426 | 11.8 | 3.6 | 1.5 | 0.3 | 0.0 | | 5.4 | 6.4 | 14.74 | 1.0245 | 8.4 | 5.603 | 2.382 |
| 17 | 55 | 11.4 | | 1.0216 | 5.922 | 18.7 | 1.0454 | 62.44 | 3.0 | 9.115 | 11.4 | 3.5 | 1.5 | 0.2 | 0.2 | | 5.4 | 6.0 | 13.76 | 1.0237 | 8.8 | 5.347 | 2.315 |
| 16 | 55 | 13.9 | 18.5 | 1.0223 | 6.167 | 26.2 | 1.0498 | 58.12 | 2.6 | 9.266 | 11.2 | 3.5 | 1.5 | 0.2 | 0.1 | | 5.3 | 6.9 | 10.04 | 1.0274 | 8.0 | 5.971 | 2.311 |
| 16 | 55 | 13.9 | 18.5 | 1.0223 | 6.167 | 26.2 | 1.0478 | 56.40 | 2.5 | 9.564 | 11.9 | 3.3 | 1.6 | 0.2 | 0.1 | | 5.2 | 6.7 | 10.28 | 1.0269 | 7.6 | 5.783 | 2.259 |
| 18 | 55 | 11.4 | | 1.0210 | 6.009 | 22.3 | 1.0498 | 59.74 | 3.2 | 10.422 | 12.2 | 3.7 | 1.3 | 0.3 | +0.2 | —0.1 | 5.1 | 7.1 | 10.64 | 1.0275 | 7.6 | 6.289 | 2.224 |
| 16 | 56 | 13.9 | 18.5 | 1.0223 | 6.167 | 26.2 | 1.0514 | 65.20 | 4.0 | 9.567 | 12.4 | 3.4 | 1.6 | 0.5 | 0.1 | | 5.6 | 6.8 | 14.54 | 1.0270 | 8.6 | 5.842 | 2.390 |
| 16 | 56 | 13.9 | 18.5 | 1.0223 | 6.167 | 26.2 | 1.0509 | 64.60 | 4.0 | 8.858 | 12.4 | 3.1 | 1.7 | 0.6 | 0.2 | | 5.6 | 6.8 | 14.42 | 1.0268 | 8.6 | 5.848 | 2.395 |
| 17 | 56 | 11.4 | | 1.0216 | 5.922 | 18.7 | 1.0475 | 57.34 | 2.4 | 9.428 | 12.0 | 3.1 | 1.8 | 0.2 | 0.1 | | 5.2 | 6.8 | 10.22 | 1.0268 | 7.6 | 5.873 | 2.259 |
| 17 | 56 | 11.4 | | 1.0216 | 5.922 | 18.7 | 1.0498 | 60.10 | 2.6 | 9.979 | 12.4 | 3.4 | 1.7 | 0.1 | 0.0 | | 5.2 | 7.2 | 11.00 | 1.0278 | 7.4 | 6.160 | 2.345 |
| 18 | 56 | 11.4 | | 1.0210 | 6.009 | 22.3 | 1.0487 | 66.52 | 4.4 | 11.110 | 12.3 | 3.7 | 1.5 | 0.3 | 0.0 | 0.1 | 5.7 | 6.6 | 14.60 | 1.0262 | 11.2 | 6.070 | 2.543 |
| 20 | 56 | 13.1 | | 1.0230 | 5.650 | 18.0 | 1.0429 | 56.904 | 4.5 | 8.606 | 10.7 | 3.6 | 1.1 | 0.2 | 0.0 | | 4.9 | 5.8 | 12.92 | 1.0227 | 9.6 | 5.278 | 1.968 |
| 20 | 56 | 13.1 | | 1.0230 | 5.650 | 18.0 | 1.0542 | 71.288 | 4.8 | 10.750 | 13.1 | 3.4 | 1.8 | 0.7 | 0.1 | | 6.0 | 7.1 | 16.24 | 1.0287 | 12.0 | 6.493 | 2.590 |
| 17 | 57 | 11.4 | | 1.0216 | 5.922 | 18.7 | 1.0529 | 70.24 | 2.7 | 10.614 | 13.1 | 4.0 | 1.5 | 0.3 | 0.1 | | 5.9 | 7.2 | 13.54 | 1.0279 | 7.4 | 6.264 | 2.558 |
| 17 | 57 | 11.4 | | 1.0216 | 5.922 | 18.7 | 1.0509 | 66.32 | 2.4 | 10.076 | 12.5 | 3.5 | 1.7 | 0.3 | 0.2 | | 5.7 | 6.8 | 13.78 | 1.0263 | 7.4 | 6.023 | 2.543 |
| 18 | 57 | 11.4 | | 1.0210 | 6.009 | 22.3 | 1.0463 | 62.02 | 2.8 | 9.962 | 11.5 | 3.9 | 1.2 | 0.2 | +0.1 | —0.1 | 5.2 | 6.3 | 12.76 | 1.0247 | 7.6 | 5.781 | 2.318 |
| 18 | 57 | 11.4 | | 1.0210 | 6.009 | 22.3 | 1.0400 | 52.26 | 2.4 | 8.705 | 10.0 | 3.7 | 0.9 | 0.2 | +0.1 | 0.0 | 4.7 | 5.3 | 11.24 | 1.0213 | 6.0 | 4.948 | 1.909 |
| 19 | 57 | 12.9 | | 1.0232 | 5.541 | 16.5 | 1.0474 | 60.984 | 3.0 | 8.539 | 11.7 | 3.6 | 1.3 | 0.4 | 0.1 | | 5.4 | 6.3 | 12.86 | 1.0240 | 8.8 | 5.805 | 2.266 |
| 19 | 57 | 12.9 | | 1.0232 | 5.541 | 16.5 | 1.0472 | 60.476 | 3.0 | 8.465 | 11.5 | 3.3 | 1.5 | 0.4 | 0.0 | | 5.2 | 6.3 | 12.48 | 1.0246 | 8.8 | 5.951 | 2.274 |
| 18 | 58 | 11.4 | | 1.0210 | 6.009 | 22.3 | 1.0479 | 71.81 | 3.2 | 10.996 | 11.7 | 3.8 | 1.3 | 0.1 | 0.0 | 0.0 | 5.2 | 6.5 | 29.26 | 1.0258 | 7.2 | 6.204 | 2.218 |
| 18 | 58 | 11.4 | | 1.0210 | 6.009 | 22.3 | 1.0497 | 81.48 | 2.6 | 11.006 | 12.4 | 3.9 | 1.4 | 0.1 | 0.0 | 0.0 | 5.4 | 7.0 | 31.12 | 1.0275 | 6.3 | 6.484 | 2.117 |
| 19 | 58 | 12.9 | | 1.0232 | 5.541 | 16.5 | 1.0523 | 83.152 | 3.0 | 9.679 | 12.7 | 3.5 | 1.4 | 0.4 | 0.1 | | 5.4 | 7.3 | 32.28 | 1.0285 | 7.8 | 7.196 | 2.421 |
| 19 | 58 | 12.9 | | 1.0232 | 5.541 | 16.5 | 1.0540 | 87.192 | 3.0 | 10.598 | 13.3 | 3.5 | 1.5 | 0.6 | 0.1 | | 5.7 | 7.6 | 34.12 | 1.0300 | 9.2 | 7.483 | 2.500 |
| 20 | 58 | 13.1 | | 1.0230 | 5.650 | 18.0 | 1.0553 | 87.792 | 2.5 | 11.180 | 13.2 | 3.2 | 1.8 | 0.6 | 0.1 | | 5.7 | 7.5 | 33.80 | 1.0300 | 10.0 | 7.063 | 2.456 |

by the Bureau of Internal Revenue) and from the sugar content before and after fermentation and the specific gravities of the mash and beer along with the alcohol content of the latter it was possible to calculate the fermentation efficiencies and yields. Since about 2.5 per cent of the total alcohol in the beers is obtained from the molasses solution, which is the medium in which the yeast is propagated, and which is added with the starting yeast, the fermentation efficiencies are all high but serve well for comparative purposes, since the error is practically a constant one.

In addition, it permits of the expression of yields in the same way that they would be obtained commercially, since in either case about 1 per cent by volume of the total mash consists of the starting yeast solution. Tables I and II, showing the fermentation record and fermentable sugar and alcohol yields,

wood was 400 to 100 and the ratio of acid to dry wood was 1.8 to 100. In view of better fermentation conditions, some of the above work was repeated and in addition the following variables were studied: (1) ratio of water to dry sawdust, (2) ratio of catalyzing agent to dry sawdust, (3) concentration of catalyzing agent in the water added. The first variable was carried from 4 water : 1 dry wood (called 400 per cent water) down to 1 water : 1 wood. The best operating condition finally chosen was 125 per cent of water. This was done: (1) To insure a better mixture of acid and wood, which is easier to accomplish with increasing amounts of water, (2) to use the maximum amount of water possible, and still obtain a digested sawdust that had no drip; *i. e.*, no free water or liquid should be present after digestion. This is highly desirable from an operating standpoint and, although 100 per cent added water is to be

TABLE II—SUGAR AND ALCOHOL YIELDS FROM WHITE SPRUCE

| | Total reducing sugar Per cent of original wood | Per cent of total reducing sugar | | | ALCOHOL IN BEER | | Per cent of total sugar obtained as alcohol | ALCOHOL YIELDS | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cook No. | | Fermentable | Non-fermentable | Fermentation efficiency | Actual alcohol yield | Theoretical alcohol yield | | Per cent of original dry wood | Gallons absolute per dry ton | Gallons 190 Proof per dry ton allowing 5 per cent distillation loss |
| 55 | 18.06 | 82.35 | 17.65 | 98.95 | 2.311 | 2.330 | 81.48 | 7.520 | 22.746 | 22.703 |
| 55 | 18.06 | 81.41 | 18.59 | 100.88 | 2.259 | 2.239 | 82.11 | 7.580 | 22.927 | 22.884 |
| 55 | 18.06 | 81.82 | 18.18 | 99.11 | 2.259 | 2.289 | 81.09 | 7.485 | 22.640 | 22.597 |
| 55 | 18.06 | 81.37 | 18.63 | 98.34 | 2.345 | 2.381 | 79.02 | 7.294 | 22.062 | 22.021 |
| 55 | 18.06 | 80.04 | 19.96 | 95.53 | 2.224 | 2.328 | 76.45 | 7.058 | 21.348 | 21.308 |
| Average | | 81.40 | 18.60 | | | | | 7.387 | 22.340 | 22.300 |
| 56 | 21.56 | 77.16 | 22.84 | 97.73 | 2.390 | 2.446 | 75.41 | 8.307 | 25.126 | 25.079 |
| 56 | 21.56 | 77.68 | 22.32 | 98.09 | 2.395 | 2.440 | 76.20 | 8.395 | 25.392 | 25.345 |
| 56 | 21.56 | 76.63 | 23.37 | 98.75 | 2.382 | 2.412 | 75.67 | 8.338 | 25.220 | 25.172 |
| 56 | 21.56 | 77.53 | 22.47 | 97.80 | 2.315 | 2.367 | 75.82 | 8.355 | 25.271 | 25.224 |
| 56 | 21.56 | 77.56 | 22.44 | 101.11 | 2.543 | 2.515 | 78.42 | 8.641 | 26.136 | 26.087 |
| 56 | 21.56 | 76.85 | 23.15 | 91.83 | 1.968 | 2.143 | 70.57 | 7.778 | 23.520 | 23.475 |
| 56 | 21.56 | 76.66 | 23.34 | 97.73 | 2.590 | 2.650 | 74.92 | 8.256 | 24.972 | 24.925 |
| Average | | 77.15 | 22.85 | | | | | 8.295 | 25.09 | 25.04 |
| 57 | 21.08 | 80.26 | 19.74 | 93.46 | 2.558 | 2.541 | 75.01 | 8.082 | 24.446 | 24.400 |
| 57 | 21.08 | 78.73 | 21.27 | 100.07 | 2.543 | 2.468 | 78.78 | 8.488 | 25.674 | 25.625 |
| 57 | 21.08 | 79.00 | 21.00 | 96.86 | 2.318 | 2.393 | 76.52 | 8.249 | 24.951 | 24.904 |
| 57 | 21.08 | 78.09 | 21.91 | 95.16 | 1.909 | 2.006 | 74.31 | 8.006 | 24.216 | 24.170 |
| 57 | 21.08 | 78.43 | 21.57 | 97.09 | 2.266 | 2.334 | 76.15 | 8.204 | 24.815 | 24.768 |
| 57 | 21.08 | 78.91 | 21.09 | 97.64 | 2.274 | 2.329 | 77.05 | 8.301 | 25.108 | 25.060 |
| Average | | 78.90 | 21.10 | | | | | 8.222 | 24.87 | 24.82 |
| 58 | 22.82 | 60.62 | 39.38 | 98.84 | 2.218 | 2.244 | 59.92 | 6.989 | 21.140 | 21.100 |
| 58 | 22.82 | 60.98 | 39.02 | 87.52 | 2.117 | 2.419 | 53.37 | 6.225 | 18.829 | 18.793 |
| 58 | 22.82 | 60.29 | 39.71 | 99.43 | 2.421 | 2.435 | 59.95 | 6.992 | 21.149 | 21.109 |
| 58 | 22.82 | 59.95 | 40.05 | 98.62 | 2.500 | 2.535 | 59.12 | 6.895 | 20.855 | 20.816 |
| 58 | 22.82 | 60.56 | 39.44 | 95.38 | 2.456 | 2.575 | 57.76 | 6.737 | 20.377 | 20.339 |
| Average | | 60.48 | 39.52 | | | | | 6.768 | 20.47 | 20.43 |

preferred to 125 per cent added water when steam consumption is taken into account, it was felt that the better mixture of acid and wood obtained with the 125 per cent water outweighed the small increased steam consumption and justified its adoption as a standard in our work.

Table III shows no great differences in yields resulting in the reduction of the added water from 400 to 125 per cent, which is of exceeding importance commercially.

TABLE III

1.80 to 1.85 Per Cent $H_2SO_4$ 0 Minute Time 7.5 Atmos. Pressure

| Water Per cent of dry wood | Total Sugars | Per Cent of Total Sugars Fermentable | Per Cent Alcohol |
|---|---|---|---|
| 100 | 21.09 | 60.68 | 6.440 |
| 125 | 21.96 | 59.29 | 6.805 |
| 250 | 23.75 | 55.31 | 6.648 |
| 300 | 23.16 | 54.87 | §6.096(*a*) ¶6.645(*b*) |
| 400 | 22.24 | 56.19 | 6.154 |

(*a*) Actual average, containing one poor fermentation.
(*b*) Result recalculating poor fermentation to a normal efficiency.

Sulfuric acid was used as a catalytic agent in amounts varying from 0.5 per cent to 4 per cent of the dry weight of the wood. The results obtained with a zero minute cooking period and 125 per cent water cooked at 7.5 atmospheres pressure are given in Table IV, which shows that not only total sugars increase with increasing acidity, but especially that the portion which is fermentable increases so that the alcohol yields increase proportionally.

TABLE IV

| Concentration $H_2SO_4$ | Total Sugar Per Cent | Per Cent of Total Sugars Fermentable | Per Cent Alcohol |
|---|---|---|---|
| 0.5 | 17.42 | 43.13 | 4.172 |
| 0.75 | 21.83 | 56.03 | 6.085 |
| 1.00 | 21.68 | 56.43 | 6.506 |
| 1.40 | 23.09 | 53.93 | 6.502 |
| 1.83 | 21.53 | 59.98 | 6.623 |
| 2.50 | 22.11 | 63.16 | 6.927 |
| 4.00 | 21.10 | 66.63 | 7.000 |

A consideration of the above two variables will show that the concentration of the catalytic agent expressed in terms of dry wood is the single and great determining factor and this is especially true when the following work on the effect of time of cooking is studied. The concentration of acid expressed in terms of the added solution is without effect (contrary to a number of patents that have been granted) except where such variation also varies the ratio of acid to dry wood. In the paper referred to in the beginning of this communication, the conclusion was reached that "a cooking period of 0 minute, that is, blowing off from $7\frac{1}{2}$ atmospheres as soon as that pressure was obtained, was advantageous." This was the result of a study of total sugars only, as shown in Figure 3 of that paper where the total sugar obtained from a series of cooks varying from 0 to 30 minutes varied less than a few tenths of 1 per cent. A repetition of that work has shown practically the same results

TABLE V

7.5 Atmos. Pressure and 125 Per Cent Water

| Time of Cook Minutes | Total Sugar Per cent | Per cent of Total Sugar Fermentable | Alcohol Per Cent of Dry Wood |
|---|---|---|---|
| | With 1.40 Per cent $H_2SO_4$ | | |
| 0 | 23.09 | 53.93 | 6.502 |
| 10 | 23.45 | 55.08 | 6.456 |
| 30 | 22.34 | 63.22 | 6.862 |
| | With 2.50 Per cent $H_2SO_4$ | | |
| 0 | 22.11 | 63.25 | 6.927 |
| 10 | 22.36 | 68.53 | 7.662 |
| 20 | 23.61 | 71.44 | 8.537 |
| 45 | 21.56 | 77.15 | 8.295 |
| 90 | 18.06 | 81.40 | 7.387 |

so far as the total sugar is concerned, but careful fermentations have shown a decided difference in composition of that sugar under different conditions. This difference is shown particularly when the acid concentration is fairly high, as in the case of the 2.5 per cent acid, although the rise in fermentable sugars is noticeable even in 1.4 per cent acidity.

Table V shows these variations and fermentable sugar and alcohol yields. In addition it will be noticed that with 2.5 per cent acid there is a gradual decrease in total sugar as the length of the cook is largely increased (beyond 20-minute cooking periods), even though the portion that is fermentable increases quite decidedly. The causes and explanations of these differences have not been fully worked out, although a number of lines of attack suggest themselves, and we hope to take up this phase of the problem in detail in a subsequent publication. This brief summary of results is given purely for its technical value for the assistance that it may give in the proper choice of operating conditions as determining those prime variables which affect the total and fermentable sugar yields.

CONCLUSION

From an operating standpoint, and taking into consideration, (1) economic operation, which includes acid cost, lime or other neutralizing cost, and steam consumption; and (2) plant depreciations, we feel that the following cooking conditions give the greatest yields of alcohol:

I—Pressure of cook, $7\frac{1}{2}$ atmospheres.
II—Time of cook, about 20 minutes.
III—Water to dry wood ratio, 125 to 100.
IV—Acid to dry wood ratio, $2\frac{1}{2}$ to 100.

The writer wishes to thank the E. I. du Pont de Nemours Powder Company, and Mr. John Boyt and Mr. J. S. Groves, Superintendent and Chemist, respectively, of the alcohol plant of the du Pont Company at Georgetown, S. C., for the many courtesies and suggestions rendered in the yeasting and fermentation work. The writer further wishes to thank Mr. Homer Cloukey, of the Forest Products Laboratory, for the patience and skill exercised in the many hundred analyses required in the study of this problem.

FOREST PRODUCTS LABORATORY
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## THE MANUFACTURE OF ETHYL ALCOHOL FROM WOOD WASTE—III. WESTERN LARCH AS A RAW MATERIAL

By F. W. KRESSMANN

The logging of western larch (*Larix occidentalis*) shows a woods loss of 8 per cent due to butting off the lower portion of the tree.[1] This practice is due chiefly to the presence of shakes in the butt. In addition, the base of the tree is usually swelled. The swelled portion is denser than the rest of the trunk and usually sinks, thus preventing rafting. The lengths of the "butts" left in the woods vary from 4 to 8 feet, although occasionally a 16-foot piece is rejected.

The utilization of this waste material up to the present time has not met with success and it was hoped that it might be profitably employed as a raw material in the production of ethyl alcohol.

A sample of sawdust from a butt log was cooked with 1.8 per cent sulfuric acid, 125 per cent of water, at 7.5 atmospheres pressure for 10 minutes. A yield of sugar equal to 29.72 per cent, and of total solids equivalent to 35.18 per cent, of the dry weight of the wood was obtained. Under the same conditions, white spruce would yield about 22 per cent of sugar, of which from 60 to 65 per cent would be fermentable, making an alcohol yield of 6.8 to 7 per cent of the dry weight of the wood, or from 20 to 21 gallons of absolute alcohol per dry ton. The extracts obtained from the hydrolysis of the larch were fermented under standard conditions, the fermentation records and alcohol yields being given in Tables I and II.

The larch yielded about 35 per cent total sugar more than spruce and yet only 37.9 per cent of that sugar fermented compared with 60 or 65 per cent from spruce. Mr. A. W.

[1] U. S. Department of Agriculture, *Forest Service Bulletin* **122**, "The Mechanical Properties of Western Larch," O. P. M. Goss.

TABLE I —FERMENTATION RECORD—WESTERN LARCH

| Fermentation No. | Yeast: Seed yeast: Cook No. | Yeast: Seed yeast: Brix. | Yeast: Seed yeast: Acidity. | Yeast: 96 Hours yeast: Sp. grav. at 15° C. | Yeast: 96 Hours yeast: Alcohol. % by weight | Yeast: 96 Hours yeast: Acidity | Mash before fermentation: Fermenter set. Date | Mash before fermentation: Hours filling fermenter | Mash before fermentation: Hours fermenting, including time of filling | Mash before fermentation: Sp. grav. at 15° C. | Mash before fermentation: Reducing sugar Grams per liter | Mash before fermentation: Acidity | Mash before fermentation: Total solids Per cent | Mash before fermentation: Brix record Decrease in Brix: Brix | 1st day | 2nd day | 3rd day | 4th day | 5th day | Attenuation Degrees Brix. 4th day | Beer: Distillation Date | Beer: Reducing sugar Grams per liter | Beer: Sp. gr. at 15° C. | Beer: Acidity | Beer: Total solids % by weight | Beer: Alcohol. % by weight |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 50 | .. | .. | 1.0243 | 6.170 | 18.6 | 1/21/15 | 32.5 | 128.5 | 1.0495 | 94.92 | 3.2 | 10.301 | 12.1 | 3.1 | 0.3 | +0.1 | —0.2 | 0.0 | 3.5 | 8.6 | 1/26/15 | 56.28 | 1.0341 | 7.0 | 7.207 | 1.4707 |
| 11 | 50 | .. | 22.0 | 1.0262 | 5.398 | 26.4 | 2/11/15 | 32.5 | 128.5 | 1.0543 | 97.936 | 2.4 | 12.325 | 13.3 | 3.0 | 0.5 | 0.2 | 0.2 | 0.0 | 3.9 | 9.4 | 2/16/15 | 61.744 | 1.0392 | 7.2 | 9.490 | 1.598 |
| 14 | 50 | .. | 22.5 | 1.0235 | 5.784 | 24.5 | 3/18/15 | 32.5 | 128.5 | 1.0440 | 83.38 | 2.8 | 9.190 | 11.0 | 2.9 | 0.4 | 0.3 | +0.2 | 0.0 | 3.4 | 7.6 | 3/23/15 | 51.264 | 1.0302 | 5.6 | 6.438 | 1.320 |

TABLE II—SUGAR AND ALCOHOL YIELDS FROM WESTERN LARCH

| Species of wood | Cook number | Total reducing sugar in per cent of dry original wood | Per cent of total reducing sugars fermentable | Per cent of total reducing sugars non-fermentable | Fermentation efficiency | Alcohol in Beer: Actual alcohol yield | Alcohol in Beer: Theoretical alcohol yield | Per cent of total sugar obtained as alcohol | Alcohol Yields: Per cent of original dry wood | Alcohol Yields: Gallons of absolute per dry ton | Alcohol Yields: Gallons of 190 proof per dry ton allowing 5% distillation loss |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Western larch.... | 50 | 29.72 | 37.70 | 62.30 | 85.77 | 1.320 | 1.539 | 32.34 | 4.970 | 15.033 | 15.004 |
| Western larch.... | 50 | 29.72 | 39.83 | 60.17 | 79.85 | 1.470 | 1.841 | 31.80 | 5.048 | 15.269 | 15.240 |
| Western larch.... | 50 | 29.72 | 36.04 | 63.96 | 92.23 | 1.578 | 1.711 | 33.24 | 4.912 | 14.857 | 14.829 |
| AVERAGE..... | | | 37.89 | 62.11 | | | | | 4.977 | 15.05 | 15.03 |

Schorger, of this laboratory, has analyzed both of these woods with the following results:

| | Western Larch (Base) Per cent | White Spruce Per cent | White Spruce (4 Samples) Average |
|---|---|---|---|
| Soluble in ether | 9.75 | 0.90 to 1.95 | 1.36 |
| Soluble in cold water | 14.47 | 0.82 to 1.45 | 1.12 |
| Soluble in hot water | 16.52 | 1.88 to 2.52 | 2.14 |
| Soluble in 1 per cent NaOH, 10 min. heating | 32.72 | 6.72 to 8.84 | 7.70 |
| Soluble in 1 per cent NaOH, 60 min. heating | 38.58 | 11.18 to 13.87 | 12.21 |
| Pentosan | 6.99 | 10.04 to 10.78 | 10.39 |
| Methyl pentosan | 3.42 | 3.08 to 3.95 | 3.55 |
| Cellulose | 42.57 | 51.95 to 58.47 | 56.17 |
| Volatile oil | 0.84 | ... | ... |
| Ash | 0.36 | 0.285 to 0.326 | 0.307 |

It will be noticed that the larch contains a large amount of water-soluble material and a proportionally small amount of cellulose. In all cases, the above analyses were made on a fresh sample taken from the same lot. In a subsequent paper, Mr. Schorger will take up the composition of this water-soluble material, the chief constituent of which is a galactan which yielded approximately 10 to 12 per cent of the dry weight of the wood of galactose, which in turn accounts for the high sugar yields obtained from the larch.

It has been suggested by Körner,[1] although disputed by Gallagher and Pearl,[2] that in the acid hydrolysis of cellulose-containing material, the source of the fermentable sugars and, therefore, the alcohol, is the cellulose itself.

If the sugar yield for the larch is recalculated so that it is proportional to the cellulose content, assuming 22 per cent of sugar from the spruce, we would have then 16.7 per cent of sugar instead of 29.7 per cent, as actually obtained. However, as noted above, about 10 or 12 per cent of galactose was obtained, which subtracted from the total sugar yield of 29.7 per cent, would leave from 17.7 to 19.7 per cent of sugar comparable to that obtained from spruce. Under normal conditions, with a 94 per cent efficiency and a yield of that per cent of the theoretic amount of alcohol formed, which is 51.1 per cent, we get for 60 or 65 per cent of total sugar fermentable the following alcohol yields:

$$16.7 \times 0.511 \times 0.94 \times 0.60 = 4.83 \text{ per cent alcohol}$$
$$16.7 \times 0.511 \times 0.94 \times 0.65 = 5.23 \text{ per cent alcohol}$$

The actual alcohol yield is 4.977 per cent, which corresponds to about 62 per cent of total sugar fermentable, which is the average of the above figures chosen for spruce. It appears, therefore, that the yield of fermentable sugar and alcohol is proportional to the cellulose content of the wood, irrespective of other materials that may be contained therein. In addition, western larch butts will be a good raw material for the production of ethyl alcohol if a yeast is found which will ferment the galactose as well as the dextrose within the time limit and other limitations as prescribed by the Bureau of Internal Revenue. This phase of the subject has been reserved and will be taken up in the near future.

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[1] *Zeitschrift für angewandte Chemie*, **1908**, 2353.
[2] *Proc. Eighth Intern. Cong. Appl. Chem.*, **13**, p. 147.

## THE APPLICATION OF THE DAVIS SPOT TEST IN THE PRELIMINARY EXAMINATION OF CREOSOTES

By HOMER CLOUKEY

The tests undertaken and included in this report were run for the purpose of verifying the "absorption spot test" given in an article by T. H. Davis on "The Examination of Creosote,"[1] and described in this article as follows:

*"Absorption Spot*—Allow six drops of the sample to fall from a burette upon the surface of clean, white blotting paper. If tar, carbon, or dirt is present, it is very easily observed, as it quickly segregates at the center. The paper should be laid away, in a flat position, for several hours, in a place free from dust. If then examined, foreign matter will be observed in a distinct zone at the center of the spot; the outer zone very readily indicates the character of the oil."

In order to establish some idea of the sensitiveness of this test for carbon and dirt in creosote and make it fairly quantitative a series of spots was made from a carbon-free creosote with definite graduated amounts of carbon in the form of lampblack added.

This series comprises six mixtures of creosote and lampblack as follows:

| Per cent lampblack added | 0.0 | 0.005 | 0.01 | 0.05 | 0.10 | 0.50 |
|---|---|---|---|---|---|---|

This series is shown in Fig. I. The results obtained show an increasing gradation in the density of the free carbon ring at the center and indicate that 0.005 per cent is easily shown by this test. In heavier percentages than 0.5 per cent, the amount in an unknown sample would be difficult to estimate by comparison.

The appearance of several authentic samples of various creosotes and oils used for wood-preserving purposes is shown in Fig. II. No. 1 shows coal tar creosote with the characteristic brown gradually shading on the edges to a lighter zone: if carbon and dirt are present, these are segregated in an inner circle which is the size of the original spot before diffusion. No. 2 is a characteristic water gas tar creosote with the large spot and outer yellow zone characteristic of this oil. No. 3 illustrates the character of the spot afforded by a paraffin base crude oil used for wood-preserving purposes: this is almost colorless

[1] *Oil, Paint, and Drug Reporter*, February 14, 1910.

0.000 0.005 0.01 0.05 0.10 0.50

FIG. I—SPOTS MADE WITH CREOSOTE AND LAMPBLACK. PERCENTAGES GIVEN
Reduced a little over one-half. Color—Light brown with black centers

Coal Tar Creosote (Brown) | Crude Oil Paraffin Base (Pale Gray) | Water Gas Tar Creosote (Brown and Black) | Water Gas Tar (Dark Brown) | Hardwood Tar Creosote (Dark Gray) | Coal Tar (Dark Brown and Black)

FIG. II—SPOTS OF VARIOUS OILS USED FOR WOOD PRESERVING
Reduced a little over one-half. Colors as noted

while an asphaltic base crude oil shows a browner center. No. 4 shows the characteristic dead gray-black of creosote made from hardwood tar. No. 5 is the even dark brown spot of a typical water gas tar: this tar is often used in creosote tar mixtures at the present time. No. 6 is the spot of a coal tar with the heavy carbon in the center and the small diffusion of the pitchy mass.

The spots given in Fig. II represent only the typical spots of the various oils used for wood-preserving purposes. In actual practice, these oils are used in more or less admixture with each other and a large number of spots can be obtained grading from one of these types to another.

The admixture of tar can be determined roughly from the size (smaller) and the general character of the spot. The heavy tar does not diffuse with the speed of the lighter creosote oils.

CONCLUSIONS

I—The presence of dirt and free carbon in creosote oil is indicated in very minute quantities by this test.

II—If the creosote spot shows a dense black center it will probably be necessary to run a free carbon analysis to determine if the creosote passes the free carbon specification.

III—The various types of wood-preserving oils can be easily distinguished from each other by this test when they are true type samples.

IV—In the large number of intermediate or mixed commercial oils, the value of this preliminary test will depend on the experience of the one applying it together with the possession of a large number of authentic samples for comparison. On applying this test to a number of oils compounded from known authentic samples it was possible to tell the constituents with a reasonable degree of accuracy.

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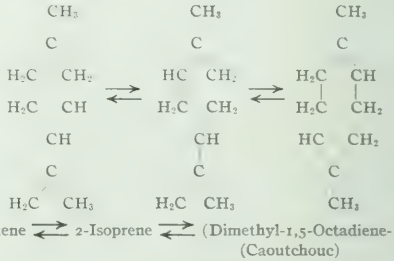
## ISOPRENE FROM β-PINENE

By A. W. Schorger and R. Sayre

The discovery during the latter half of the past century of a close relation between isoprene, the terpenes, and caoutchouc has naturally directed considerable attention toward the utilization of the terpenes as a source of isoprene. This relation may be represented by the following reversible reactions:



Dipentene ⇌ 2-Isoprene ⇌ (Dimethyl-1,5-Octadiene-1,5)$_x$
(Caoutchouc)

It was to be expected that attempts would first be made to utilize α-pinene as a raw material, since, in the form of turpentine, it can be more easily and cheaply obtained than any of the other terpenes. The results of former experiments clearly indicate, however, that only comparatively low yields are possible from turpentine. Tilden,[1] by passing turpentine through a red-hot tube, obtained about 20 cc. of isoprene from a liter of turpentine. By means of his isoprene lamp, Harries[2] obtained about 1 per cent of isoprene from commercial pinene and attributed even this small amount to the presence of dipentene in the turpentine employed. Herty and Graham[3] obtained 5.5 per cent (by volume) of isoprene from turpentine and 8.0 per cent from a fraction boiling between 155 and 156°. These authors are of the opinion that the isoprene obtained from turpentine is not due to dipentene present in the turpentine as asserted by Harries, an opinion that we believe is fully justified.

Apparently the only terpene yielding considerable amounts of isoprene is limonene (dipentene). Harries[2] obtained 30 to 50 per cent of isoprene from commercial limonene while Herty and Graham obtained 12 per cent from a limonene fraction. Staudinger and Klever[4] found that by working at a pressure of about 4 mm., a yield of 60 per cent of exceptionally pure isoprene could be obtained from limonene.

According to patents held by Schering and Company,[5] con-

[1] *Chem. News*, **46** (1882), 220.
[2] *Ann.*, **383** (1911), 228–9.
[3] THIS JOURNAL, **6** (1914), 803–4.
[4] *Ber.*, **44** (1911), 2242.
[5] German Patent 260,934. K. Stephan. U. S. Patent 1,057,680 (1913) (Assignor to Schering & Co.).

siderably larger yields of isoprene can be obtained from β-pinene than from α-pinene. As has been previously shown by one of us,[1] the oil from the oleoresin of western yellow pine (*Pinus ponderosa*, Laws.) consists mainly of β-pinene with small amounts of α-pinene and limonene. Large stands of this species are available for tapping purposes on the Pacific Coast and to our knowledge offers the only cheap source of β-pinene. Since no data was available on the yields of isoprene to be obtained from β-pinene, it was determined to investigate this point. The above oil would be additionally promising, owing to the presence of limonene.

It was found, however, that α-pinene and β-pinene gave approximately the same yield of isoprene when both terpenes were passed through the same apparatus for the purpose of direct comparison.

## EXPERIMENTAL

The isoprene lamp of Harries[2] offers a convenient means of "cracking" terpenes in the laboratory. After considerable experimentation to avoid certain mechanical disadvantages a modified form of apparatus of the type shown in the accompanying Fig. I, *A*, was employed. The heating coil consisted of a platinum wire 150 cm. long wound in the form of a spiral through two parallel rows of holes in the edges of a strip of "transite," a heat-resisting, insulating material, composed of asbestos and cement; the temperature of the wire was regulated by means of a sliding rheostat, the best results being obtained at a low red heat.

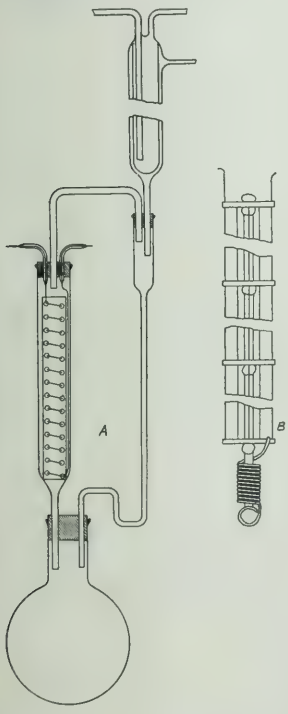


FIG. I

The vapors after passing the coil entered the Hopkins condenser where the less volatile portions were condensed and returned to the boiling flask through the trap as indicated. The vapors passing through the Hopkins condenser, passed in turn through a second condenser fed with cold water, then through a spiral glass tube surrounded by a freezing mixture of salt and ice, and finally into a receiving flask likewise surrounded by a freezing mixture.

The turpentine employed was obtained by rectifying ordinary gum turpentine. The β-pinene employed was obtained by repeated fractionation of the oil of western yellow pine.

At first the boiling was continued until the contents of the flask had completely polymerized, but it was found that practically no isoprene was formed after the first three or four hours. Although great pains were taken to secure complete condensation, it was evident that some of the isoprene escaped with the non-condensable gaseous decomposition products. Immediately after the completion of a run the distillate was fractioned by means of a 12-inch Hempel column, filled with glass beads, and the fraction boiling between 35–37° considered as isoprene. To what extent the crude isoprene was possibly contaminated with trimethylethylene was not determined. The results of some typical runs are given in Table I.

TABLE I

| No. | Original Material | Weight Grams | Time hrs. | Per Cent of Original Residue | Total distillate | Loss | Yield of isoprene % by weight |
|---|---|---|---|---|---|---|---|
| 1 | Turpentine | 400 | 6 | 31.7 | 35.1 | 33.2 | 8.1 |
| 2 | Turpentine | 283 | 5 | 46.7 | 35.3 | 18.0 | 10.3 |
| 3 | β-Pinene (b. p. 162–165°) | 300 | 6 | 40.0 | 37.4 | 22.6 | 9.4 |

The production of isoprene in the experiments described above would appear to be due largely to the catalytic effect of the platinum, since a nichrome wire was found to act in an entirely different manner. In order to use a long wire in a compact space a nichrome wire was stretched back and forth between perforated disks of transite fastened on a glass rod Fig. I, *B*.

Owing to the great elongation on heating, the wires sagged, thereby causing short circuits. This difficulty was successfully overcome by attaching a section of strong steel door spring to the lower disk to take up the slack in the manner illustrated. When the terpene vapors came in contact with the nichrome wire, heated to the same intensity as the platinum wire, thick deposits of carbon were formed immediately. The wires were short-circuited so quickly by the masses of carbon deposited that it was impossible to continue the experiment beyond this point.

Several experiments were performed by passing the terpene vapors through an iron tube filled with pumice stone and heated in a combustion furnace. With an apparatus of this type it is difficult to return the unchanged terpenes to the boiling flask. Owing also to the difficulty of temperature control, the terpenes in some cases passed through largely unchanged while in others considerable amounts of tar and members of the naphthalene series were formed from too high temperatures. The results are accordingly not comparable with those obtained with the isoprene lamp.

The small yields of isoprene obtained by Tilden were probably due to the small positive catalytic effect of the iron tube. To obtain the desired catalytic effect platinum black was deposited in the pores of the pumice by reduction of potassium chlorplatinate. It was found advisable to boil the liquid very gently and maintain the tube as nearly as possible at a barely visible red heat. Some of the results obtained with the tube method are given in Table II (no platinum black was deposited in the pumice used in Experiment No. 1).

TABLE II

| No. | | Per Cent of Original Residue | Distillate | Loss | Yield of isoprene % by weight |
|---|---|---|---|---|---|
| 1 | Turpentine | 6.7 | 85.6 | 7.7 | 3.5 |
| 2 | Turpentine | 6.0 | 74.2 | 19.8 | 8.0 |
| 3 | β-Pinene (b. p. 163–166°) | 3.6 | 64.2 | 32.2 | 9.6 |

It will be noted that the yields of isoprene obtained from turpentine are considerably higher than those obtained by Herty and Graham. This may be due to the employment of a larger catalytic surface in our experiments.

## CONCLUSIONS

The results obtained show that turpentine and β-pinene under the same conditions yield about the same amount of isoprene, approximately 10 per cent.

The isoprene obtained from turpentine is certainly not due to the cracking of dipentene or limonene originally present in the turpentine; but the opinion is advanced that the isoprene results indirectly from dipentene. It is a well-known fact that α-pinene can be converted into dipentene by heat; the condition

[1] Schorger, *Bull.* **119**, U. S. Forest Service (1913).
[2] *Ann.*, **383** (1911), 228–9.

obtaining in the apparatus would be favorable to such a transformation. The changes may be represented thus:

PINENE ⟶ DIPENTENE ⟶ ISOPRENE

Since the first reaction would probably not proceed to a great extent under the conditions of the experiment the yield of isoprene would necessarily be low.

It is not probable that either $\alpha$-pinene or $\beta$-pinene can be made to yield directly sufficient isoprene for the commercial production of rubber. However, since good yields of isoprene are possible from dipentene, an attempt to obtain an approximately quantitative conversion of pinene into dipentene is worthy of further consideration.

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## THE DISTILLATION OF DOUGLAS FIR AT HIGH TEMPERATURES

By BAILEY TREMPER

Inasmuch as the cost of manufacturing illuminating gas from coal and oil is gradually increasing in the small plants, the possible substitution of wood as the raw material is of interest. This is especially the case in sections of this country such as the Pacific Northwest, where thousands of cords of mill waste are destroyed in mill incinerators. For several years an experimental gas plant using sawmill waste has been in operation in this state, and recently several plants have been, or are being, constructed for commercial operation. It is the purpose of this paper to present some of the results obtained in one of these plants, located at Auburn, Washington.

The plant is patterned closely after standard coal-gas installations. Benches of four 9-ft. clay retorts are used. These are connected in turn to a hydraulic main, condenser, exhauster, and dry scrubbers; thence through the station meter to the holder.

The big stumbling block in wood-gas manufacture has been the accumulation of tar in the pipes, especially near the offtake. This has been overcome by waterjacketing the standpipes from mouthpiece to bridge pipe. Special design of the mouthpieces provides for drainage of the condensed liquor. Particles of tar and pitch are readily removed by the action of the thin liquor resulting from the condensation of portions of the gas. Trouble from stoppage further on is also minimized.

The wood for gas making is bought in 4-ft. lengths. It is tied into bundles of such size that two may be placed side by side in the retort, each retort requiring four bundles. The bench is maintained at 1400 to 1600° F. The exhauster is regulated so that there is neither vacuum nor pressure on the retorts. The time of carbonization is one hour and forty to fifty minutes.

Both the quantity and the quality of the gas vary with the grade and variety of the wood used. In commercial practice Douglas fir only is used but trial runs were made with red cedar and Western hemlock.

Forest wood cut from live trees, seasoned three months, fairly resinous, and weighing 3700 lbs. per cord, an average of the butt of a tree, produced 25,000 cu. ft. of gas per cord of 128 cu. ft.; 19,000 cu. ft. of this gas had an average heating value of 538 B. t. u. per cu. ft. as determined with a Junkers calorimeter. The average of the entire run was 482 B. t. u. per cu. ft. The maximum heating value during the run was 560 B. t. u. Bark alone from this wood gave 17,000 cu. ft. per cord, averaging 494 B. t. u., with a maximum of 567 B. t. u.

From unselected mill waste, thoroughly air-dried, weighing 3300 lbs. per cord, 18,000 cu. ft. of gas were obtained as the average yield per cord during two months' operation. The average heating value of the gas is 470 to 480 B. t. u. In each run a maximum heating value of about 515 B. t. u. is attained when the run is one-third over.

From hemlock mill waste, very wet, and weighing 4000 lbs. per cord a yield of from 15,000 to 17,000 cu. ft. of gas with an average calorific value of 414 B. t. u. was obtained. Cedar gave the same yield with a heating value of 460 B. t. u.

A typical analysis of the gas as determined with the Morehead apparatus is as follows:

| | Per cent |
|---|---|
| Carbon dioxide ($CO_2$) | 17.4 |
| Illuminants | 6.0 |
| Oxygen ($O_2$) | 0.0 |
| Carbon monoxide (CO) | 31.5 |
| Methane ($CH_4$) | 21.7 |
| Hydrogen ($H_2$) | 18.3 |
| Nitrogen ($N_2$) | 5.1 |

The calculated heating value of the gas is 500 B. t. u. and the calorimeter test of the same sample was 509 B. t. u.

It will be seen from this analysis that the gas resembles more or less closely carbureted water gas in composition, and it is of value to consider the reactions in the retort in this light. Wood charged into the hot retort soon acquires a coating of charcoal. Water vapor driven out from the wood comes in contact with the hot carbon and is decomposed. Inasmuch as the initial temperature is comparatively low, the layer of charcoal thin, and steam greatly in excess, the formation of carbon dioxide is favored. The resinous and oil-forming portions of the wood, on vaporization, are apparently cracked and partially converted into permanent gases, thus forming the enriching constituents.

It has been observed that during the first part of a run there is considerable cooling of the retorts due to evaporation of moisture. During the latter part of the run, the exothermic character of the reaction brings the retorts to their former temperature. Temperatures below 1300° F. do not give as good results as outlined, while, from somewhat incomplete data, it appears that temperatures above 1800° cause the breaking down of the richer constituents of the gas. For bark alone, however, a higher temperature seems suitable, as the gas contains a very high percentage of carbon dioxide when formed at medium temperatures.

Attempts have been made to reduce the high content of carbon dioxide in the gas, which under poor conditions of operation has reached 22 per cent. The formation of carbon dioxide is decreased with increase of temperature, but the sample containing 17.4 per cent was generated at as high a temperature as is practicable in the ordinary bench. It was thought that the carbon dioxide might be reduced by drawing the gas through beds of charcoal in the front part of the retort. The results showed, however, that decomposition of water vapor, under conditions favoring the formation of carbon dioxide, took place to such an extent that there was no reduction in its amount. In other words, the gas was diluted with a rather poor water gas.

The nitrogen content of the gas is due to bench gas working into the retort through small cracks. The more or less porous new retorts do not become coated with carbon as is the case in coal-gas manufacture. This demonstrates the need of extreme care in heating the benches so that the formation of even the finest cracks may be avoided as much as possible.

A bench of four 9-ft. retorts will hold a charge of one-fourth cord. Twelve charges can be made in twenty-four hours, giving a gas output of 60,000 cu. ft., or 15,000 cu. ft. per retort, an amount somewhat in excess of coal-gas practice.

The by-products of wood-gas manufacture are chiefly tar and charcoal. Wood alcohol, acetic acid, acetone, and part of the tar are largely decomposed under the temperature of distillation. Analysis of the aqueous distillate shows 1.0 to 2.5 per cent acetic acid, 0.2 per cent wood alcohol and acetone, and less than 1 per cent soluble tar.

The yield of tar varies from 14 to 22 gallons per cord according to the quality of the wood, the temperature of distillation, and the pressure on the retorts. The tar is much more easily recovered than when produced by low temperature distillation, and settles out in eight hours, carrying less than 5 per cent

water. On redistillation it yields 1.5 per cent wood spirits, boiling below 100° C. and 2.5 per cent light oils boiling below 150° C. It is completely dehydrated at 150° C. This tar sells readily in local markets for 12.5 cents per gallon.

By employing a lower temperature the yield of by-products is increased. While a lower heating value of the gas results, it would still be useful for industrial purposes.

Charcoal is obtained at the rate of 700 to 800 lbs. per cord, for which a good market does not at present exist in the Northwest. Its quality is impaired by the presence of charcoal from bark, but as the latter is a good producer of gas, it is not feasible to remove it from the sawmill waste. The amount of charcoal obtained is ample to furnish fuel for open-fired benches and with regenerative furnaces an excess would be produced. This excess quantity or the entire amount can be used in water-gas manufacture, as demonstrated by trial runs made in a 3-shell Lowe water-gas set at the plant of the Tacoma Gas Company. The charcoal held its heat so that 3-minute periods of run and blast could be maintained. The same amount of oil was used as with coke. A yield of 1000 cu. ft. of carbureted gas was obtained from each 25 lbs. of charcoal as opposed to 40 lbs. of coke. The clinker formed was practically negligible and did not show signs of fusion with the generator lining. Whereas one hour out of every eight is generally required for clinkering coke, shaking grates would probably eliminate clinkering entirely, with charcoal. The use of the latter would therefore result in the production of more gas, with a saving in labor and periods of shut-down, as well as increase the life of the furnace. Very little dust was blown into the carburetor and all of it could probably be eliminated by baffles.

Kiln-drying of wood to remove the considerable amount of water still held after air-drying would doubtless still further increase the heating value of the gas and the capacity of the retorts, as well as decrease the fuel required.

SUMMARY

1—From Douglas fir forest wood, 25,000 cu. ft. of gas with a calorific value of 482 B. t. u. is obtained per cord of 37000 lbs.; 19,000 feet of this gas has a heating value of 538 B. t. u.

2—From Douglas fir mill waste 18,000 cu. ft. of gas with a calorific value of 475 B. t. u. is obtained per cord of 33000 lbs.

3—Enough tar is obtained to pay for the cost of wood at the plant.

4—The exothermic character of the reaction favors low fuel consumption.

5—Water gas can be produced satisfactorily from charcoal at the rate of 1000 cu. ft. per 25 lbs. of charcoal.

6—Wood gas and charcoal are especially available for metallurgical operations at mines located far from fuel supplies other than wood.

AUBURN GAS COMPANY
AUBURN, WASHINGTON

## THE PRODUCTION OF ACETONE FROM PYROLIGNEOUS ACID[1]

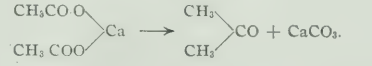
By Marc Darrin

The purpose of the work reported in this paper is to show the yield of acetone that can be obtained from pyroligneous acid by means of a continuously operated electric furnace, containing a catalyzer, which converts the acid directly into acetone without necessitating the intermediate production of the acetate.

The raw material consisted of pyroligneous acid obtained by the destructive distillation of Douglas fir mill waste at the half-cord wood distillation plant designed by the author,[1] and erected cooperatively by the University of Washington and the U. S. Forest Service. Before treatment, the pyroligneous acid was distilled in order to separate and recover the turpentine, oils, tar, alcohol, acetone, etc., since it was thought that these substances might have an injurious effect on the catalyzer and since these by-products are necessarily separated and recovered in commercial practice, up to the point where the re-distilled acid is neutralized with milk of lime for the manufacture of the gray acetate. At this stage, the present practice is to mix the pyroligneous acid with the lime in large tanks until the neutralization is complete, as shown by the color change. The principal acid constituent of pyroligneous acid is acetic acid.

$$2CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + 2H_2O.$$

It is then evaporated to a pasty consistency, dried, and shipped away as "gray acetate of lime" to the acetone plant, where it is destructively distilled in steel retorts, breaking down into acetone and calcium carbonate.



$$CH_3CO\cdot O \quad Ca \longrightarrow CH_3 \quad CO + CaCO_3.$$
$$CH_3\,COO \qquad\qquad CH_3$$

The acetone is condensed, washed and refined in column distillation apparatus.

### APPARATUS

The apparatus used for these experiments is shown in the accompanying illustration. Its operation is as follows: The pyroligneous acid is introduced into the reservoir *A* and allowed to drop slowly into the round bottom flask *B* regulated by means of the cock *C*. The acid in the flask is heated by a carefully regulated burner *B*, which is so controlled as to cause the liquid to evaporate at the same speed with which it is dropping into the flask. The acid vapors pass through the tube *E* into the electric furnace *V*, which consists of a quartz tube *G*, surrounded by insulating material *J*, containing the electric heating element. The interior of the quartz tube is filled with the catalyzer *H*, and it is in this region that the conversion takes place. The entrance and exit connections to the heated quartz tube are made by asbestos stoppers, *F F*. The vapors leaving

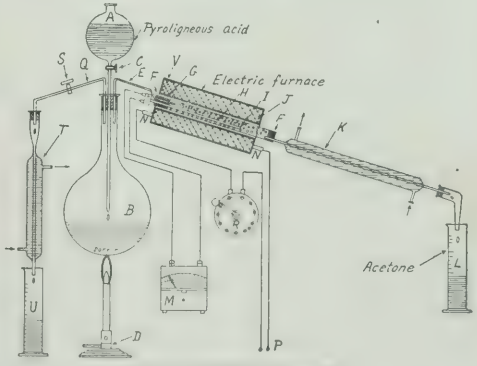



FIG. 1 ACETONE APPARATUS

[1] REFERENCES U. S. Pat. (1910), 933,107: Formation of acetone from zinc, barium and magnesium carbonates at 575° C.

*Pharm. Ztg.*, **54** (1910), 880: Formation of acetone by passing over base heated at a high temperature at 300–350 mm. pressure.

German Pat. (1910), 214,151. Addition to patent 198,852: Manufacture under reduced pressure.

*Ber.*, **43** (1911), 2821: Acetone and ketone formed to extent of 10% when passed through pumice heated to 500–600°.

Brit. Pat. (1907), 13,263: Generation of acetone.

Ger. Pat. (1908), 198,853: Generation of acetone under reduced pressure.

Fr. Pat. (1908). Addition to 6,531 to 361,379: Generation of acetone under reduced pressure.

[1] For design of plant, see THIS JOURNAL, **5**, 935.

the furnace are condensed in the condenser $K$, and the liquid caught in the graduate $L$. The temperature within the interior of the electric furnace is measured by means of the thermocouple $I$, which records the temperature on the millivoltmeter $M$. The electric furnace is connected at $N$ $N$ to 110 volt switch, $P$. The temperature within the electric furnace is regulated by means of the rheostat $R$, connected in series with the furnace. A sample of the pyroligneous acid vapors before treatment is taken from the flask $B$, by means of the tube $Q$, the amount being regulated by means of the cock $S$, so as to be the same as that coming out of the condenser $K$. These sample vapors are condensed in the condenser $T$, and caught in the graduate $U$.

### ANALYSIS

The two distillates in graduates $L$ and $U$ were analyzed separately for their acidity, by titration with $N/2$ KOH, using phenolphthalein as an indicator. The acidity of the liquid in each graduate was computed to the per cent by weight of pure acetic acid, $CH_3COOH$. The difference in the per cent of acetic acid, that the liquid in graduate $L$ was less than that in graduate $U$, measured the amount of acetic acid that had been decomposed in the electric furnace.

The two distillates in the graduates $L$ and $U$ were also analyzed separately for the acetone, by titration[1], with $N/2$ $Na_2S_2O_7$, using starch solution as an indicator, after first adding an excess of alkaline KI solution and $N/2$ NaOCl, and neutralizing with 6 per cent HCl. The solutions of $N/2$ $Na_2S_2O_7$ and $N/2$ NaOCl were standardized every day against a standard acetone solution of known strength. A small amount of higher ketones, aldehydes, and similar bodies, which react with the NaOCl, are estimated as acetone. To eliminate the error that this would cause in the acetone determination while working with the pyroligneous acid, the blank tests for acetone were made on the untreated acid in the graduate $U$. Subtracting the amount of ketones which were determined in the untreated acid, from the amount of acetone determined in the treated liquid, gave the actual per cent by weight of acetone which had actually been formed in the furnace.

### CALCULATIONS

The maximum amount of acetone that can be obtained theoretically from the decomposition of acetic acid is shown by the following equation:

$$\begin{matrix} CH_3CO\vdots OH \\ CH_3\,COO\,H \end{matrix} \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CO + CO_2 + H_2O.$$

$$120.06 \quad = 58.05 \quad + 44.00 + 18.01$$

The figures below the chemical equation show the relative weights of the products formed; that is to say, 120.06 g. of acetic acid have a maximum theoretical yield of 58.05 g. of acetone.

The decomposition of the acetone does not always proceed as in the above equations, except under the proper control of temperature and other factors. For instance, too high a heat causes the acetone to break down into methane, free carbon, etc. It was found that by a second treatment of the liquid, any acetic acid would be decomposed that had not broken up on the first treatment. For this reason it was assumed, in the following computations of theoretical yields, that the amount of acid concerned in the reaction was only that portion indicated by the difference of the percentages between the treated and untreated liquids. The method has the further advantage of eliminating the error which is caused by the presence of other acid bodies than the acetic acid, but which the analysis computes as acetic. The theoretical yield is, therefore, computed from the analysis by means of the following formula:

[1] Kebler's method, see THIS JOURNAL, **19**, 316.

$$Y = 100\frac{(B_2 - B_1)}{(A_1 - A_2)} \frac{120.06}{58.05} = \frac{(B_2 - B_1)}{(A_1 - A_2)} 207$$

where $Y$ = per cent of theoretical yield of acetone,
$A_1$ = per cent of acetic acid in the untreated acid,
$A_2$ = per cent of acetic acid in the treated acid,
$B_1$ = per cent of acetone in the untreated acid,
$B_2$ = per cent of acetone in the treated acid.

### ACETIC ACID

Before the work was taken up with pyroligneous acid, the exact conditions under which the reactions best took place were carefully studied, using pure acetic acid. Altogether, 57 different samples of acetic acid were tested under various conditions of control. These were tested continuously, at the rate of about 2 a day, the entire operation on pure acetic acid extending over a period of a little over a month.

During this time the effects of various types of catalyzers were studied, the influence of the initial acid concentration was observed, and the effect of speed and temperature carefully noted. The effect of steady and intermittent heating of the electric furnace caused by the automatic breaking of the circuit at intervals of two seconds was also studied.

Table I is an extract of the analytical data, after the control conditions had been adjusted to run in a satisfactory manner.

TABLE I

| Run No. | Per cent acetic acid in Untreated acid | Treated acid | Per cent acetone in Untreated acid | Treated acid | Per cent of theoretical yield of acetone |
|---|---|---|---|---|---|
| 33 | 3.09 | 0.33 | 0.00 | 1.25 | 94.0 |
| 34 | 3.78 | 0.48 | 0.00 | 1.34 | 84.2 |
| 35 | 3.69 | 0.48 | 0.00 | 1.52 | 98.0 |
| 36 | 3.00 | 0.21 | 0.00 | 1.07 | 79.2 |
| 52 | 2.49 | 0.33 | 0.00 | 0.87 | 83.5 |
| 53 | 2.34 | 0.24 | 0.00 | 0.87 | 86.0 |
| 54 | 2.43 | 0.12 | 0.00 | 1.02 | 91.5 |
| 55 | 2.80 | 0.09 | 0.00 | 1.07 | 81.8 |
| 56 | 3.18 | 0.15 | 0.00 | 1.22 | 83.0 |
| 57 | 5.58 | 0.60 | 0.00 | 1.98 | 82.4 |
| AVERAGE | 3.24 | 0.30 | 0.00 | 1.22 | 86.4 |

When working with 2 to 4 per cent solutions of pure acetic acid, the electric furnace is able to convert 86.4 per cent of the maximum theoretical into acetone. The original strength of the acetic acid has little effect on the process as equally good results were obtained with 50, 25, 10, 5 and 2 per cent solutions. The majority of the tests were made on 2 to 4 per cent solutions.

### PYROLIGNEOUS ACID

Having established the conditions under which the maximum yields were obtained working with pure acetic acid, a study was made of the yields from pyroligneous acid. Operating under the same conditions of temperature, speed, etc., that were found to give the best results for the pure acid, the data given in Table II were obtained.

TABLE II

| Run No. | Per cent acetic acid in Untreated acid | Treated acid | Per cent acetone in Untreated acid | Treated acid | Per cent of theoretical yield of acetone |
|---|---|---|---|---|---|
| 58 | 2.52 | 1.14 | 1.07 | 1.45 | 57.8 |
| 60 | 2.43 | 1.23 | 0.71 | 0.95 | 40.9 |
| 61 | 2.52 | 1.08 | 0.53 | 0.81 | 48.5 |
| 62 | 2.49 | 0.93 | 0.71 | 1.05 | 45.4 |
| 63 | 2.58 | 0.69 | 0.71 | 0.99 | 30.2 |
| 64 | 3.18 | 0.72 | 0.66 | 1.42 | 63.6 |
| 66 | 3.99 | 0.48 | 0.66 | 1.38 | 42.2 |
| 79 | 2.04 | 0.99 | 0.53 | 0.98 | 87.5 |
| 81 | 3.18 | 0.24 | 0.55 | 1.35 | 52.0 |
| 86 | 4.68 | 0.27 | 1.08 | 2.32 | 58.3 |
| 92 | 2.88 | 0.36 | 0.47 | 1.24 | 63.0 |
| AVERAGE | 2.95 | 0.74 | 0.70 | 1.27 | 53.6 |

Because of the small size of the furnace (capable of treating about 25 cc. of the acid per hour), it was impossible to control the speed of the distillation as accurately in proportion to the size as could be done with a commercial apparatus treating several hundred gallons per hour. Consequently small variations which were followed by similar variations in temperature within the furnace, caused local overheating, resulting in a loss of acetone. It is this variation which is the principal cause for the different yields found in various runs shown in Table I. Probably in a larger apparatus with the speed and temperature

properly controlled the yield would be higher than 86.4 per cent, approaching 100 per cent as a maximum.

Applying the same line of reasoning to the yields from pyroligneous acid as shown in Table II, a larger apparatus would produce a yield about 15 per cent higher than that shown in the data, or would approach a maximum of about 65 per cent.

There is still another factor which the author believes, if looked into more thoroughly than the scope of this investigation permitted, would show that the actual yield was even greater than 65 per cent; *viz.*, that the higher ketones, aldehydes, and similar bodies present in the untreated pyroligneous acid are decomposed to a considerable extent by the temperature of the furnace. If this is the case, the true amount of acetone formed by the furnace is not the *difference* between the determinations before and after treatment, but the *whole* amount after treatment. With the assumption that half of the higher ketonic bodies are destroyed in passing through the furnace, the average yield of acetone computed from the data in Table II would be 86 per cent. This is approximately the same figure as that obtained from the pure acid. The assumption that the higher ketonic bodies are destroyed in the furnace is further supported by the observation that the cloudy, yellow iodine compounds, caused by certain higher, ketonic bodies in the untreated acid, do not appear in the acetone determination of the treated acid, the iodoform settling in a flocculent state and leaving a clear, supernatant liquid.

### CONCLUSIONS

I—The percentage of the theoretical yield that can be obtained by treating acetic acid in a continuous electric furnace is a little over 85 per cent, approaching 100 per cent as a maximum, under favorable conditions.

II—The yield from pyroligneous acid is similar to that from pure acetic acid, being around 85 per cent.

III—The concentration of the solution being treated has little effect on the operation.

IV—The temperature and speed are the principal factors influencing the yield, the most suitable for the apparatus employed being approximately 435° C. at a speed of 25 cc. per hour.

V—The catalyzer can be used continuously with little deterioration, a sample of barium acetate having been used continuously a little over thirty days.

VI—The process of the direct and continuous conversion of pyroligneous acid into acetone in an electric furnace containing a catalyzer is adaptable to commercial usage in plants treating several thousand gallons of pyroligneous acid per day.

VII—The advantages over the ordinary method of making acetone from the acetate, are considered to consist chiefly in:

1—Higher yields in acetone.

2—Lower operating expenses.

3—Elimination of the large consumption of lime.

4—No drying of the acetate with attendant losses.

5—Continuous operation, converting the pyroligneous acid directly into acetone without intermediate handling.

6—Low cost of apparatus.

7—Easy control of apparatus, adapting itself to an automatic thermostate arrangement, assuring uniform results.

SEATTLE, WASHINGTON

## WASTE PINE WOOD UTILIZATION

By JOHN E. TEEPLE

This is an old, old industry. As far back as we have definite information, people were using tar on their cordage and pitch on their ships. Even Noah's ark you recall was "pitched within and pitched without," and the ark of bullrushes that supported the baby Moses was "daubed with pitch." We lack positive assurance that a pure pine pitch was used in these cases, but it may easily have been cypress pitch, which is not so widely different. Since the industry is such an old one, the chemist is not to be either censured or credited with its results until within the last thirty years, and more especially within the last ten or fifteen years. The method commonly used formerly was to pile the wood in large heaps, cover it with earth, and by burning a portion of the wood accomplish a destructive distillation of the remainder. The products were tar and charcoal, although some few attempts were made to recover the volatile spirit for use as an illuminant.

About thirty years ago the use of iron retorts was introduced, and this made possible the recovery of an unsatisfactory turpentine, a little of the natural pine oils, and considerable tar oil, creosote oil, pitch and pyroligneous acid, in addition to tar and charcoal. The turpentine had a vicious odor, but being in small amount, it could usually be worked off by persuasion. Tar was a standard commodity, but the trade soon began to differentiate between this retort tar and ordinary kiln tar, and the purchaser demanded a reduction in the case of the former, or refused it. Charcoal could be sold for household fuel provided the plant was located in the neighborhood of a fair-sized city. Otherwise it was used to fire the retorts. Gas was also at a time recovered and burned under retorts. When pitch was not readily salable it could be dissolved in the tar oils or creosote oils and sold as tar, but these various light and heavy distillation oils accumulated, and, depending on his ingenuity, the manufacturer worked them up into paint oils, mixed paints, insecticides, disinfectants, fungicides, embalming fluids, medicinal products, and so on until the catalogue becomes alarmingly long. This destructive distillation industry still exists. It is one of the two methods of treating wood to obtain Naval Stores that has been able to operate continuously under even the present very adverse conditions. Many improvements have been made in the type of the retort, in the regulation of heat, and in the separation and preparation of products for the market. In many cases the turpentine now obtained is of excellent odor and of surprisingly good quality, but its success has usually depended on the ability of the manufacturer to work up his oils into lines of specialties under carefully established trade names, and thus protect himself from too vigorous competition. He has improved his retort tar so that now it commonly commands the same price as kiln tar, and is sometimes quoted at a higher figure. With the present high prices ruling for acetate of lime, due to the strong demand for acetone, he is even proceeding in some instances to the manufacture of this product from his pyroligneous acid. A considerable part of these improvements has, of course, been due to chemists, but it must be admitted that a further very considerable part of the preparation of products for the market has been due rather to business men who are good observers but were not primarily trained as chemists. It seems to me that the destructive distillation of wood is wrong in principle, with our present knowledge of its composition, but at the same time the fact that some of these plants have been continuously operating for many years indicates that they are not to be abolished with the speed that advocates of some of the newer processes have assured us.

Of other processes that have been suggested—distillation with superheated steam, extraction with rosin bath or tar and pitch bath, distillation with water, distillation with hot gases, digestion with soda and application of vacuum have all had their trial in a commercial way, and a number of them have seemed to operate successfully for a while, due usually to special market conditions, but for the present these have all passed into history. It is very doubtful whether any of them will appear again, at least alone, even under improved conditions. While they lasted, each one found vigorous supporters and provoked much discussion. The question, for example, whether the steam should preferably pass upward or downward through a retort,

was considered of considerable moment, but now it hardly arouses our interest. Some chemist usually took an active part in developing all of these processes, but the fact that none of them are operating to-day should not be laid entirely against him. In many cases he was responsible only for the laboratory results, and plants were constructed without the aid of chemical engineers, or, in fact, of chemists or engineers of any kind. In many other cases he had no first-hand knowledge of the industry himself, and relied on faulty information as to cost of wood and market conditions, supplied by men who were promoting the plants. In any case, in developing these processes the chemist and chemical engineer accumulated, and frequently put on record, a fund of very valuable information which is not at all lost, but which will have an important bearing on the future development of the industry.

In one important respect the chemist performed valuable service during this period of development. For the first time there was produced under his supervision a quantity of wood turpentine and pine oil sufficient to have an appreciable effect on the market. He succeeded in making a wood turpentine of a much higher and more uniform grade than had ever been attained before, and by his knowledge of its uses he overcame the prejudice against it, due to its different odor and different source, in enough places so that a firm and steady outlet on good prices was obtained for all that could be supplied. For the first time, too, there was a very considerable amount of the heavy natural oils of the wood, known as pine oil, to be disposed of. This had no regular market, and he succeeded in finding a use for it in a very wide range of industries, where it has so firmly established its value that at the present time the supply cannot begin to equal the demand.

The one other process which has apparently proved of value, and which is still in operation today under adverse market conditions in at least two or three plants, is that of extraction by means of a volatile solvent. This method was at one time very extensively employed, producing more Naval Stores from waste wood than all other systems combined. The amounts of turpentine and pine oil were large and of good quality, and one new product was added from the wood—rosin. This was ultimately refined to a grade approximately corresponding to F and G grades of gum rosin. At first, progress in marketing this was rather difficult, but the oils and tarry matters affecting its use were in part eliminated, and in part the customer was taught what changes were necessary in order to use it as satisfactorily as gum rosins, so that to-day again the demand exceeds the supply.

The worst feature, of course, in the development of this industry during the last few years has been the wide fluctuation in prices. In 1911 F rosin reached a high price of $8.45 per barrel of 280 pounds, at Savannah: to-day it is $3.00—scarcely more than one-third of the high figure, and it has been lower. In 1911 turpentine reached a high price of $1.07 per gallon at Savannah: to-day it is 38c. and has been lower. Most of these plants were built on the assumption that turpentine would not go below 50c. per gallon, nor rosin below $5.00. These conditions were freely predicted at the time by people who had spent their lives in the Naval Stores industry, and so probably the chemist should not be blamed too much for the failure of processes to operate successfully at much lower figures, when he had based all his calculations on the higher figures and on the best judgment of people well informed as to conditions.

Now as to the future of the industry: Let us look first at the composition of the material with which we have to deal. Assuming that this is what we know as fat lightwood or as fat lightwood stumps, it contains rosin, turpentine, pine oil and the wood fiber. The problem is: in what way can all these products be extracted and placed on the market to bring the largest net amount to the manufacturer? In some places where the timber has been very largely the long-leaf pine, there is the additional factor of so locating his plant that he can entirely clear the land and largely enhance its value at the same time that he is furnishing his plant with raw material. In the future this will no doubt have an important bearing on the establishment of plants, but it will not be considered here. Suppose we have 5000 lbs. of very rich, fat lightwood stumps. Suppose this contains 20 per cent, or 1000 lbs., of rosin; 40 gallons or 300 lbs. of turpentine and pine oil, and 15 per cent, or 750 lbs., of water. This leaves nearly 3000 lbs. of wood fiber. Now if we subject this 5000 lbs. of fat lightwood to destructive distillation, no matter how carefully, we shall not get all the turpentine and we get only a small portion of the pine oil, before the rosin and the wood itself begin to decompose. The rosin would be valuable if we could get it, or its decomposition product, rosin oil. The pine oil would be valuable if we could get it, but before either the rosin oil or the pine oil leave the retort in any quantity they become thoroughly mixed with the tar and tar oils from the decomposition of the wood fiber, and there is no convenient way of ever separating them again in marketable conditions from the resulting mess. If we investigate any of the other methods that have been discussed above, we find an important loss in some one or more of the products originally present in the wood. If we digest with soda there is a very fair recovery of the turpentine and a moderately good recovery of the pine oil, but the rosin and resinate are not in good marketable condition, and it would be very difficult to get them in any condition for anything but very special markets. On the other hand, if we use a volatile solvent, properly selected and properly applied, we can recover nearly the whole of the rosin, turpentine and pine oil, and have left the wood fiber unchanged. The rosin, the turpentine and the pine oil will be in such condition that they can be made into the best grades it is possible to produce from wood. The wood fiber is free of rosin, and is in just the condition required for digestion to manufacture wood pulp. According to information and experiments it gives a good yield of a very strong-fibered pulp. Probably it will work up best into what is known as Kraft pulp, or undercooked pulp, and this 3000 lbs. of wood fiber remaining should furnish about 1500 lbs. of good marketable pulp.

Our wood fiber has two disadvantages as a source of pulp. In the first place it cannot be entirely freed from the charcoal and charred and burned wood, and in the second place it will not be entirely free from bark, but there is no question that it will produce a good grade of brown wrapping paper, and with this addition we have made a very complete utilization of our 5000 lbs. of wood. The difficulty heretofore has been that the Naval Stores manufacturer has approached the problem with the view of making the wood pulp plant an annex to his existing plant. The wood pulp plant is the more expensive, requires the more skilled labor, and is by far the more important, so that the rosin and turpentine production should be considered rather as an annex to the pulp plant, or, better still, the whole should be considered as one complete proposition. Many people have this combination of rosin, turpentine, pine oil and wood pulp in their minds at the present time. There is no doubt that it will be tried before long. It is only to be hoped that when it does receive its trial it will be under the supervision of men thoroughly acquainted with both the wood pulp industry and the wood extraction industry, and with the aid of the most competent chemical engineers there are available. In this way it can build on the mistakes of its predecessors, and it seems to me to stand an excellent prospect of success. There has too much good work gone into this industry, and there is too much accumulated information available to allow it to languish. I feel sure it has an important future, and when its success ultimately comes, very large credit will be due to the chemists and chemical engineers who have made it possible.

CHEMISTS' BUILDING, 50 EAST 41ST ST.
NEW YORK

# SYMPOSIUM ON THE CONTRIBUTIONS OF THE CHEMIST TO AMERICAN INDUSTRIES

Papers presented at the 51st Meeting of the AMERICAN CHEMICAL SOCIETY, Seattle, August 31 to September 3, 1915

## CONTRIBUTIONS OF THE CHEMIST TO THE NAVAL STORES INDUSTRY

By JOHN E TEEPLE
Consulting Chemist and Chemical Engineer

The Naval Stores Industry includes primarily the production of rosin and turpentine, and secondarily that of tar, pitch and various oils. The raw material in this country is the long-leaf pine and some similar pines in the South Atlantic and Gulf States. The United States produces more turpentine and rosin than all the rest of the world, our total annual production being probably worth over $40,000,000; our exports in one year exceeded $27,000,000, and are usually above $20,000,000.

The industry is not a new one. When America was discovered, Russia was furnishing tar and pitch and turpentine for the cordage and ship building industries, and in our own country we were exporting turpentine and rosin in considerable quantities before the year 1800. Nearly forty years ago our exports were nearly half in quantity what they have been in recent years, though having only about one-fifth the present value.

Notwithstanding the magnitude and age of the Naval Stores Industry, however, it developed largely without the aid of the chemist. Only within the last ten or fifteen years can he claim to have played more than a minor part, but recently his contributions have been of extreme importance. We may discuss the chemical contributions under four heads:

1—Improving the quality and quantity of rosin and turpentine produced from the living tree.

2—Providing standards, and detecting and preventing adulteration.

3—Finding new uses and enlarging the markets, particularly for rosin.

4—Utilizing the rich dead pine (lightwood) and various pine wastes for the manufacture of Naval Stores.

This last field is usually classed as wood distillation, or wood extraction, and as there is a special symposium on that subject at this meeting it will not be further discussed here. When this utilization reached its maximum in 1911 to 1913, it is probable that it furnished over 10 per cent of the total Naval Stores production of the United States, and it seems likely to increase in importance in the future when conditions and prices have readjusted themselves.

The methods of producing rosin and turpentine from the living tree made very little progress during the whole nineteenth century. Timber was plenty, land, leases and labor were cheap, there was a profit to be had by existing methods, so why worry. The method consisted in hollowing out a cavity near the base of a pine tree, and cutting away bark and wood, to leave a smooth face for a few inches above it. Then every week from Spring till Fall a V-shaped chip about an inch wide was cut through bark and wood above this face, each chip being just above the preceding one. Thus inch by inch the scarred face crept up the tree, to the extent of say thirty inches a year, and at each chipping the oleoresin from the wound flowed down the scarred face till it reached the cavity at the bottom, whence it was dipped out for distillation with water over direct fire, to produce volatile turpentine and non-volatile rosin. Every year the thick, gummy exudate had to flow over a longer stretch of discolored scarred face, and be exposed to longer evaporation of turpentine before it reached the collecting cavity at the bottom. And so every year the producer's rosins were darker colored, and his yield of turpentine smaller.

But conditions began to change. Many lumber men refused to have their trees bled for turpentine, as it decreased the value of the lower end of the tree for lumber, and very largely increased their loss of timber from forest fires and from windstorms. Timber was not so plentiful as had been supposed. Prices of lands, leases, labor and materials were all rising. The cost of producing turpentine and rosin to-day is probably three times what it was twenty-five years ago. So the producer called for help. He looked first to France. There they were able to bleed a tree for many years—one is said to have survived two hundred years—while here four years was about the limit of profitable operation. There they planted large orchards of pine trees for the express purpose of turpentining them. There they made much narrower gashes in the trees, used a cup and gutters to collect the oleoresins, instead of allowing them to flow long distances over the scarred face into a hole in the tree, and there they accordingly made lighter colored, higher priced rosins, and bleached them still further in shallow pans in the sun, changing for example a K rosin into the much more valuable water-white rosin.

A study of the French methods seemed, however, to show that they were not, as such, applicable to existing conditions here. But there was an idea there, and to C. H. Herty is due the credit first of working out that idea in a scientific and practical way to fit conditions here, and second, what was probably much more difficult, of persuading the operators to use his methods for their own good. Herty conducted careful comparative scientific experiments, and showed clearly:

I—That there was no physiological reason for the marked coloration of rosins during the later years of operation as compared with the first or virgin year, but that this coloration was due to oxidation of the resin acids during the longer flow from the point of exudation to the receptacle, "the box," a large hole cut with an axe in the base of the tree, and especially to the absorption by the fresh oleoresin of the old oxidized resin on the face of the tree scarified during the previous years. By using an outside receptacle attached to the tree and moving it annually up the tree near the point of scarification, only the best grades of rosin were obtained.

II—The flow of the oleoresin over long surfaces resulted in heavy loss of the volatile spirits of turpentine.

III—The cutting of "the box" resulted in destruction of much of the timber by fire, wind and insects.

IV—Most important of all, it was demonstrated that the unboxed pine tree would produce 25 per cent more crude turpentine than the boxed tree, due to greater vitality of the tree.

The total value of the annual Naval Stores output is approximately $40,000,000. It is easily seen, therefore, that the above losses in material, both as to quantity and quality, represent an annual waste of from $10,000,000 to $15,000,000.

Early commercial confirmation of the experimental results led to the rapid substitution of the long used "box system" by the practical, cheap and efficient "cup system." The use of the cup system was not thoroughly efficient for several years, as was evidenced by the low yields of early Spring as compared with the later yields. The explanation of this shortcoming was apparent when Tschirch, of the University of Berne, published his views on resin flow and then by a slight modification of woods practice the difficulty was overcome and a further annual increase of crude turpentine valued at a half million dollars was effected.

But the end is not yet in sight, for, according to Herty, laboratory experiments on perfectly fresh specimens of crude turpentine show that its normal content of spirits of turpentine is approximately 30 per cent, while under most favorable methods

of collection and distillation at present yields of only 18 to 20 per cent are obtained. This loss of at least one-third of the volatile oil by evaporation remains still to be overcome.

Some chemists have established new industries, and many have coöperated to improve old ones, but this work of Herty's in making, practically alone, such a change in an industry that had been stationary in methods for a hundred years, is almost unique.

As to other improvements in manufacture, not much progress has been made. The French method of bleaching rosin seems too slow and laborious, and many chemical methods have been suggested instead, but up to the present have not made much headway. Methods of distillation without the use of direct heat, such as using superheated steam, or distillation in vacuum have been suggested but have had little influence as yet on methods of manufacture. The United States Bureau of Forestry has recently been studying the question of chipping, and has published results indicating that a $^1/_2$ inch chip gives about as good a flow of oleoresins as an inch chip, besides being less injurious to the tree. They further recommend chipping every four days instead of once a week, thereby increasing the yield in a season. It has been objected that the tree may not be able to stand this excessive bleeding. The method is still to be tried in practice.

When turpentine was comparatively high in price, many substitutes, chiefly from petroleum distillates, and many methods of adulteration were found. Presumably we must give the chemist credit for these too. The question of adulteration particularly became a serious problem and provoked a flood of literature devising tests for various impurities and additions. Most of the large consumers finally evolved specifications to fit their requirements, and many states have passed laws for preventing and punishing adulteration, so that conditions now are much improved, for which we may also thank the chemist. There is still much work to be done, however, in standardizing turpentine specifications to fit the consumers specific requirements. As they now stand, with rather arbitrary figures on specific gravity and distillation, we, no doubt, often include material he really does not want, and exclude material he could perfectly well use.

Rosin has usually been too cheap to suffer from adulteration except with dirt or brickbats. The chemist has little to do with its purity or grading. Recently, however, the United States Bureau of Chemistry has proposed a series of permanent standards, for the different grades of rosin, based on definite transmissions of red and yellow light for each grade.

In extending the markets for Naval Stores the chemist has done little for turpentine. It has had three uses for many years: (1) As a solvent for gums in the manufacture of varnishes; (2) as a vehicle in the manufacture of paints; (3) as a thinner in the application of paints. The chemist has more often striven to avoid its use in these fields than he has to extend it. Two new fields have been opened within recent years, by chemists—one the manufacture of synthetic camphor. This has been carried on to a considerable extent in a commercial way, and will be again, whenever satisfactory relations exist between the market prices of turpentine and camphor. If the yields of camphor could be made more satisfactory it would no doubt become a permanent industry. But at present, with the price of the raw material, turpentine, and of the finished product, camphor, independent variables, and no large margin in any case existing above the fixed manufacturing cost, the outlook is not enticing to the investor. The second new field opened by the chemist is the manufacture of synthetic rubber. Synthetic rubber can be made from isoprene, and isoprene can be made from turpentine, but whether this is the best way to make synthetic rubber, and whether turpentine is the best source of isoprene, and whether synthetic rubber can compete with natural rubber in the long run anyway, are still open to discussion.

With rosin the chemist has had more opportunity. He puts it into shrapnel shells and sometimes into varnish. In the presence of an alkali, rosin acts as an acid, forming resinates. Combined with an amount of soda insufficient to saponify the whole, it forms rosin size, extensively used in the manufacture of papers, where the rosin deposited in the paper prevents the spreading of ink and moisture. This accounts for a very considerable amount of the medium grades. A somewhat higher grade of rosin, when saponified, forms a valuable constituent of, or addition to, many soaps. Combined with zinc, manganese or the alkaline earths, rosin gives resinates used extensively in varnishes.

A very large amount of rosin, particularly of the lower grades, is distilled for the production of rosin oil. The lower grades of rosin oil when mixed with lime, set to form a semi-solid mass (axle grease) extensively used as a lubricant. Better grades are used extensively in the manufacture of printing ink, so that the marvelous increase in printing and paper during the last fifty years has furnished an outlet for rosin in two directions. All of these varnish, soap, paper and printing industries have furnished abundant fields where the chemist has exercised and continues to exercise his ingenuity on rosin and its products.

In the manufacture of rosin oil the yields and quality are not always what they should be. Recent suggestions of different methods of distilling promise much larger yields of better quality oil with smaller amounts of by products.

To conclude, we find the chemist has been particularly valuable in three departments of the Naval Stores Industry. He has improved largely the quality and quantity of product, has standardized grades and prevented adulteration, and has been very successful in finding products and derivatives to fit the markets, or in finding markets to fit his products. This last field especially is far from worked out. There is still a wide scope for the energies of the chemist.

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## CONTRIBUTIONS OF THE CHEMIST TO THE STEEL INDUSTRY

By Geo. W Sargent
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To demonstrate the service that chemistry has rendered to an industry such as that of steel, whose whole foundation is chemistry, and where even the messenger boys about the works speak of carbon, phosphorus, sulfur, silicon, etc., almost as freely as they use the terms of the baseball field, would require volumes. In fact, volumes have been published on the part taken by one element alone. To present, therefore, in a brief outline the success that chemistry has achieved in this tremendous industry is a most difficult task, and it is with considerable hesitation that this paper is presented. Perhaps by picturing the past at a time when the chemist was an almost unheard of factor in the iron and steel industry, in contrast with the present conditions, the object of this paper might be attained.

Harking back somewhat more than half a century with an old furnace man who possessed a mind as active and clear as it was at the time of which he spoke, despite his ninety years, he made the following statement: "A water wheel at the flour mill ran the blower, supplying air to us at the forge several hundred feet distant. Here the pig iron, brought up in canal boats from a charcoal furnace forty miles down the river, was melted in the run out, subsequently tapped into two forge fires, there worked to nature, and forged into blooms under a trip hammer run by the old-fashioned overshot water wheel... The blooms were cut in two pieces about 80 to 100 pounds each and then shipped by canal to Pittsburgh to be rolled into sheets, bars or rods, and then into wire; or to be melted in crucibles and made into steel. Charcoal was the fuel we used. It made mighty fine iron and steel, and that without your chemists. Two tons was a day's output, but we made it right and never had any rejected."

Picture the forge with its two "fires," but little larger than fire-places, its "run out" an enlarged blacksmith's forge on top of a hearth or crucible, and its ten men coming to work at 3 A.M. and quitting at 3 P.M. with two tons of good iron, then worth almost $250, to the credit of the sweat of their brows and twenty cords of wood sent up in smoke. Then remember that before this iron became steel it must be heated, forged or rolled into bars, cut up, charged into crucibles, melted, cast and again hammered into bars at the expense of much time and labor. This was the iron and steel business previous to 1860, with wood for fuel and no chemist. The product was expensive and its use limited; only 40,000 tons of cast steel were produced in 1872, sixteen years after the introduction of Henry Bessemer's process.

In the year 1915, with this picture in our minds, we walk through the latest steel plant, wherein are embodied the experience of the many previous years of the chemists and the engineer's efforts.

The locomotives are placing drafts of cars of 50 tons capacity, so that their contents may be added to the almost mountainous piles over which moves what appears to be a bridge without any approaches, but which is a huge crane capable of handling 2500 tons every 12 hours. It scoops up, at each mouthful, tons from the piles and quickly places the ore, limestone and coke in the respective bins from which definite measured quantities are being continually taken and by means of an inclined elevator carried to the top of a blast furnace stack and dumped into its capacious mouth, fully 85 feet above the ground. Every twenty-four hours this stack has produced 500 tons of iron of definite predetermined composition and at a fuel efficiency of 60 per cent, the highest so far obtained from any heating furnace using fuel. The molten slag, instead of being thrown over the dump, is granulated and used for making cement or as a fertilizer. The waste gases from the stack, after all possible heat has been abstracted, are burned to generate steam for the turbines producing the electricity used about the plant. To keep this blast furnace in operation requires engines for blowing 40,000 cu. ft. of air per minute at 15 to 20 lbs. per sq. in. pressure, a condensing pump, ten 350 H. P. boilers, and a water purifying plant with a capacity of 60,000 gallons per hour.

The molten iron as it comes from the blast furnace is caught in ladles holding 30 tons each and hauled by a locomotive to the open hearth department 1000 yards away. This department is contained in a building almost 1000 ft. long × 175 ft. wide × 90 ft. high. It includes, in addition to the 500-ton electrically tilted mixer, ten 75-ton open hearth furnaces. Into the mixer the molten iron is poured as one would pour cream from a pitcher, and from this mixer or reservoir a weighed quantity of molten iron is poured into a smaller ladle and charged into the open hearth furnace together with definite predetermined quantities of scrap steel, iron ore, and limestone or sand.

The steel making is begun, and after about eight hours of boiling, as it were, the requisite amounts of ferro-manganese, ferro-silicon or aluminum are added; then the 75 tons of steel are teemed into ingots weighing from 3 to 8 tons. As soon as the steel has solidified the ingots are stripped from the moulds by a huge machine, almost human in its action, then carried off to the soaking pits where they are kept hot until ready to be rolled and cut into billets. The capacity of this department is over 2000 tons of ingots per day. In the meantime drillings from a test ingot have been analyzed by the chemist, thus checking the efforts of the melter to produce steel of a definite desired composition, and the ingots are bloomed to the correct size for the next step. This blooming is done in a building over 300 ft. long × 75 ft. wide, containing, in addition to the soaking pits at one end, a blooming mill equipped with the necessary mechanical handling devices, operated by a 20,000 H. P. reversing engine and also hydraulic shears capable of cutting a 20 × 20 in. bloom.

Following our product from the blooming mill to the bar mill, we see it charged, perhaps in the form of billet 4 in. × 4 in. × 11 ft. into a continuous furnace of a capacity of 150 tons per day; thence it emerges, almost automatically, at the opposite end heated to the correct rolling temperature, and twisting and writhing like a snake it passes from one set of rolls to another and then loops back and forth through another set of rolls, finally emerging a bar over 300 ft. long, 2 in. wide and 0.260 in. thick. This mill will turn out 300 tons of this per day in straight lengths, and varying in thickness not more than 0.010 in. from the size mentioned.

The steel mill just pictured is the home of small things as well as large, and just as the efforts of the engineer have produced the 500 tons per day furnace, the 20,000 H. P. engine and the trains of rolls weighing tons in themselves, seemingly so rough or crude, and just as these in turn have enabled the manufacturer to turn out bars of steel with a variation in size of 0.010 in. and less from the desired thickness, so have the efforts of the chemist been bent towards not only estimating and controlling those elements which are found in steel in large quantities, but also those to be found there in the most minute amounts, all with the greatest accuracy and speed.

Steel would not exist were it not for the element carbon; therefore, the determination of this elment is most frequent. Although the most obvious method was to burn the metal and collect the $CO_2$, it was not until the last five years that this was done with assurance—a result attained through the high temperature obtainable with the electric furnace, the development of refractories and the ease with which oxygen can be obtained. Fifteen to twenty minutes after the sample is taken the melter is advised of the carbon content of his 75 tons of molten steel, the necessary additions are made and steel to the required analysis is cast; and this whether or no that analysis includes simply the usual elements, carbon, manganese, phosphorus, sulfur and silicon or the elments chromium, nickel, vanadium, tungsten, titanium or any of the other elements which are used in the production of the alloy steel. For so has the analytical chemist improved his methods that to-day the estimation of almost all the afore-mentioned elements is but a matter of minutes, and the accuracy a few thousandths of one per cent.

The extent of the analyst's work may be judged from a consideration of the data in Table I.

TABLE I INGOTS AND CASTINGS—GROSS TONS

| Years | Bessemer | Open hearth | Crucible | Electric and all other | Total |
|---|---|---|---|---|---|
| 1898..... | 6,609,017 | 2,230,292 | 89,747 | 3,801 | 8,932,857 |
| 1899..... | 7,586,354 | 2,947,316 | 101,213 | 4,974 | 10,639,857 |
| 1900..... | 6,684,770 | 3,398,135 | 100,562 | 4,862 | 10,188,329 |
| 1901..... | 8,713,302 | 4,656,309 | 98,513 | 5,471 | 13,473,595 |
| 1902..... | 9,138,363 | 5,687,729 | 112,772 | 8,386 | 14,947,250 |
| 1903..... | 8,592,829 | 5,829,911 | 102,434 | 9,804 | 14,534,978 |
| 1904..... | 7,859,140 | 5,908,166 | 83,391 | 9,190 | 13,859,887 |
| 1905..... | 10,941,375 | 8,971,376 | 102,233 | 8,963 | 20,023,947 |
| 1906..... | 12,275,830 | 10,980,413 | 127,513 | 14,380 | 23,398,136 |
| 1907..... | 11,667,549 | 11,549,736 | 131,234 | 14,075 | 23,362,594 |
| 1908..... | 6,116,755 | 7,836,729 | 63,631 | 6,132 | 14,023,247 |
| 1909..... | 9,330,783 | 14,493,936 | 107,355 | 22,947 | 23,955,021 |
| 1910..... | 9,412,772 | 16,504,509 | 122,303 | 55,335 | 26,094,919 |
| 1911..... | 7,947,854 | 15,598,650 | 97,653 | 31,949 | 23,676,106 |
| 1912..... | 10,327,901 | 20,780,723 | 121,517 | 21,162 | 31,251,303 |
| 1913..... | 9,545,706 | 21,599,931 | 121,226 | 34,011 | 31,300,874 |

Included in the total for 1913 are about 714,357 tons of ingots and castings which were treated with ferro-vanadium, ferro-titanium, ferro-chrome, nickel, or other alloys, of which about 625,430 tons were ingots and about 88,927 tons were castings, as compared with about 892,501 tons in 1912, of which about 689,392 tons were ingots and about 103,109 tons were castings. Of the total in 1913 about 74,924 tons were Bessemer steel ingots or castings, about 599,890 tons were open hearth, about 28,279 tons were crucible, about 11,254 tons were electric, and about 10 tons were miscellaneous. Of the total production of steel ingots in 1913 about 625,430 tons were treated with ferro-vanadium, ferro-titanium, ferro-chrome, nickel or other alloys, of which about 53,751 tons were Bessemer ingots, about 535,577 tons were open hearth, about 25,281 tons were crucible, and about 10,821 tons were electric.

Therefore, assuming the sizes of the heats of steel made by the respective processes to average 10, 50, 1.5 and 6 tons, and each heat to have required one determination of each of the five usually estimated elements, we would have for the year 1913 the interesting data in Table II, in which round figures only are used.

TABLE II

| DETERMINATIONS | Bessemer | Open hearth | Crucible | Electric |
|---|---|---|---|---|
| Carbon | 954,000 | 432,000 | 81,000 | 5,700 |
| Manganese | 954,000 | 432,000 | 81,000 | 5,700 |
| Silicon | 954,000 | 432,000 | 81,000 | 5,700 |
| Sulfur | 954,000 | 432,000 | 81,000 | 5,700 |
| Phosphorus | 954,000 | 432,000 | 81,000 | 5,700 |
| Nickel | ..... | 7,000 | 3,400 | 1,800 |
| Chromium | ..... | 5,400 | 7,700 | 900 |
| Vanadium | ..... | 2,700 | 1,700 | 500 |
| Titanium | 5,300 | 1,100 | | |
| Total | 4,775,300 | 2,176,200 | 417,800 | 31,700 |

GRAND TOTAL ..... 7,401,000 determinations

These figures are startling, and yet they do not, by any means, wholly represent the analytical work connected with the production of the steel itself. It is not to be understood that these figures represent the actual conditions, for it is very questionable if one-half the Bessemer steel heats are analyzed; on the other hand, however, many companies make two and three check determinations on a single heat of open hearth steel. The figures as a whole are very probably far short of showing the work of the analytical chemist associated with the production end of the steel industry. The analyses connected with the blast furnace, such as those of pig iron, ores, slag, coal, coke, gases, refractories and water, should be added to these and also those determinations made upon the ordinary or regularly used ferro-alloys and metals, not to mention those necessary for the production of alloy steels containing chromium, nickel, vanadium, titanium, cobalt, tungsten, copper, molybdenum, and perhaps uranium, either singly or in combination.

Frequently much of this steel when it reaches the consumer is again analyzed so that the part analytical chemistry plays in the steel industry is seen to be extensive and absolutely indispensable. Without it we could not ride from New York to Chicago in twenty hours nor drive with safety in an automobile at a fair rate of speed, nor would we have our high structures, huge bridges or viaducts, nor any of the modern mechanical equipment for operating our factories.

To obtain the high fuel efficiency of the blast furnace, the control of the Bessemer converter and of the open hearth furnace has necessitated an extensive and careful study of the weights and volumes of gases, high and low temperature measurements, heats of combustion of gases and fuel. Thus physical chemistry is seen to be an essential aid, since the metallurgy of steel involves principles which are not only chemical but also physical and mechanical. The mositure of the air was of sufficient economic importance to the efficiency of the blast furnace that its removal by refrigeration was undertaken, following a study of the physical chemistry of the blast. In the Talbot open hearth furnace, a bath of molten steel is used to excite the reaction between molten pig iron and iron ore, with a saving of fuel, since the materials themselves burn each other as it were, an achievement following the study of the thermochemical reaction between carbon and oxide of iron.

Not only has inorganic chemistry in its analytical, physical and thermo phases played a highly important part in the steel industry, but also organic chemistry is entering the field. The production of coke is accompanied by the making of coal tar which is the source of benzol and many other valuable bases used throughout the chemical and allied industries. It is now proposed by one of the largest steel producers, to take up this feature and develop it.

In concluding this presentation, which, on account of the broadness of the subject is necessarily very incomplete, mention should be made of the part electricity has more or less recently played. While the process of making steel with electricity is primarily electrothermic, an extensive chemical study of refractories and electrodes was necessary before the process attained its present status. The high temperature which could thus be gotten enabled the use of hitherto impossible combinations for slags with the result that steels of a greater purity became possible and these from scrap or iron containing high percentages of objectionable elements such as phosphorus and sulfur; the chemist was thus also enabled to produce ferro-alloys otherwise impossible.

It is hoped that this article may give to those unfamiliar with the metallurgy of iron and steel some idea of the all-important part chemistry has had in the success of one of the greatest of the world's industries.

PITTSBURGH, PA.

## CONTRIBUTIONS OF THE CHEMIST TO THE IRON AND STEEL INDUSTRY

BY ALLERTON S. CUSHMAN

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The contribution of chemistry to the iron and steel industries may be said to have begun with the introduction of the great pneumatic processes of steel making in the latter part of the 19th century. The Bessemer process, brought out in 1863, and the Siemens-Martin open hearth process which followed soon after, produced a revolution in the iron industry that gave the chemist his first opportunity. Before the days of steel, iron making was largely an empirical art, and no one considered the estimation or control of the impurities which usually accompany the metallurgy of iron to be a matter of vital importance. It was, of course, known through the operation of the puddling and crucible processes that certain elements could be depended upon to confer hardness and toughness, but the very important quantitative rôles in the metallurgy of iron played for good or ill by the ever-present five elements—carbon, manganese, sulfur, phosphorus and silicon—were not understood. It was by means of his original researches into the methods for determining and controlling these so-called impurities that the chemist began to force his coöperation upon the more or less unwilling body of contemporary metallurgists. Even within the metallurgical memory of the present writer, which does not comprise more than a third of a century, iron masters were loathe to recognize the necessity for well-equipped laboratories under the charge of college-bred chemists.

After the ore is mined and shipped, the iron industry begins in the blast-furnace in which chemical reactions involving enormous energy exchanges take place. Just as soon as the professional chemist was allowed to win his way from the laboratory into the works, revolutionary changes in output and economy were very soon accomplished. This move forward constitutes, in the opinion of the writer, the first great contribution to the iron industry made by the chemist.

In the meantime, the steel maker, in charge of the rapidly developing pneumatic processes, required to know and follow the content of carbon, manganese and other impurities during the progress of a heat. Analytical chemistry came to the rescue by devising quick methods of analysis. So rapid has been the development along this line of chemical contribution that the modern metallurgist can literally obtain his information while he waits and thus modify and control the degree and duration of his heats. The writer has information that by a recent method even carbon by combustion can be accurately determined in eight minutes from the time the sample drillings are delivered to the laboratory. The development of modern methods of rapid and accurate analysis may be held to constitute another great contribution of chemistry to the metallurgy of iron and steel.

Modern metallurgy has not been satisfied with the development and improvement of ordinary carbon steels, for modern industrial requirements have demanded the production of alloy steels possessing marvelous and, until very recently, unheard of and undreamt of physical properties. The ores of the rarest elements have been unearthed to produce these wonderful

alloy steels, and the chemist has been called upon to devise ways and means for their development and study. This evolution has indeed presented many a knotty problem to the analyst as well as to the chemist in the works. It is no easy chemical task to separate, estimate and control such elements as tungsten, chromium, vanadium, titanium, nickel, cobalt, molybdenum and tantalum as every-day constituents of steel.

Space will permit of only the briefest reference to the very important place that the curious alloys have made for themselves in the metallurgy of iron and steel. The tungsten, chromium, cobalt and molybdenum alloys of varied composition constitute the modern "high speed" steels which have revolutionized machine shop practice. Vanadium and chromium are used in the manufacture of the so-called anti-fatigue steels for springs and other rapidly moving machine parts. At the New York meeting of the Eighth International Congress of Applied Chemistry, in 1912, Dr. Carl Duisberg referred to the use of some of these new alloys as follows:

"Of great importance are those alloys of iron with chromium, tungsten and vanadium which possess a high degree of hardness even at 400–500° C. They are needed by engineers for the construction of steam turbines, for the embossing and spraying of metal objects when heated to redness, a process which has lately found extensive application. Chemists use these kinds of steel wherever chemical reactions are carried out at high temperatures and pressure, as in the synthesis of ammonia according to Haber's process."

According to Dr. Duisberg, the very latest alloy manufactured by Krupp for the manufacture of safety vaults and safes can neither be drilled nor exploded nor can it be cut by the oxyhydrogen flame. In the light of subsequent events we are led to presume that the manufacture of safes was not the only purpose in the minds of our chemist-colleagues across the water. It is interesting to note in passing that unless the chemists of Germany had worked out the synthesis of nitrogen compounds from atmospheric nitrogen as well as the special steels suitable for the construction of the necessary apparatus, the present great world war would have to be brought to an early close.

Another important contribution of chemistry to the iron industry which may be called purely American is along the line of the manufacture of pure iron on the same scale which is usual in steel production. This development, which the writer is in large measure responsible for, has had to win its way against many difficulties and even much prejudice and hostility. Many hundred thousand tons of commercially pure iron are now produced annually in this country and are in demand for many purposes for which iron is more suitable than steel. Pure iron is soft and ductile with a high electrical conductivity and useful magnetic properties; for many deep drawing and enamelling purposes it is unequalled, while its slow rusting qualities have given it a wide-spread reputation and use. Some years ago the demand for pure iron could be filled only by the importation of Norway and Swedish charcoal irons; at the present time the industry is fully established in this country on the large scale which our industrial and economic conditions demand. That the chemist has contributed to this line of development there can not be the slightest doubt. It has been found necessary to eliminate the gaseous as well as the solid impurities from these pure irons, and this difficult problem has engaged the closest coöperation between the men in the laboratory and the mill.

In a brief review of this nature it is possible to touch only lightly on the many contributions of chemistry to the iron and steel industry, but the writer's experience is that unless the divisional superintendents in a modern iron and steel plant are themselves chemists as well as metallurgists, they can not be depended upon to carry on progressive work.

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## CONTRIBUTIONS OF THE CHEMIST TO THE ART OF SOAPMAKING

By MARTIN HILL ITTNER
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Although the art of soapmaking is of long standing it has undergone considerable improvement during recent years. The advance in the science of chemistry has contributed in no small way to the number and magnitude of the successes in this field.

Soapmaking is connected almost inseparably with a number of other related industries among which the chief are the manufacture of alkali, glycerine, edible fats and oils, and perfumery, while the manufactures of candles and lubricants are industries closely associated with soapmaking.

Although many of the larger soap manufacturers make their own caustic soda from soda ash, the manufacture of alkali is a great industry in itself. I would be neglectful, however, if I failed to state here that the manufacture of alkali has advanced so that most of the alkali now on the market is of very high quality and is sold at a very reasonable price.

It was only a comparatively few years ago that the greater portion of the glycerine formed during the process of soapmaking was wasted. It was thrown away with the spent lyes in the process of making "curd" soap, or was left in the soap in the so-called "cold-made" soap. An increased demand for pure glycerine for the manufacture of explosives, confections, and pharmaceuticals has stimulated the soapmaker to recover his glycerine and an article that was once a neglected by-product has now assumed so much importance that no soapmaker could operate with any degree of success without recovering his glycerine, and the profit from the recovery of glycerine is frequently greater than that from the manufacture of soap itself. A knowledge of the physical and chemical properties of glycerine has been utilized in the various processes which have been devised to recover and purify this valuable body. The most important part of these processes is the distillation of the glycerine by means of steam *in vacuo*. It is not necessary to operate at a temperature sufficiently high to cause any decomposition of glycerine, as was the case in older methods, and improvements in processes employed have worked economics in yield and cost of production. Glycerine of the highest degree of purity is now regularly made on an enormous scale from soap lyes.

During the operation of soapmaking the glycerine is gradually removed from the soap by successive washes. Chemical analysis enables the soapmaker to estimate the total amount of glycerine possibly obtainable in a given operation. Chemical control and a consideration of the cost of operation taken together with the value of glycerine enable him to ascertain the most economical conditions of working.

The process of making "settled" soap, carried on under chemical control, enables the soapmaker to readily produce soap of uniformly high quality.

With an aim to the simplification of the process of soapmaking and the realization of greater economy, new methods of hydrolyzing fats and oils have been devised. In some of these methods, notably those in which sulfo-fatty acids are used, the hydrolysis is effected at atmospheric pressure. Hydrolysis by means of enzymes is also used to some extent. By these processes the larger part of the glycerine is readily recovered and fatty acids suitable for soapmaking are produced. When materials of poor quality are used, as, for instance, cottonseed soapstock, the fat may be hydrolyzed into fatty acids and glycerine, the glycerine recovered, and the dark acids subjected to distillation with steam *in vacuo*, whereby white fatty acids, suitable for making good quality soap, may be obtained.

A new method of lime saponification gives a lime soap that is brittle and readily pulverizable and which is insoluble even in boiling water. By this method, which requires somewhat

more mechanical handling than other methods, all of the glycerine may be recovered and the lime soap may be converted into soda soap by means of soda ash, giving a soap of good quality.

The soapmaker is not blessed with a market in which he can obtain at will a steady supply of fats and oils of uniform quality at uniformly reasonable prices. His supplies must be drawn from all over the world and consist of animal and vegetable fats and oils. They include tallow, lard, cotton oil, peanut oil, soya-bean oil, olive oil, cocoanut oil, palm oil, marine animal oils, etc. His principal competitor in the markets of the world is the manufacturer of fat and oil food products. In some cases the soapmaker is also a manufacturer of edible products and at times converts a large part of the fats and oils which he handles into first-class food products, and sells them as such. It has thus become necessary for the soapmaker to develop methods of refining and purification whether the product is to be used as food or to be made into soap. A knowledge of the physical and chemical properties of various fats and oils used in soapmaking makes it possible to get a uniform and satisfactory result by the proper employment of different combinations, thus enabling the soapmaker to utilize the cheaper materials available at any given time. If he could not accomplish this result he would be a more serious competitor to the manufacturer of edible fats, with the result that both our edible fats and oils, and soaps would cost more to the consuming public.

The process of hydrogenating soft oils whereby hard fats may be obtained, has been worked out by a number of soapmakers. Although hydrogenated oils have been and are used on a comparatively large scale in soapmaking, their principal employment up to the present time has been in the manufacture of edible fats.

The soapmakers are the largest consumers of perfume materials in the world. Most of the soaps on the market, even the cheaper grades, are perfumed. There is a popular misconception that perfume material is used to cover up inferior materials. If this was ever the case it can scarcely be so considered now. Perfumes are added to soaps for two reasons: to make them more attractive to the consumer, and because of the fact, well known to all soapmakers, that practically all of the perfume materials exercise a preservative action on soaps, keeping them sweeter than they would be if no perfume material was used.

The manufacturers of toilet soaps include the largest perfumers in the world and the chemical study of perfume materials has come within the province of the soap manufacturer, while some of these manufacturers have entered the field of the distillation of essential oils and the manufacture of synthetic perfume materials.

The successes which have been realized in the soapmaking industry through the aid of chemistry and engineering have been of inestimable value but they are not final. The practice in this industry, however much it may have been improved, has not been perfected, and the wide-awake manufacturer is more than ever convinced by each new improvement that chemistry and engineering must be employed and followed if continued success is to be realized.

COLGATE & COMPANY, JERSEY CITY, N. J.

## CONTRIBUTIONS OF THE CHEMIST TO THE PERFUMERY AND ESSENTIAL OIL INDUSTRY

By EDWARD T. BEISER
Perfume Chemist, F. W. Fitch Company

As in many other fields, the contributions of the chemist to the domain of perfumery constitute a glorious romance which would fill many volumes of no small size.

Once secluded to the adornment of the royalty, perfumery has been augmented in volume and lowered in cost until today the most meager toiler may revel in "amber scents of odorous perfume." This is due to the many improvements manufacturing processes have undergone and our advanced knowledge of chemistry.

The synthesis of flower oils has, without a doubt, been the greatest achievement made in elevating the art of perfumery. With all due credit, however, to the perfumer, without whose highly trained sense of smell perfumery perfection could not be attained, yet when it comes to making plain extract of civet cat masquerade as the delicate perfume of a spring Nosegay, we have just simply got to hand it to the chemist. Through his untiring efforts we need no longer depend upon cow dung, or the vomit of the whale as the source of ambergris, but ambrein, the odor constituent of ambergris, in a fine state of perfection, is now produced in the laboratory, and from substances which have a very different effect upon our gustatory functions.

One of the first synthetic materials to find successful application in perfumery was vanillin—the flavoring constituent of vanilla beans. In 1876 Tiemann took out his first patent on a process to produce this methyl ether of protocatechuic aldehyde by means of the acetylation of eugenol and its subsequent oxidation.

The first vanillin sold for nearly $800 per pound. Through advances in chemical discovery, improved manufacturing processes, increased consumption and the opposition of rival patentees this price has been gradually reduced until today vanillin can be bought for less than one one-hundredth the introductory price.

A later discovery which gave renewed impetus to the industry of synthetic perfumery was that of Tiemann and Kruger. These chemists, after many years of patient research, finally succeeded in preparing an artificial violet perfume which they called ionone.

Ionone was formed by condensing the olefinic aldehyde citral with acetone. The olefinic ketone in the presence of alkalies formed pseudoionone of the formula $C_{13}H_{20}O$. By inversion with dilute acid pseudoionone was converted into ionone. This methyl ketone, a straw-colored oil, had such a powerful violet odor that one pound of it was equal to the perfume contained in all of the violets that you could pack into a fair sized room. Perfumers who, up to the time of this discovery, refused to admit the value of synthetic perfumes, were soon won over by the exquisite rendering of the violet made possible with this valuable chemical invention.

In rapid succession, one discovery followed another, until to-day the modern perfumer can choose from several hundred important aromatic chemicals and produce thousands of fine combinations satisfying to the most fastidious. Synthetics have made possible the perfection of many old perfumes and enable the perfumer to produce new scents undreamed of heretofore.

As mere traces of impurities will often seriously alter the basic odor of a synthetic perfume, it must, besides being chemically pure, respond to the olefactory test. And while the sense of smell in man is inferior to that developed in animals, it is nevertheless marvelously delicate. It has been found that air containing one twenty-three billionth of a milligram of mercaptan to the cubic centimeter could be detected, and it was estimated that only one four-hundred-sixty millionth of a milligram of this substance was necessary to excite the sensation of smell.

So, to pass the cultivated nose, great care is exercised by the chemist to free his laboratory creations from detrimental impurities.

Few of the natural flower oils are made up of a single aromatic substance, but are very complex, some oils having upwards of half a hundred individual constituents. Some of these constituents, while having a decided effect upon the character of the complete odor, are present in minute traces only, making recognition exceedingly difficult. But in spite of these many handicaps the chemist has produced a number of artificial flower oils which compare favorably in quality, are always uniform, and in every instance very much cheaper than the oils extracted from the flowers.

In the essential oil field also the chemist has rendered great service. It is no longer necessary to depend wholly upon the nose test in judging the value of an essential oil. Such progress has been made in the way of analysis that the perfumer is enabled to obtain not only pure oils, but such that are rich in active constituents. The composition and properties of the essential oils are so well understood to-day that the Pharmacopoeias have adopted requirements concerning them which are specific and exacting.

While not an extremely large industry, perfumery does figure in the daily life of the average American, and without a doubt brings occasional aesthetic delights to every living being who is blessed with the sense of smell. In the United States, the value of finished products, in which perfumery plays an important part, amounted to several hundred million dollars last year.

Just as the chemist has found the delightful fragrance of new mown hay to be due to the crystalline lactone coumarin, so in time he will discover and synthesize the refreshing odor of the sea-borne breeze, the exhilarating fragrance abounding within the forest after a warm rain, and the many charming odors which prevail at the various seasons in the fields.

712 THIRD STREET, BOONE, IOWA

## CONTRIBUTIONS OF THE CHEMIST TO THE LEAD INDUSTRY

By G. W. THOMPSON

Chief Chemist, National Lead Company

To start with, we must admit that the possibilities for accomplishment in the lead industry by the chemist are, for obvious reasons, much more limited than in some of the newer industries. Lead smelting and the manufacture of most lead compounds was fairly well developed before modern chemistry began. Lead was known to the ancients, as well as were most of the lead compounds, which are now produced in large quantities. The great help modern chemistry has afforded is in the direction of preventing losses and systematizing smelting and manufacturing operations.

In the smelting of lead, there have been no radical departures due to the influence of chemistry. The old methods of oxidation and reduction are still in vogue. Many attempts have been made by chemists, particularly electrochemists, to develop simpler methods for the production of lead from its ores. None of these, however, has been commercially successful.

The principal influence of the chemist, as indicated above, has been in the study of the losses incident to smelting and the reducing of these losses to a minimum. The chemist has therefore contributed here principally to a better understanding of the operations of smelting. His influence has also been felt in the development of methods for the concentration of lead from its ores. Most of these methods are, however, distinctly mechanical, and while the modern methods of oil flotation may be considered chemical, their influence upon lead concentration has not been so great as it has been with other metals. It is true also that the chemist has done his part in those operations connected with the recovery, utilization and production under controlled conditions of fumed products, particularly in the production of basic sulfate of lead and the leaded zinc oxides.

In the refining of lead the chemist has helped through the introduction of electrolytic methods, as in the Betts process. This process, however, could hardly compete in cost with the older methods devised by Pattinson and Parkes, which methods, while involving principles of physical chemistry, can hardly be considered as distinctly chemical processes. The use of the Betts process has been particularly serviceable in the recovery of bismuth from metallic lead, which bismuth remains as a slime or mud.

It can hardly be said that the uses of metallic lead have been increased through the help of the chemist. Sheet lead and lead pipe have, of course, been used to a large extent in most chemical operations, particularly in the manufacture of sulfuric acid, and the chemist has assisted considerably in determining the best leads for such purposes. The development of lead alloys since modern chemistry has made its influence felt has been comparatively slight. Metallographical work has thrown a great deal of light upon these alloys and indicated many things with regard to their constitution and possible usefulness. It has helped in the determination of relative values. It cannot be considered, however, that chemistry has developed new lead alloys of great commercial value. The uses of metallic lead have increased considerably, more, however, through the development of other branches of science.

When we come to the compounds of lead and their uses, we find that here too most of the processes now in general operation were developed before the advent of modern chemistry. White lead is still made by the old Dutch process, and while in Germany and France the chamber and precipitation processes have been developed, no new qualities of value have been imparted to white lead by these processes, and Dutch process white lead is still considered the standard. In this country the manufacture of white lead by the Carter process has shown considerable growth, and it was the understanding of the chemical reactions taking place in the manufacture of white lead by the Dutch process that brought about the final development of the Carter or cylinder process, as well as the more recent so-called "mild" process invented by Rowley.

Chemistry has indeed been a great help in the understanding of all of the reactions that take place in the manufacture of white lead and it has helped here to reduce manufacturing costs and save losses. All of these things have been accomplished simply because of the better understanding of the reactions which take place. No specifically great improvement, however, has resulted from this better understanding of reactions. The oxides of lead, litharge and red lead, are manufactured practically as they were before the advent of modern chemistry. It is true that in the manufacture of nitrite of soda by the lead method, a considerable amount of litharge was made until the advent of cheaper methods of manufacture of nitrite of soda as a by-product of the nitrate industry in Norway. The development of the storage battery industry has created a great demand for red lead and litharge, and as the storage battery industry is electrochemical in its character, it may be considered with propriety that in this branch of industry chemistry has been of great assistance. The use of lead oxides in the curing and vulcanization of rubber goes back to the time of Goodyear, and it is very doubtful if at that time or even at the present day, the function which lead oxides perform is properly understood. The best information obtainable indicates that the lead oxides act as catalyzing agents, producing greater uniformity in vulcanization, carrying on reactions which are started either with or without heat and bringing the curing and vulcanization about with more uniform results. The oxides of lead which are used in the glass industry are made by the old methods. The glass industry itself follows the old empirical methods, in which chemistry has had little part in improving results. The study of glass, however, has resulted in the development of a better understanding of what glass is and how it can be made more suitable and permanent.

The function of lead salts in driers in the paint industry is practically chemical, and much information has been obtained as to the action of driers, giving quantitative knowledge, which has helped in the preparation of better driers and product containing them. The influence of the chemist upon the paint industry involving the use of lead compounds has been entirely subordinate to the practical results obtained. Undoubtedly the influence of the chemist has been felt in the better understanding of paint problems, but progress in this direction has been unfortunately handicapped by the development of many

fallacious hypotheses, which the chemist is only now beginning to overcome. Very few new salts of lead have been developed having commercial value or importance. Acetate of lead and nitrate of lead are still manufactured by the old processes and chemistry has helped in their manufacture only to a slight extent. The use of arsenate of lead as an insecticide having qualities superior to the ordinary arsenates and arsenites of copper, etc., has grown within the last few years, with promise of still greater progress. Arsenate of lead has the advantage over other arsenical compounds of not injuring foliage to as great an extent, and remaining where it is put for a longer time.

It will be seen, therefore, that what I stated in the beginning is true. The chemist's principal influence in the lead industry has been in the better understanding of chemical reactions involved in the production, manufacture and use of lead and its compounds. Chemistry has helped in the modification of lead products to make them better and more suitable for use. It cannot be said, however, that outside of lead refining by the Betts process, the use of lead compounds in storage battery manufacture and in the production of arsenate of lead, that chemistry has had a conspicuous part. Chemistry has undoubtedly been responsible for many lead industries being able to hold their own in competition with other products, but beyond this and the part which this has in the general application of chemical knowledge, chemistry has done little.

129 York Street, Brooklyn, N. Y.

## CONTRIBUTIONS OF THE CHEMIST TO THE PAINT AND VARNISH INDUSTRY

By Maximilian Toch
Director of Laboratory of Toch Brothers

The contribution of the chemist to the paint and varnish industry is not a very long story, for prior to twenty-two or twenty-three years ago the paint and varnish industry was based on rule of thumb entirely, and it is only within the last ten years that the raw materials pertaining to the manufacture of paint have been systematically classified and illustrated by photomicrographs.

If you take the example of white lead, which has been mentioned by Pliny as having been used four hundred years before Christ, re-invented by the Dutch over three hundred years ago, it will be found that this material was empirically made and in a "hit or miss" fashion. It is only within the last few years that the large lead concerns have employed able chemists who have systematized the manufacture of white lead so that all batches are uniformly produced.

It was the custom in the paint industry that dry color manufacturers, whose business really was the manufacture of high type chemicals, had practical men who owned formulas and guarded them as zealously as the alleged secrets of the masonic order are hidden. I knew a well-known manufacturer of chrome green, which in the paint industry is a mixture of prussian blue and chrome yellow, who was entirely at the mercy of his foreman because his foreman never would divulge the actual working formula of the green that he made.

For many years I have enjoyed the confidence of many of our competitors, and it would not be amiss to cite a single example of the method by which the paint or dry color industry was conducted in former years. A very large manufacturer of chrome yellow came to me one day and told me that he made upwards of one million pounds per year and did not make any money. He showed me the cost of his raw materials and the cost of his labor and could not understand where his loss came in. I examined his factory, calculated for him the amount of acetate of lead necessary to react upon a given amount of potassium dichromate and then made an analysis of the waste water from his factory, and showed him that 40,000 pounds of sugar of lead solution were going into the sewer every year, simply because he had no man in charge who knew what he was doing scientifically. I could give many instances of this kind, and it is a gratification for me to know that many of the chemists now employed in the paint and varnish industry have been originally selected by me, and that my firm, though really insignificant as compared with some of the large paint concerns, has, at this writing, five chemists including myself, and that we have had some slight measure of success is due to the scientific control of the products that we make.

Fifteen years ago I doubt whether there was any large varnish concern in the United States who had a chemist; in fact, chemists were then as they are now—frowned down upon by the practical superintendent, who always desired to surround his doings with a witchcraft and chicanery that made him imposing in the eyes of his principal; but fortunately those days have passed and the varnish foreman is more or less dominated now by the chemist. I have been so personally identified with the chemistry of paints and varnishes that those who read or hear this will know that there is absolutely no egotism in what I am saying: In the old days of the Chemists' Club, the late Professor Morris Loeb and I were the targets of every unemployed chemist in the City of New York, at least that is the way it appeared: the present existing Bureau of Employment was started by me with the help of Professor Loeb, and many of the paint and varnish chemists today owe their positions to this Bureau of Employment. This has been further reaching than the paint and varnish industry, because the oilcloth, linoleum, leather and printing ink industries, all of which use paint and varnish in different forms, are now more or less conducted on scientific principles, and many such large works are supervised by competent chemists who were originally recommended by the Bureau of Employment of the Chemists' Club.

I think this small contribution will indicate what a tremendous influence the chemist has had upon the paint, varnish and allied industries, particularly the paint chemist, who was unknown only a few short years ago.

320 Fifth Ave., New York

## CONTRIBUTIONS OF THE CHEMIST TO THE PHOTOGRAPHIC INDUSTRY

By Francis C. Frary
Professor of Chemistry, University of Minnesota

If we ask what the chemist has done for photography within the last quarter-century, we may well receive the answer, "everything." For indeed there is little in modern photography which is more than a quarter-century old, and it is the developments of the last two decades that have popularized photography and at the same time wonderfully increased its usefulness to science.

Among the pioneers in the development of the modern "gaslight" papers, with their wonderful adaptability and variety, we are proud to number one of the foremost chemical engineers in this country; and none of the host of competing papers which has since arisen, could have been produced without the chemist. Careful chemical control of the quality of the paper-stock, the gelatine, and the silver salts used, is one of the first requisites in the manufacture of any photographic paper. The older printing-out paper, with all of its beauty of detail and gradation, required negatives of a quality which the average amateur seldom obtains; and it requires a modern paper to make a satisfactory print from the under-timed "snap-shots" which are the inevitable result of the popularizing of photography. Moreover, the possibility of making prints by any common artificial light has placed photography within the reach of thousands who could never have used the older papers.

The successful manufacture of the photographic film has been a great achievement for the chemist. Especially is this the case when the motion-picture film is considered. The problem of making thousands of miles of the support, of uniform high quality, and coating this with an emulsion of uniform and maximum sensibility and satisfactory stability, is one with which the chemist has had many a struggle, and for the solution of which he is entitled to much credit.

The advance in the manufacture of dry-plates in the quarter-century has been remarkable. In uniformity, keeping power, speed, and most of all in color-sensitiveness, their quality has been steadily improving. Much of this improvement has been due to the careful chemical studies of the emulsion, both in the factories and in the K. K. Graphische Lehr- und Versuchs-Anstalt, in Vienna, where a notable group of chemists have devoted themselves to a thorough study of all phases of the photographic industry. It is due to chemical research work of a high order, that we now have panchromatic plates which are sensitive over practically the whole range of the visible spectrum, and can even photograph the infra-red rays which our eyes do not perceive. The beautiful three-color work in our modern magazines would no more be possible without the panchromatic plate, than would modern press photography without the high-speed plate.

In color photography we have made considerable progress. The solution, by the Lumière Brothers, of the problem of the manufacture of a plate combining a permanent screen in three colors with a stable panchromatic emulsion, first brought natural-color photography within the reach of any well-informed photographer. Many similar plates have been introduced, and the results with this type have had a great value in many lines, particularly in medical science. Other processes for transparencies, such as those of Ives and the Eastman Kodak Co., and several for the production of natural-color prints on paper, owe their development and perfection to chemical research of a high order. Suitable aniline dyes for sensitizing the panchromatic emulsion are of course the fundamental need of all such processes, but the proper selection and adjustment of filters, color-screens, and other factors to the characteristics of the panchromatic emulsion chosen, involve a mass of careful work.

The chemist has made for us a large number of new developing agents, which have many advantages over the old-fashioned pyrogallic acid and ferrous oxalate. Improvements in the quality and uniformity of other chemicals have been greatly appreciated.

As yet we are somewhat in the dark as to the exact nature of the latent image, the theory of the action of some of the constituents in the developer, and many similar things, for enlightenment on which we must turn to the chemist. It is a very encouraging sign of good things to come, that one of the largest photographic manufacturers in the world has installed and is maintaining a large research laboratory, where chemical and physical research work on all phases of photography is being carried on by a corps of thoroughly trained men who are in touch with actual manufacturing conditions. We may certainly expect that the next twenty-five years will bring us many more great developments in photography, through the work of these and other chemists and physicists.

UNIVERSITY OF MINNESOTA, MINNEAPOLIS

## CONTRIBUTIONS OF THE CHEMIST TO THE MANUFACTURE OF PHARMACEUTICAL PRODUCTS

By FRANK R. ELDRED
Chief Chemist, Eli Lilly & Company

The manufacture of medicines is not confined to pharmaceutical houses, since they do not produce many of the medicinal chemicals, volatile oils and other products which may be said to constitute a large portion of their raw materials. Many of these products, however, must pass through the hands of the pharmaceutical manufacturer in order that they may be put in a form suitable for use. It is not easy to draw the line between pharmaceutical manufacturing and the closely allied industries as their fields of activity will frequently be found to overlap; for instance the study and manufacture of certain alkaloids have been left almost entirely to pharmaceutical chemists and manufacturers although most of the alkaloids have been produced by distinctively chemical manufacturers.

Few industries have been as dependent upon the work of the chemist as that of pharmaceutical manufacturing. Many industries have been developed up to a certain point without the direct assistance of the chemist but the very beginnings of pharmacy and chemistry were closely linked together and pharmaceutical manufacturing was made possible by the work of the early chemists. It is true that pharmaceutical manufacturing has not always kept pace with the progress in chemistry, yet the chemist, although at times very imperfectly trained, has always been an indispensable factor in the development of the industry and to-day the successful manufacturers are those who are making use of the most recent discoveries in chemistry and medicine and to that end have built up organizations of well trained and highly specialized scientific workers.

The work of the chemist in the pharmaceutical industry has been characterized by the development of new products and improvement in the quality of products already established rather than by any reduction in manufacturing costs, although at the present time much attention is also being given to the latter problem. For many years it has been the custom of the more progressive pharmaceutical manufacturers to devote considerable sums of money to research along the various lines connected with their business and for this reason much of the credit for the development of our present materia medica should be given to them. Chance and uncertainty in pharmaceutical manufacturing have been largely eliminated, and while ten or fifteen years ago much of the routine manufacturing could be carried on without the direct supervision of the chemist, it is now necessary to have every crude material thoroughly examined, every process controlled and every finished product assayed or inspected by competent chemists.

Among the earlier improvements, due entirely to the pharmaceutical chemist, the standardization of preparations made from vegetable drugs deserves especial mention. The crude drugs were found to vary enormously in strength and as their active principles became known and assay processes were developed the manufacturers adjusted their preparations so that they were always of uniform strength. At that time the only pharmacopoeial standard for such preparations was the fixed amount of drug used in their manufacture and the preparations when finished of course varied according to the strength of the drug from which they were made. The standards established by the manufacturers were based upon the strength of an average prime drug and the quantity of drug required varied inversely with its strength. Most of these standards were adopted by the Pharmacopoeia many years later. This like many other improvements made by the chemist in this industry resulted in increased costs not only on account of the analytical work required but also because of the greater care necessary to maintain these standards.

Thousands of different products are manufactured by every pharmaceutical house, and it has been the duty of the chemist during the past twenty-five years to study these products in order to discover their faults and improve them by modernizing the methods of manufacture. On account of the great number of products to be studied and the diverse problems involved, progress may seem slow but if we look back even ten years we

cannot fail to recognize the great improvement which has been made in the general line of pharmaceutical products. The keeping qualities of many products have been thoroughly studied although only a few years ago very little was known in regard to the stability of medicines. Much remains to be done and progressive manufacturers are sparing no effort to improve the quality and raise the standards of their products.

Many of the older classes of pharmaceutical products, however, are rapidly giving way to new medicinal agents which are established on a scientific foundation. This necessitates research with the object of developing new products to take the place of those which are falling into disuse, for the manufacturer who neglects this will see his business gradually going to his competitor who is awake to this necessity. Extracts and tinctures made from vegetable drugs can hardly be considered scientific products even though standardized to a definite content of the active principles since they always contain many other substances which are either inert or possess undesirable physiological activity. Alkaloids and other definite principles isolated from vegetable drugs have already, to a large extent, taken the place of the various extracts and we may expect even greater progress in this direction during the next few years. The preparation of active extracts and definite principles from the ductless glands is one of the remarkable developments of the last fifteen years. Most of us have witnessed with interest the increase in synthetically prepared medicines from a very small beginning to a point where they are made to meet almost every therapeutic indication. The continued advance along the line of rational and exact medication has led the manufacturer to develop many of these new and improved therapeutic agents.

In one respect the position of the pharmaceutical manufacturer differs from that of manufacturers in other lines. The U. S. Pharmacopoeia, a book of standards published under the authority of a convention whose members are appointed by various medical and pharmaceutical bodies, and the National Formulary, published by the American Pharmaceutical Association, have been made the legal standards for all preparations and substances described by them. It is evident that such legal standards are necessary and that the manufacture of medicinal products should be very carefully controlled. This being granted it is very important that the standards be correct and the control judicious. The U. S. Pharmacopoeia is revised decennially by a revision committee chosen by the convention already referred to. In making this revision the committee draws upon the published or privately communicated work of chemists and pharmacists and to some extent upon work carried on under its own direction. Much of the work of chemists for the manufacturing houses has been utilized in the compilation of the Pharmacopoeia. Since the revision committee is a representative body in which all classes interested in the preparation and use of medicinal products have a voice, probably no better standards could be established, but it must be recognized that the progress which necessitates the revision of the book every ten years also renders many of the old standards obsolete long before the new edition appears. The National Formulary is a valuable book which was designed to serve as an unofficial guide in preparing commonly used preparations which were not described by the Pharmacopoeia and its elevation to the rank of a legal standard seems to have been due to a misconception of its function.

While these two standards have been legalized by the Federal Food and Drugs Act a very wise clause was inserted in the act which provides that preparations may differ from the standards so established if the standard be *plainly* stated on the label. This clause allows uninterrupted progress during the interval between revisions of the Pharmacopoeia and insures new material and improved standards for the use of each revision committee. It is this clause which now enables the chemist to contribute actively to the manufacture of medicinal products.

In some quarters the repeal of this provision of the law has been advocated and since it has such an important bearing upon the relation of the chemist to pharmaceutical manufacturing, it should receive our careful consideration. The repeal of this clause would make it unlawful to market any product which differed in any way from the product described by the Pharmacopoeia or National Formulary; manufacturers therefore could not profit by any improvement which they might make and all research tending toward the improvement of such products would be discontinued. When it is remembered that the most important medicines are described in the Pharmacopoeia, that many are included in the National Formulary which afterward find their way to the Pharmacopoeia, and that many of the articles dropped from the Pharmacopoeia are subsequently inserted in the National Formulary, it will be seen that no more effective bar to progress in the production of medicinal products, than the elimination of this clause from the law, could be devised. It may be pointed out that the standardization of extracts and tinctures as well as many other improvements could never have been introduced by manufacturers if no variation from pharmacopoeial standards had been allowed. Under such a law while manufacturers in every other line would be stimulated by competition to improve their products, the manufacturer of medicines would be legally prohibited from doing so. The contributions of the chemist to this industry would then be confined to routine analytical work and to the development of products which could be protected by patents; all improvements in medicinal substances now included in the National Formulary and Pharmacopoeia would have to be made by the committees of revision with limited time and facilities and without manufacturing experience. It seems doubtful if such a law could be enforced but if the matter is placed before our law makers in the proper light there can be no doubt that the federal law will remain unchanged and that the state laws will conform to it in this respect. If this course is followed the progress in this industry, which has never been as rapid as at the present time, will be uninterrupted.

INDIANAPOLIS, INDIANA

## CONTRIBUTIONS OF THE CHEMIST TO THE HARDWOOD DISTILLATION INDUSTRY

By S. W. KATZENSTEIN
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The hardwood distillation industry has been brought to popular attention of late, on account of the rapid increase in value of one of its products, acetate of lime, which is being converted, in large amounts, into acetone for the manufacture of smokeless powder. This recent impetus has been a great boon to the industry for, with low prices for wood alcohol since the passage of the denatured alcohol act, overproduction and low prices for acetate of lime and a constantly decreasing premium for charcoal pig iron, the outlook for the industry has not been brilliant for the past few years.

It was the last named condition which made the advent of the chemist into the wood distillation industry imperative. Necessity called him in to show how efficiency of operation, with low prices, might replace obsolete processes, stimulated by high prices. He came into the industry as efficiency engineer.

It has been in the treatment of the crude pyroligneous acid resulting from the wood distillation and in the recovery and refining of the valuable products that the contribution of the chemist has been of greatest value. Although he has shown the importance of temperature control of carbonization; of the physical condition of the wood; of the proper condensation and scrubbing of the non-condensable gases; although he proved beyond question the necessity of the abandonment of the old

kiln process and the adoption of the more efficient oven or retort system; yet it has been in the treatment of the products of wood distillation that he has served the industry most usefully.

To outline this treatment of the pyroligneous acid, we have the following steps, after the settling of the crude liquor for the purpose of removing the insoluble wood tar:

1—Distillation of the crude acid liquor for the purpose of removing the tar in solution.

2—After neutralization of the crude acid liquor by means of milk of lime, separation of the volatile products, *viz.*, methyl alcohol and acetone, from the acetate of lime of the neutralized liquor.

3—Concentration and drying of the acetate of lime.

4—Concentration and refining of the wood alcohol.

The primary distillation of the crude liquor was usually a simple distillation under atmospheric pressure, carried out in copper stills, fitted with cylindrical steam coil, copper goose and vertical tubular condenser. The operation consisted of feeding the crude liquor into this still continuously, while the process of distillation was carried out by means of live steam in the coil. This was continued ordinarily for three days when the addition of crude liquor was stopped and the distillation continued until no further product was obtained. Then live steam was entered in the still and a further amount of distillate, containing a large percentage of acetic acid was obtained. The matter of keeping the coils of these stills free from tar and carbon deposit was a difficult one, especially where the liquor was obtained from the kiln process. For the retort plant, it was necessary only once a week to enter a charge of settled tar which, in this process, contains a large amount of oils.

The crude liquor generally entered these primary stills at the temperature at which it was obtained from the retort or kiln condenser. Seldom were preheaters, operated either by the use of the steam condensate from the coil or the heat in the distilling vapor used. When it is remembered that substantially 90 per cent of the crude liquor is distilled, it will be readily seen that the process was a very costly one, not only on account of the high steam consumptoin, but also on account of the large investment in copper stills, coils and necks, all of which required frequent renewal.

The separation of the volatile constituents, *viz.*, methyl alcohol, acetone and methyl acetate, from the acetate of lime of the neutralized liquor was carried out by a simple distillation in the so-called "Lime-Lees" stills—vertical iron tanks, fitted with copper coil on the bottom, with a vertical goose, consisting of an iron pipe of varying heights, leading to a surface condenser, similar in construction to that used in the primary stills. The operation of these stills consisted of alternately filling the still with the neutralized liquor and, by means of live steam in the coil, distilling the volatile constituents until the watery distillate showed, by hydrometer test, no further alcohol content. According to the nature of the liquor, that is, if from retort or kiln and also depending on the nature of the goose, the distillate obtained in this process would vary from 5 to as high as 50 per cent alcohol.

The weak acetate of lime solution remaining in the Lime-Lees stills was then pumped or drawn into storage tanks, settled and fed to open, double bottom graining pans. The solution was evaporated down and grained, with the necessary stirring or "spudding" to secure proper grain of the final product. The final drying of the acetate of lime was then carried out, either on the brick tops of the retort setting by means of the waste heat from the retort, or on an iron dry floor, set on brick flues and heated at one end by coal fire, or by means of waste boiler gases. This process required a large amount of labor in the graining and raking of the drying acetate on the floor.

The watery alcohol distillate from the Lime-Lees stills was generally concentrated in intermittent stills, consisting of an iron still, fitted with scroll coil, the vapors passing through copper columns, of various design, frequently built with perforated plates and return pipes, with tubular separator and condenser at the top for increasing the proof of the distillate by means of fractional condensation. Frequently, the refining distillations are carried out in columns built of plates, with a large number of boiling pipes and caps for the purpose of better separating the more volatile acetone from the methyl alcohol.

The process indicated above involved, in some plants, as many as seven separate distillations from the pyroligneous acid to the refined alcohol; and, where carried out with live steam under atmospheric pressure, it resulted, of course, in great fuel consumption and excessive amounts of water required for condensing and cooling purposes. To these may be added the constant loss of products, due to the rehandling of the volatile material, especially when it is remembered that, even in the northerly plants, the available water frequently rises in temperature in the summer months to a point at which losses of volatile material may be considerable. The improvements undertaken, therefore, in the last few years have had these objects in view:

1—Economy of steam in evaporation and distillation.

2—Economy of water for condensing and cooling.

3—Greater simplicity of operation involving the elimination of repeated condensations and consequent redistillations in the step-up process.

The greatest steam consumer was the first step in the process, the distillation of the acid for the removal of the tar in solution. The first departure, therefore, from the atmospheric evaporation, was the introduction of vacuum evaporators. With the recognized advantage of single- or multiple-effect evaporation, the introduction into this industry was long delayed for various reasons. In many plants which operated in connection with sawmills, refuse has been sold to the chemical plant at a round figure, generally quite favorable to the chemical plant. With the large excess of waste available, the necessity of steam economy was, therefore, not present at these plants and it was at the plants without this favorable connection or at which the utilization of lumber was closer, that the introduction was first made.

The nature of the problem involving the evaporation of a liquid containing volatile products (methyl alcohol and acetone) together with an acid (acetic) with a tarry residue, in solution and held colloidally, presented many new conditions for the builder of evaporators. Generally, their work had involved the concentration of a dilute aqueous solution, in which case the removal of the distillate at a high temperature was permissible. With pyroligneous acid, however, the presence of methyl alcohol and acetone necessitates the use of very efficient condensing and cooling apparatus to prevent losses of these valuable products. Again, the tar in solution presents a substance which rapidly forms a coating on the evaporator tubes, quickly reducing the heat transference and decreasing the boiling and circulation in the evaporator. The following conditions were essential, therefore:

1—Complete accessibility of all evaporator tubes for cleaning, inside and out. The cleaning problem varies with the nature of the crude liquor: that is, if derived from retort or kiln process, and the matter of keeping the evaporator clean is the most serious problem met with in the use of the vacuum evaporator. It is at this point that the attention of the chemist is most necessary, for it is his duty to indicate, judging from temperature and pressure conditions, in the different vapor chambers of the several effects, just where the accumulation of tar has brought about the decrease in heat conductivity.

2—Efficient condensing and cooling apparatus is of vital

importance on account of the difficulty of complete condensation, while working under the high vacuum. The design of the condensing apparatus, therefore, in this case, should involve a considerable length of path for vapors and gases before the non-condensable gas is allowed to escape from the apparatus.

3—The prevention of entrainment is important on account of the possible contamination of the distillate by a small amount of tar which might be thrown over and which causes difficulty in the later drying of the acetate of lime solution. Hoods, built within the evaporator body, itself, where the evaporator tubes are vertical, have lately been found to be of great advantage in this regard and permit rapid circulation in the boiling chamber, without fear of entrainment.

Again, in the concentration of the dilute acetate of lime liquor, the introduction of the vacuum evaporator has brought about great savings in steam and consequent lowering of costs. Here, also, the possibility of losses by entrainment was present, but has been completely eliminated by the use of horizontal tubes in the construction of the evaporator. The particular type of evaporator introduced has depended upon the saving to be brought about, in other words, upon the availability of exhaust steam or sawmill refuse. Hence, the single- or double-effect evaporator would be introduced where considerable exhaust steam was available or where fuel was cheap, while the triple-effect would find its place where coal at a high price was used for fuel. Combination evaporators have been introduced with success in several plants. Thus, a common type is a double-effect evaporator, the first effect of which is an iron pan, equipped with horizontal tubes, serving to concentrate the acetate of lime solution, while the second effect, operated by the vapors from the acetate pan, is a copper pan with steam chest equipped with vertical tubes for the distillation of the pyroligneous acid. Further economy has been secured by the introduction of preheaters for the crude liquors, which use the various waste condensates as the heating medium.

The final drying of the concentrated acetate of lime solution from the evaporators is now carried out very efficiently by means of mechanical driers which have eliminated the high labor costs of the old dry floor process. Rotary cylindrical driers, operated with steam within the cylinder, with the concentrated solution without, and fitted with scrapers to remove the acetate mud, have been eminently successful, the final drying taking place on horizontally moving canvas belts traveling over a series of pipes heated by exhaust steam or, better, the wet material is fed into a continuous wire belt moving vertically counter to a current of waste gases from blast furnace stoves, or boilers, reduced to the proper temperatures for drying. The latter arrangement produces a uniform product, especially free from dust, with one-quarter the labor previously used on dry floors and with a considerable saving of steam.

Returning to the second step of our process, the separation of the volatile components from the acetate of lime solution, we find that the introduction of continuous columns has halved the amount the steam formerly used in the old Lime-Lees and the distillate is brought to high proof in one operation, thereby eliminating the step-up process of intermittent distillation. These continuous columns are of various types, frequently of plates equipped with boiling pipes and caps, the preheated neutralized liquor entering at the middle part of the column, the lower half then serving to deprive the neutralized liquor of the volatile products, the upper half concentrating the volatile distillate continuously. An improved arrangement which has been put in successful operation during the last few weeks consists of two separate columns, the first one serving only to remove the alcohol from the neutralized liquor and discharging a low-proof vapor into the middle of the second column, which, operating on this vapor, produces a high-proof distillate, miscible with water, while discharging waste oils and watery condensate from its base. This latter arrangement is a considerable improvement over previous columns in that this latter discharge will not dilute and contaminate the acetate solution, as has been the case heretofore.

In refining the crude wood alcohol, continuous columns have, in some plants, replaced the intermittent stills to a considerable extent. Columns are now in successful operation which separate the acetone from the methyl alcohol, so that a 50 per cent solution of acetone and, simultaneously, methyl alcohol containing under 0.1 per cent of acetone, are obtained continuously. The chemist's ingenuity in the production of various special solvents and mixtures has been of great value in the creation of new uses for methyl alcohol, which to-day are of great importance in disposing of the product, when the market for the regular grades is poor.

It is not within the scope of this paper to mention the work that has been done in the further development of wood distillation products, namely the manufacture of acetone and acetic acid from acetate of lime; of formaldehyde from methyl alcohol and of wood creosote from wood tar. We need only mention that these are purely chemical developments and their increasing importance to-day is a tribute to the American chemist.

Thus, the work of the chemist is apparent at every important step of the hardwood distillation industry and it may safely be said that the introduction of the improved apparatus described and its successful operation would never have been accomplished without the guidance of the chemist.

MANCELONA, MICHIGAN

## CONTRIBUTIONS OF THE CHEMIST TO THE PACKING HOUSE PRODUCTS INDUSTRY

By ARTHUR LOWENSTEIN
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The modern large packing house is composed of a group of industries. The packing phase itself consists usually of the slaughter of animals, resolving the carcasses into various commercial cuts, curing, smoking, canning, assorting the various by-products and their conversion into finished products, the manufacture of sausage and other meat food products, etc., etc. In addition to this phase, however, many of the large packers are engaged in a number of specialized industries on a good-sized commercial scale, which are distinctive in themselves. Some of these are: the cottonseed oil industry; the poultry industry; manufacture of "compound" (a substitute for lard), oleomargarine, fertilizers—both animal and mineral (acid phosphate), sulfuric acid, glue, hair felt, curled hair, anhydrous ammonia (from ammoniacal liquor from coal), creamery butter, canned specialties, soda-fountain products, soap and toilet specialties, pharmaceuticals—from animal products, glycerine refining, etc., etc.

The contributions of chemists to some of these specialized industries referred to have already been ably discussed in papers presented earlier in this symposium and others are to be discussed at this meeting. That which follows in this paper will therefore deal largely with the contributions of the chemist to essentially the packing house phase of the subject rather than its allied industries in which the packing house chemist and chemical engineer today actively participate.

It may be interesting to quote from a book entitled the "Modern Packing House" by F. W. Wilder under the caption "Chemical Department:" "This is a department which in all of the large well-regulated packing houses is considered very essential and the information obtained therefrom in the saving and the turning into commercial value of the by-products, as well as in determining the value of the products already produced is turned to good account. Laboratories in the larger plants are fitted up for making exhaustive tests as to the value

of the products as well as for ascertaining the most practical methods for manufacturing, and many of the departments of the modern packing house had their origin in the chemical laboratory."

Another book entitled "Packing House Industries" of the International Library of Technology, after discussing the importance of the application of artificial refrigeration to these industries says: "In addition to artificial refrigeration, another most potent factor in developing the modern scientific packing industry is applied chemistry. Were it not for the ingenuity of the chemist in finding a way to utilize the offal of slaughtered animals, the price of meat would necessarily be very high. The chemist has turned into practical channels of income what was in former times not only waste, but a source of expense for its removal."

This group of industries, certainly from the time when it can be termed "modern," does not date back more than thirty-five to forty years. Chemists and chemistry have played an important part in its development almost from its inception. It is interesting to note that the leading pioneer chemists in this industry are living to-day. They have generously responded to the request of the writer for authentic information relative to the early contributions of the chemist to this industry but unfortunately, owing to the limited time and space provided for this paper, only a small portion of this evidence can be included.

In 1886, H. B. Schmidt was the first chemist to be regularly employed by a packer in the Union Stock Yards, Chicago. In the same year Dr. Rose was employed as a consulting chemist by another packer and prior to 1886 one of the packers had employed Prof. Haynes in a consulting capacity in a suit brought against them by the owners of the Mege Mouries patents for the making of oleo oil. This date, then, marks the beginning of the application of chemistry to the packing house industry in this country by the packers themselves through their own chemists. Prior to this date, however, they disposed of some of their by-products in a crude or unfinished state to concerns who employed chemists. Pressed, undried tankage and blood, glue in jelly form, evaporated tank water commonly termed "stick" are examples. Also steam-rendered lard which in those days was frequently discolored, was first improved by a chemist, W. B. Allbright, in 1879–1880, although not at that time identified with a packing house. Mr. Schmidt's description, with dates of installation of improved machinery for evaporating, drying, pressing, refining, etc., of various by-products is exceedingly interesting. These improvements generally were the result of the combined efforts of the chemical, engineering and operating staff.

The installation of vacuum evaporators, first single-effect, and later multiple-effect, stimulated the recovery of boiled beef liquors. These evaporated liquors were at first further concentrated into paste of "solid" beef extract by drying on cast-iron steam-heated revolving roll evaporators, and it was not until some years later that vacuum kettles with agitators supplanted them. It is rather interesting to note that practically since the days of Liebig the development of the extract of meat manufacture has been under the direction of chemists.

The recovery of tank water, containing dissolved nitrogenous constituents resulting from the cooking of various kinds of packing house offal, marked an important step forward both from a sanitary as well as economic viewpoint. A concern in Hammond, Indiana, employing a chemist, Dr. Van Ruymbeke, are said to have been the first to develop the evaporation of tank water, which was evaporated in a Yar Yan double-effect evaporator to a jelly form. This work was done under the supervision of Dr. Van Ruymbeke, who was the first to do this work in the Stock Yards. The material was then shipped to Hammond and mixed with copperas and dried in pans. This latter treatment with sulfate of iron was patented by Jobbins and Van Ruymbeke. Later O. T. Joslin, a chemist for one of the packers, substituted a process of his own, wherein the evaporated tank water was coagulated with a ferric sulfate solution and dried on the roll invented by him. This roll system was devised in 1892–93 and is in general use to-day.

"The refining of tallows was started in 1886 and the pressing of tallows into tallow oil and stearine and the refining of the tallow oil into acidless grade was started possibly a year later in 1887. The refining of tallow and oils by means of the fuller's earth treatment was then coming into vogue in the Stock Yards and in the next year or two became universal."

Somewhat later naphtha extraction of tankage and bone was experimented with and at first met with obstacles in the way of insurance restrictions, but was later developed to its present status. Its general adoption was somewhat slow because of the low grade of grease recovered and the fact that there was only one concern in this country at that time capable of refining this product.

In 1887–88 one of the other packers engaged Manwaring as their first chemist and in 1889 O. T. Joslin was engaged as the first chemist for another packer. J. P. Grabfield and A. G. Manns were also active pioneer chemists in the early days. E. K. Nelson became identified with the industry a little later on, as did W. B. Allbright, some of whose early contributions to this industry we shall describe briefly in a moment. It has been principally under the direction of these men and of the chemists actively connected with the industry today, that the contributions of the chemists to this industry have been made.

As previously mentioned, in 1879–80 W. B. Allbright first applied chemical treatment (in this country) to Prime Steam Lard to improve its color. This treatment consisted in the use of caustic soda. To quote Mr. Allbright: "This made so much soap, that in studying for a more economical method I hit upon fuller's earth." This is the first record of employing fuller's earth for this purpose.

Mr. Allbright very interestingly describes the origin of "compound," a substitute for lard, which resulted from the gross adulteration of cuban lard by eastern refiners, until one of the large western refiners put a product on the market consisting solely of cottonseed oil and oleo stearine. This product was so well received that, with subsequent improvements in its manufacture, notably the invention of the lard roll or cooling cylinder by Allbright, and of the deodorization process for cottonseed oil, this firm discontinued the refining of pure lard entirely. To give some idea of the extent of this compound industry to-day, in 1910, the Bureau of Animal Industry reported 671,526,107 pounds to have been inspected and passed by them.

The following paragraph of a letter from Dr. J. P. Grabfield is of interest: "Most of the discoveries and improvements in the packing house on the various by-products was brought about by necessity to find utilization for same. Referring to fats and oils, it was always an effort to manufacture a product that would bring a better price. It was really the chemist who first began to develop the various products in the packing industry. There was so much for the chemist to do in those days that it was simply a question of what pleased him best to work on. There was scarcely a line in the entire packing industry that was not open to an improvement by the chemist."

The following excerpt from correspondence with A. G. Manns bearing on this subject is of interest: "The employment of chemists by the packers was of course the means whereby it became possible for the packers to progress along the various lines that have been developed. The activities of the sales departments were, however, the real stimulant. Without this coöperation, or I might say their leadership, little would have been accomplished."

E. K. Nelson says: "The manufacture of neat's foot oil

in its various grades, lard oils, tallow and tallow oils, etc., was improved if not by the chemist, at least with his coöperation. All the daily runs were checked up constantly in the laboratory until the quality of the products was worked up to a high standard. This same thing applies to all by-products as you know."

The work of the present-day chemist, chemical engineer or technologist in these industries in addition to analytical work for control of product and supplies, may be summed up as follows:

I—Waste prevention.

II—Improvement of existing methods and processes of operation.

III—Utilization or recovery of products in a more valuable form.

IV—Initiation of new processes.

V—Direction of industrial research and application of the results of the researches until placed on a commercial basis.

VI—Investigation of and putting on a commercial basis new industries and lines of activity allied and associated with the packing industry.

UNION STOCK YARDS, CHICAGO

## CONTRIBUTIONS OF THE CHEMIST TO THE ELECTROCHEMICAL INDUSTRY

By W. S LANDIS

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When I was first requested to say something about the relation of the chemist to the electrochemical industry I thought I was being handed one of Goldberg's Foolish Questions. The spontaneous answer that occurred to me—he has been the foundation and is at present the mainstay of the industry, however, on mature thought requires reconsideration, for while his present status is well provided for, we should pay some attention to the growing tendency of the industry to replace his services by other classes of engineers.

An analysis of the industry, directing our attention only to that part concerned with the production of compounds, in distinction to the branch concerned with the extraction of metals, shows it to be of comparatively recent origin, beginning largely with the installation of the Niagara power developments in 1896. Most of the men who founded the industry are still alive and occupying prominent positions in the operating departments of the present plants. No one seems to have cared about compiling their biographies, though an attempt was once made in the first volume of "Electrochemical Industry." For some reason only five Americans were included in the series before the work was abandoned. Of these five, three possessed special chemical training, and while the other two would be more properly classed as electrical engineers, they were men well versed in chemical principles and were closely associated with other well-known chemists. It is unfortunate that this series of biographies was so abruptly terminated, for it would have made this note of mine superfluous.

As before mentioned, the chemist played by far the most important part in the development of the industry, and to-day I estimate that he occupies over 90 per cent of the more prominent positions in the plants in the Niagara district, which I take as typical of the industry as a whole. He grew with the industry, and with a few exceptions where others have been brought in for office, sales, and executive positions as the plants enlarged, all the staffs are still predominated by men of essentially chemical training.

But among the younger men now taking their places in the Niagara plants one notes an increasing number of men with mechanical training. This seems to surprise many not directly informed as to the present status of the industry, for next to the chemist it is not unnatural to suppose that the electrical engineer would closely press the chemist for place. It must, however, be remembered that the power companies maintain most highly organized electrical engineering staffs, which at all times are available for consultation, and many times force, I may add, almost unwelcome attention upon us when in our endeavor to push things we unbalance their circuits, or cause some other equally unintelligible trouble. It is thus seen that there is really no need for the chemical plants to carry highly specialized electrical departments. They have standardized their electrical equipment to forms of installation which demand little highly skilled attention. Most of them use low tension currents with simple distribution systems, and when the electrical equipment has once been properly installed there are very few electrical problems arising. They are much more concerned with the handling of solids, liquids and gases, the transportation and preliminary treatment of raw materials, the finishing of the product, than with their power departments, all of which emphasizes the fact that in the training of the newer electrochemists too much stress can be laid on complicated and involved alternating current theory at the expense of the elementals of chemical engineering.

My experience in this field is not large, but I cannot help but remark my discouragement with many recent electrochemical graduates who seemingly are well informed about high tension electrical engineering, but cannot instal a simple pipe line for delivering a definite amount of gas or liquid under given conditions, and a conveyor system for moving a given tonnage of raw materials in some new and unheard of device. When they come into the industry they will probably find that the 10,000 volt circuits are already installed and need no further attention from the plant management, but they will meet every day with problems of moving materials faster and more cheaply, particularly as plants enlarge and efficiencies increase.

In my opinion, it is therefore necessary to the chemist, if he is to hold his own in the present development of the industry and not give way to the mechanical engineer, to familiarize himself with the advances of the industry along mechanical lines, preferably by leaving the narrow confines of the school laboratory and spending some of his time in the other departments of technical education. Analysts will always be in demand, for chemical control of the electrochemical industries is very rigid, and particularly in the field of electric furnace products is there an unlimited opportunity for highly trained analytical chemists.

The chemical engineer possessing a representative training need have no fear on first entering the industry of finding himself in foreign parts. At Niagara the sky is just as clouded with smoke as any similar chemical center in the vicinity of New York City, all of which goes to show that combustion, steam generation, heating, evaporating, crystallizing and other well-known chemical operations have not been completely replaced by electricity. The standardization of the electrical end of the plant can be assumed before his arrival, and the new agent electricity will be found a much more tractable reagent than many of the purely chemical ones he is familiar with. But this reagent rarely starts with a crude material as such, or turns out a ready finished product from the furnace or cell, and the chemical equipment used in the preparation and the finishing is the same old apparatus found in most other branches of the pure chemical industry.

My greatest regret is that the secrecy that is maintained about the electrochemical plants cannot be withdrawn just long enough to bring in the chemical faculties of our schools, so that in the formation of the courses designed to train men for this industry a proper balance of chemical, mechanical, and electrical work may be incorporated. The future of the chemist in the industry would then be assured, and not at the

expense, either, I desire to emphasize, of sacrificing that very essential of all mechanical training—fundamental general principles to specialized details.

NIAGARA FALLS, ONTARIO, CANADA

## CONTRIBUTIONS OF THE CHEMIST TO THE EXPLOSIVES INDUSTRY

By CHARLES E. MUNROE
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The explosive industry is essentially a chemical industry and is most efficiently conducted under close chemical supervision. It is true that a large part of the explosives used or proposed for use in commerce are mixtures of various components, that variations in the proportions of the components or modifications of the physical conditions of the components, or of the product, may fit it better for certain of the multifarious uses to which explosives are put, and that this has given large opportunities for the exercise of empiric ingenuity which practically controlled the industry for centuries; but modern developments have proven that these mixtures can be most economically, uniformly and satisfactorily produced when their manufacture is supervised by skilled chemists who prove the degree of purity of each ingredient and, by a systematic scientific series of tests, determine quantitatively the characteristics of the product.

As a fact, while the empiricist has dominated the industry up to recent times he has nevertheless benefited from the altruistic services of the chemist, for gunpowder, the mixture which almost alone served man's purpose as an explosive through five centuries, was brought to the attention of western nations by Roger Bacon, whom E. von Meyer includes as an alchemist in his history of chemistry, and it was brought to a higher state of usefulness and reliability through the researches of Lavoisier, Berthollet, Gay Lussac, Violette, Chevreul, Bunsen, Linck, Karoyli, Debus, and other chemists, and a variation in the oxidizer was wrought when Berthollet proposed in 1785 the substitution of a chlorate for the nitrate.

With the discovery of picric acid by Woulfe in London in 1771, its confirmation by Hausmann in 1788, its identification as trinitrophenol by Laurent in 1843 and the demonstration of its explosiveness *per se* by Sprengel in 1873 began the era of strictly chemical explosives. This was followed in 1800 by the discovery of mercuric fulminate by Howard, and the elaborate investigations of the fulminates by Liebig and his students; by the discovery of guncotton and the cellulose nitrates in 1845 by Schönbein and in 1846 by Böttger; by the discovery of nitroglycerin by Sobrero in 1846; by the discovery of diazo compounds by Griess in 1858; and by the discovery of hydronitric or triazoic acid and its salts by Curtius in 1890.

With the demonstration by Berthelot of the explosiveness of other nitrosubstitution compounds than picric acid there came a widely extended and constantly increasing use for them; and the number of different compounds made use of is constantly growing for while the cellulose nitrates, with nitroglycerine, are playing the rôle of propellants, the nitrosubstitution compounds are the explosives which are being made use of in the high explosives shell now working such devastation in the present war.

I believe I have said enough to make it obvious that only by the liberal employment of trained chemists can this industry be continued or extended, and in recent years this view has been accepted and followed by manufacturers.

It may be worth while to recall here that when the Census of the Chemical Industries was taken in 1900 an inquiry was made as to the number of chemists employed, because it was then recognized that this afforded a criterion by which to determine the intelligence and foresight with which the businesses were conducted. As shown in Bulletin No. 210 of that Census there was reported but 276 chemists employed in 1740 establishments then reporting, and that but 32 chemists were employed in the 97 explosives works from which returns were secured. It is not known what effect, if any, this inquiry had but it is understood that at present a single explosives company in the United States employs alone many times this number of chemists. This improvement is gratifying to record but it should serve only as an example to be emulated.

WASHINGTON, D. C.

# ORIGINAL PAPERS

## THERMAL REACTIONS OF PETROLEUM HYDROCARBONS IN THE VAPOR PHASE[1]

By WALTER F. RITTMAN
Received Sept. 8, 1915

One of the most widely studied and important chemical problems of the present day is the thermal decomposition or "cracking" of petroleum hydrocarbons. A considerable number of investigations have been undertaken along this line, most of which were conducted with the primary intention of developing commercial processes. The data thus obtained have been necessarily of a rather special character and, in addition, are not particularly available to the scientific world. In view of the widespread need for clear-cut and comprehensive information concerning the "cracking" reaction a series of experiments has been outlined for the purpose of studying the problem consistently and impartially in all its phases.

The first experiments[2] were conducted in connection with the problem of oil-gas production and were limited to such conditions as might apply in that field. Attention was given to the influences of temperature, pressure and concentration on the end products of the reaction, a maximum of care being bestowed upon the properties of the evolved gases. Liquid products were examined only with regard to general physical and chemical properties.

In the present experiments it has been found unnecessary to give more than a minimum of attention to quantitative relations among gaseous products. The results of the earlier experiments were so definite and so exactly in accord with theoretical considerations that little has been added to them in the present connection. It has been possible, however, to learn facts of the greatest importance concerning liquid products of the cracking reaction and, in addition, valuable information has been obtained regarding the course and mechanism of the process.

The results at hand have led to the following conclusions with regard to the cracking reaction:

1—The nature, both physical and chemical, of an oil is of secondary importance, compared with the influence of temperature, time, and pressure, in controlling the products of the cracking reaction. Under

[1] Published with the permission of the Director of the Bureau of Mines.
[2] Whitaker and Rittman, THIS JOURNAL, 6 (1914), 383 and 472.

like conditions approximately similar results have been obtained from five different oils and it has seemed that the minor existing differences may as probably be due to variation in rate of reaction as to the actual production of unlike equilibrium products.

2—From any oil it is possible to make any desired type of hydrocarbon by adjusting properly the conditions of treatment.

(*a*)—Most favorable conditions for gasoline production are temperatures of about 500° and pressures higher than 6 atmospheres.

(*b*)—Low-boiling aromatic hydrocarbons are produced best at temperatures between 600° and 700° with pressures above 4 atmospheres.

(*c*)—Higher temperatures favor the production of carbon and gas at the expense of the liquid reaction products.

3—The course of the cracking process is one of dehydrogenation.

4—The formation of aromatic compounds seems to occur in either of three ways:[1]

(*a*)—The original oil may be decomposed to small molecule compounds of the acetylene series which subsequently polymerize to form the larger aromatic nuclei.

(*b*)—There may be a simple splitting of polycyclic (asphaltic) hydrocarbons.

(*c*)—There may be a dehydrogenation of naphthene hydrocarbons.

## THEORETICAL

The characteristic feature of the present set of experiments is that cracking has been conducted in the vapor phase. The advantages of this method of procedure are considerable and, as will be shown in a later connection, have as much importance from a commercial as from a purely scientific point of view.

The primary advantage of the one-phase system is that both temperature and pressure may be controlled separately and at will. In a two-phase system each is a function of the other. The simple vapor pressure curve diagram for water (shown in Fig. I) illustrates the characteristic difference between a one-phase and a two-phase system. If liquid and vapor are in equilibrium with each other we are confined to the line representing the variation of vapor pressure with temperature. If an attempt is made to change one of these variables and keep the other constant a phase disappears. Thus any attempt to heat water above 100° C. at atmospheric pressure tends to produce entire conversion to the state of vapor. If, however, we deal with the vapor phase only we may obtain any desired combination of temperature and pressure as long as conditions are avoided which cause condensation. The vapor pressure of petroleum, which is a mixture and not a simple chemical compound, is not exactly analogous to that of water as the liquid and vapor phases differ in composition and thus permit the establishment of various conditions of equilibrium; if temperatures are raised sufficiently high, however, the liquid will disappear, as in the simpler case.

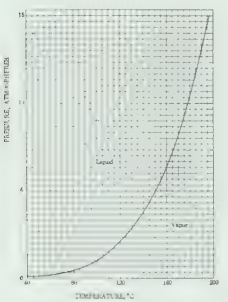

FIG. 1—VAPOR PRESSURE OF WATER

As applied to present needs the limitations of the two-phase system become evident. If it is desired to heat to 850° C. an oil boiling below 300° enormous pressure must be developed to retain the liquid phase, more pressure, probably, than apparatus of ordinary construction will withstand. Yet it is perfectly easy and simple to pass oil vapor through a tube heated to 850° and at the same time maintain in the system any desired pressure from a fraction of an atmosphere to over thirty atmospheres.

Other advantages of the vapor-phase system for heat decomposition of petroleum hydrocarbons are more mechanical than chemical. The influence due to differences among the physical properties of various original oils is eliminated. In systems which involve cracking by distillation under pressure the amount of pressure developed in getting an oil up to decomposition temperature depends upon the volatility of the oil. The total conditions and range of applicability of a process may be controlled by this factor. When, however, as in the vapor-phase system, the interdependence of the two variables, temperature and pressure, has been eliminated, the influence of volatility of the oil is a minor consideration. It is controlled by adjustment of the vaporizing device, through which the oil passes before entering the body of the cracking furnace.

The vapor-phase cracking process, as here conducted, possesses another characteristic which is advantageous, both from a scientific and from a commercial point of view. In the present work and in a majority of commercial cracking processes the production of gas is undesirable. It will be noted that the method here employed minimizes its formation. The mechanism by which this end is accomplished is as follows. In the cracking furnace we have established an equilibrium which may be represented by the following equation:

$$\left.\begin{matrix}\text{Condensable}\\ \text{Original Hydrocarbons}\end{matrix}\right\} \rightleftharpoons \left\{\begin{matrix}\text{Permanent}\\ \text{Gases}\end{matrix}\right\} + \left\{\begin{matrix}\text{Condensable}\\ \text{Cracked Hydrocarbons}\end{matrix}\right\}$$

At the lower end of the cracking tube is a Liebig condenser which removes by cooling the unreacting residuum of original hydrocarbon and the condensable products, but which does not affect the permanent gases (hydrogen, methane, etc.). As a result when more of the original hydrocarbons enter the furnace a new equilibrium is established without any further production of gas. In actual practice this condition is not attained in absolute degree but the above description indicates a strong general tendency.

The factor of safety is another important consideration. In the course of the cracking reaction only a

[1] Lewes, *Jour. Soc. Chem. Ind.*, **11** (1892), 584; R. Meyer, *Ber.*, **45** (1912), 1609; R. Meyer, and Tanzen, *Ber.*, **46** (1913), 3183; Ipatiew, *Ber.*, **44** (1911), 2978; Brooks, Bacon, Padgett and Humphrey, THIS JOURNAL, **7** (1915), 180.

small portion of oil is in the zone of action at any one time and in case of failure of apparatus to remain tight there is no large volume of hot oil to be discharged.

Valuable indications of what may be expected as products of the cracking reaction may be obtained by considering equilibrium relations between a typical hydrocarbon and its possible decomposition products. The initial substance chosen for present purposes is a hydrocarbon of the paraffin series, representative of the kerosene cut which modern commercial conditions have rendered desirable of transformation. The compound $C_{12}H_{26}$, boiling at about 215°, has been employed as a basis for a number of typical reactions (Table I), it being understood, however, that with each of the major reactions is coincident a number of minor reactions.

It is also to be understood that present considerations do not neglect the possibility of cracking polycyclic hydrocarbons directly into aromatic compounds. Here the case may be one of simple splitting, such as occurs in the transformation of a paraffin molecule to a paraffin and an olefin. By starting with a paraffin the case is made inclusive and is therefore best suited to purposes of illustration.

The possibilities of decomposition may be classified under the following four heads:

1—Paraffin formation
2—Olefin formation
3—Acetylene formation
4—Aromatic formation

The list of typical equations includes all these cases, and the approximate equilibrium relations point out general tendencies of the various reactions. It is to be noted that for all reactions save paraffin rearrangement (Equations 1 and 2) and aromatic formation (Equations 15 and 16) the effect of pressure is inimical, as the transformations are accompanied by increases in total volume. This consideration is, however, modified by the necessity of taking account of the factor of reaction velocity. According to the law of mass action, reaction velocity is proportional to concentration, and concentration is a derived function which varies in the same direction as pressure. If we allow reactions sufficient time to proceed to completion low pressure is favorable for the transformations represented by Equations 3 to 14. When, however, time is limited to a fixed amount the effect of low pressure may be unfavorable unless the reaction occurs with considerable rapidity.

All the reactions indicated, except the last two, take place with absorption of heat and therefore are favored by high temperature. This is indicated by the magnitudes of the approximate equilibrium constants which are figured according to the Nernst equation.[1]

TABLE I—QUANTITATIVE STUDY OF EQUILIBRIA

| No. | Reaction | Heat of reaction(a) | Volume change | (Formulas refer to partial pressures) | Approximate $K_{500}$ | Approximate $K_{600}$ | Approximate $K_{750}$ |
|---|---|---|---|---|---|---|---|
| 1 | $2C_{12}H_{26} \rightleftarrows CH_4 + C_{23}H_{48}$ | — 500 | 2 to 2 | $K = \frac{CH_4 \times C_{23}H_{48}}{(C_{12}H_{26})^2}$ | 0.306 | 0.308 | 0.309 |
| 2 | $2C_{12}H_{26} \rightleftarrows C_{10}H_{22} + C_{14}H_{30}$ | ± 000 | 2 to 2 | $K = \frac{C_{10}H_{22} \times C_{14}H_{30}}{(C_{12}H_{26})^2}$ | 1.0 | 1.0 | 1.0 |
| 3 | $C_{12}H_{26} \rightleftarrows CH_4 + C_{11}H_{22}$ | — 16750 | 1 to 2 | $K = \frac{CH_4 \times C_{11}H_{22}}{C_{12}H_{26}}$ | 645. | 2820. | 15500. |
| 4 | $C_{12}H_{26} \rightleftarrows C_{10}H_{22} + C_2H_4$ | — 16100 | 1 to 2 | $K = \frac{C_{10}H_{22} \times C_2H_4}{C_{12}H_{26}}$ | 1950. | 8300. | 43500. |
| 5 | $C_{12}H_{26} \rightleftarrows C_{12}H_{24} + H_2$ | — 31800 | 1 to 2 | $K = \frac{C_{12}H_{24} \times H_2}{C_{12}H_{26}}$ | 0.0044 | 0.0616 | 1.02 |
| 6 | $C_{12}H_{26} \rightleftarrows 5C_2H_4 + C_2H_6$ | — 80400 | 1 to 6 | $K = \frac{(C_2H_4)^5 \times C_2H_6}{C_{12}H_{26}}$ | $1.25 \times 10^{16}$ | $1.58 \times 10^{18}$ | $6.3 \times 10^{22}$ |
| 7 | $C_{12}H_{26} \rightleftarrows 6C_2H_4 + H_2$ | —111600 | 1 to 7 | $K = \frac{(C_2H_4)^6 \times H_2}{C_{12}H_{26}}$ | $1.2 \times 10^{14}$ | $2.0 \times 10^{18}$ | $1.6 \times 10^{23}$ |
| 8 | $C_{12}H_{26} \rightleftarrows C_2H_2 + 2C_5H_{12}$ | — 47600 | 1 to 3 | $K = \frac{C_2H_2 \times (C_5H_{12})^2}{C_{12}H_{26}}$ | $7.1 \times 10^2$ | $4.0 \times 10^4$ | $3.9 \times 10^6$ |
| 9 | $C_{12}H_{26} \rightleftarrows C_2H_2 + 2C_4H_{10} + C_2H_4$ | — 61100 | 1 to 4 | $K = \frac{C_2H_2 \times (C_4H_{10})^2 \times C_2H_4}{C_{12}H_{26}}$ | $7.4 \times 10^6$ | $1.4 \times 10^9$ | $6.2 \times 10^{11}$ |
| 10 | $C_{12}H_{26} \rightleftarrows 6C_2H_2 + 7H_2$ | 381000 | 1 to 13 | $K = \frac{(C_2H_2)^6 \times (H_2)^7}{C_{12}H_{26}}$ | $1.0 \times 10^{-20}$ | $5.0 \times 10^{-7}$ | $1.2 \times 10^9$ |
| 11 | $C_{12}H_{26} \rightleftarrows 5C_2H_2 + 6H_2 + C_2H_4$ | —336800 | 1 to 12 | $K = \frac{(C_2H_2)^5 \times (H_2)^6 \times C_2H_4}{C_{12}H_{26}}$ | $3.5 \times 10^{-15}$ | $7.1 \times 10^{-2}$ | $2.9 \times 10^{11}$ |
| 12 | $C_{12}H_{26} \rightleftarrows 3C_2H_2 + 4CH_4 + C_2H_4$ | —154400 | 1 to 8 | $K = \frac{(C_2H_2)^3 \times (CH_4)^4 \times C_2H_4}{C_{12}H_{26}}$ | $1.1 \times 10^{11}$ | $5.6 \times 10^{14}$ | $2.4 \times 10^{23}$ |
| 13 | $C_{12}H_{24} \rightleftarrows C_2H_2 + C_{10}H_{22}$ | — 29300 | 1 to 2 | $K = \frac{C_2H_2 \times C_{10}H_{22}}{C_{12}H_{24}}$ | 0.89 | 10.2 | 162. |
| 14 | $C_{12}H_{24} \rightleftarrows 4C_2H_2 + 4CH_4$ | 167600 | 1 to 8 | $K = \frac{(C_2H_2)^4 \times (CH_4)^4}{C_{12}H_{24}}$ | $5.6 \times 10^7$ | $7.1 \times 10^{13}$ | $7.8 \times 10^{20}$ |
| 15 | $3C_2H_2 \rightleftarrows C_6H_6$ | — 130700 | 3 to 1 | $K = \frac{C_6H_6}{(C_2H_2)^3}$ | $2.0 \times 10^{20}$ | $6.3 \times 10^{15}$ | $5.7 \times 10^{10}$ |
| 16 | $2C_2H_2 + C_3H_4 \rightleftarrows C_7H_8$ | —131900 | 3 to 1 | $K = \frac{C_7H_8}{(C_2H_2)^2 \times C_3H_4}$ | $6.3 \times 10^{20}$ | $2.2 \times 10^{16}$ | $1.6 \times 10^{11}$ |

(a) Whenever possible heats of reaction (for constant pressure) are based on values obtained by experimental methods. In other cases calculated values are used, based on the empirical formulae given by Thomsen. ("Thermochemischer Untersuchungen," Part IV, Chapter XIV.)

Here again it must be remembered that the case is not a simple one and that certain of the reactions take place at the expense of others. Especially is it true that the formation of hydrogen and carbon, undesirable end products, is favored by high temperature and it cannot be said, therefore, that to obtain a maximum yield of such a substance as acetylene (Equation 7) it is desirable to heat as strongly as possible.

A few specific cases deserve attention. It seems entirely reasonable to assume that olefin formation is intermediate to acetylene formation. Likewise there are clear indications to the effect that aromatic compounds are polymerization products of acetylenes. Hence the following relations seem to hold for the effects of temperature and pressure. Acetylenes are formed at moderately high temperatures and being intermediate to aromatics the latter are likewise high

[1] Nernst, "Theoretical Chemistry;" also text-books of physical chemistry —Whitaker and Rittman, *Loc. cit.*

temperature products. Acetylene formation appears to be favored by low pressure but the polymerization is a reaction helped by high pressure and this, in addition to the factor of reaction velocity, leads to the expectation that aromatic formation must be favored by pressure.

The ultimate products of the cracking reaction are carbon and hydrogen, their formation being favored by high temperature. Being inactive and undesirable end products they should be minimized by moderation in securing the latter condition.

## EXPERIMENTAL

GENERAL SCHEME OF PROCEDURE—A scheme of procedure similar to that described in an earlier paper[1] has been adopted for the present series of experiments, though the study of products has been conducted on a broader scale. The course of a single experimental unit was as follows: a quantity of oil, generally between 400 and 600 grams, was run through an electrically heated furnace in which were maintained carefully regulated and measured conditions of temperature and pressure. After the completion of the "run" the quantity of resulting oil was determined and the deposited carbon scraped out of the furnace and weighed. The evolved gas was collected in a suitable receiver and its volume read and recorded, although no use has been made of this information in the present connection.

In connection with each major experiment or run a number of supplementary determinations were necessary. Both uncracked and cracked oils were submitted to analytical distillations and specific gravities were measured for total oils and for distillation cuts. Viscosities were determined for original and recovered oils. A number of refractive indices were measured, though these, like gas volumes, are not recorded. Refractive indices have been found to agree so exactly with specific gravities[2] that these constants furnished no additional information of value.

In some cases when the presence of aromatic hydrocarbons was indicated by the gravity figures, chemical examinations were made and the reliability of the former determinations verified. The matter of chemical methods of separation has received consideration in other communications.[3] Samples of evolved gases were removed from the holder and later analyzed. This work will be described later.

The total scheme of procedure may be summarized as follows:

"RUN" OR MAJOR EXPERIMENT

1—Cracking of 400 g. to 600 g. of oil in furnace at regulated temperature and pressure.

2—Determination of quantities of oil, gas and carbon resulting.

SUPPLEMENTARY DETERMINATIONS

1—Distillations of: (*a*) uncracked oil, (*b*) cracked oil.

2—Determinations of specific gravities of uncracked oil, cracked oil and individual distillation cuts.

3—Determinations of viscosity and refractive index.

4—Chemical tests on distillates.

5—Analyses of evolved gases.

CRACKING EXPERIMENT OR "RUN"—The apparatus and general method used for making a run was the same as that described in an earlier paper.[1] The apparatus consists essentially of an electrically heated furnace body eighteen inches long and one and a half inches in diameter. At the upper end is attached an oil feed cup and a vaporizing device. Below the furnace is a Liebig condenser discharging into a receiver which is connected with either a rotary type vacuum pump or a pressure release valve. A final connection is made with a gas holder of 12 cu. ft. capacity. The whole order of the apparatus was therefore: (1) oil feed cup, (2) vaporizer, (3) furnace proper, (4) condenser, (5) first receiver, (6) vacuum pump or pressure valve, (7) second receiver in case of vacuum, and (8) gas holder. The system is a closed one and any desired pressure from a thirtieth of an atmosphere up to 30 atmospheres has been maintained. The electrical heating equipment of the furnace body permits the regulation of temperature at any desired height up to 1000° C. The temperature measurements were made by means of a thermocouple inserted in the interior of the furnace body.

DISTILLATIONS were made in flasks of 250 cc. bulb capacity, with necks $^5/_8$ in. in diameter and 6 in. long to the outlet tube. In each case the neck of the flask was equipped with a 5 in. column of the Hempel type, filled with aluminum beads. Original charges of 200 grams were distilled in most cases and cuts were made at 100° C. and therefore at intervals of 50°.

SPECIFIC GRAVITIES were determined either by means of a Westphal balance with plummet of one cubic centimeter displacement or else with Drushel type pycnometers.[2]

VISCOSITIES were measured in the Engler viscosimeter and results are expressed in Engler degrees, which represent ratios between rates of flow of oils and water.

REFRACTIVE INDICES were measured with the Pulfrich refractometer.

## GENERAL RESULTS OF EXPERIMENTS

The results of a large number of the cracking experiments appear in Table II. The necessary arrangement of figures does not render them particularly easy to interpret, and more readable tables are given in connection with the various points set forth by these experiments (see various sections of Table III). It will be noted, however, that experiments were performed with five different oils, most attention having been given to three, which were a Pennsylvania refined burning oil, an Oklahoma fuel oil and a California Kern River crude. These oils were particularly suited to the present experiments as they are devoid of low-boiling constituents; they are, therefore, of the class least valuable commercially, which renders them most promising as starting material for cracking re-

[1] Whitaker and Rittman, *Loc. cit.*

[2] Rittman and Egloff, THIS JOURNAL, **7** (1915), 578.

[3] Rittman, Twomey and Egloff, *Met. Chem. Eng.*, Oct. 1, 1915; Rittman and Moore, *Ibid.*, Oct. 15, 1915.

[1] Whitaker and Rittman, *Loc. cit.*

[2] Rittman and Dean, THIS JOURNAL, **7** (1915), 185.

actions. They are also typical of the three great fields of the country, the eastern, the mid-continent and the western. In addition to the above three Mexican and Russian crude oils were examined and sufficient data obtained to show that, in spite of their different chemical nature and physical properties, these do not vary radically in their behavior from the others. Figures for the Russian oil were so few that they have not been used in the later tables prepared for purposes of comparison.

It will be noted that the ranges of temperature and pressure are considerable, and that the entire regions of importance in the cracking reaction have been covered thoroughly. Temperatures lower than the ones used do not produce decomposition with sufficient rapidity while those higher in the scale generate as maximum end products undesirable carbon and gas. The range of pressure was as great as could be managed with apparatus of ordinary construction.

STUDY OF RESULTS (See Tables III and IV)

CARBON FORMATION—The first factor to be considered is one which, though of the greatest importance from a commercial point of view, is of but minor theoretical interest. Carbon formation was determined by the rather crude method of scraping the interior of the cooled cracking tube after each run and weighing the solid material thus removed. In spite of the roughness of the method valuable indications were obtained as to general tendencies.

A study of the data in Table III shows first that there are characteristic differences among the series run with the various original oils. These differences may be attributed to a combination of two causes, one chemical, the other physical. The chemical factor may in turn be subdivided. The four oils varied in their carbon content, partly because there were differences in the average sizes of the hydrocarbon molecules and partly because of chemical differences among the basic natures of the oils. Those of an asphaltic base have a higher carbon percentage than those of paraffin base. Hence the following order: The Pennsylvania oil, which deposited least carbon, was a "water-white" kerosene of purely paraffin base and boiling so that 90 per cent came over below 250° C. The Oklahoma oil was intermediate and was of mixed paraffin and asphaltic base; a so-called "fuel oil" of which only 22 per cent distilled below 300°. Still more carbon was deposited by the California oil, a heavy Kern River crude of asphaltic base and giving a distillation cut of only 17 per cent below 300°. The Mexican oil was lighter than the California and gave a distillation cut of 37 per cent below 300° but it had a peculiar physical property of causing much heavy tarry material to be included in the carbon deposit. As a result the figures for carbon formation are high and the yields of recovered oil and the gravities of recovered oils low.

A comparison of averages of irregular sets of figures showing such marked variations is necessarily inaccurate and is almost unscientific, yet it happens to show the result which would be expected from theoretical considerations. Carbon deposition is favored by both temperature and pressure.

VISCOSITY OF RECOVERED OIL—In a considerable number of experiments it was inconvenient to make measurements of viscosity on account of insufficiency in the quantity of recovered oil.

It will be noted that, although there are considerable differences among the viscosities of the original oils, the analogous figures for recovered oils show but moderate variations. This fact is one of a number going to show that the conditions of treatment of an oil are of much more influence than any properties, physical or chemical, which it originally possesses.

A specific comparison brings this out clearly. The ratio of viscosities between the original Pennsylvania and Oklahoma oils was about 1 : 35. The ratio between averages of the two series of recovered oils is about 1 : 3, and, by omitting two vacuum runs of Oklahoma oil, the ratio can be brought down to 1 : 1.5.

No attempt has been made to average the viscosity values, as sufficiently instructive indications can be obtained by a study of any one of the series. That for the Oklahoma oil is most complete and it has been selected for use in Table III. Here it appears that for runs up to 750° C. viscosity decreases with temperature and with pressure. It does not, however, seem probable that this rule will hold for higher temperatures and the single figure obtained for 800° goes to prove the truth of this reasonable expectation. A similar figure for California oil indicates likewise an increase in viscosity as the 800° mark is approached.

SPECIFIC GRAVITY OF RECOVERED OIL—The variation among the specific gravities of the different sets of recovered oils is likewise a factor of interest. Here, as in the case of carbon deposition, it will be noted that there are characteristic differences among recovered oils from the various sources and that these are of the same order as the gravity differences among the original oils. Pennsylvania cracked oils are lightest, Oklahoma next and California heaviest. The Mexican, on account of the tendency of heavy constituents to stick to the carbon, are a little lighter than the California, although the original oil was heavier.

Here again average values are an uncertain proposition and must be regarded with due caution. It appears definitely, however, that gravities increase with temperature. It is to be expected that they would likewise increase with pressure and there are indications that such is the case. Most of the deviations can be explained on the basis of probable experimental error.

PERCENTAGE OF OIL RECOVERED—The percentage of oil recovered is a factor of the greatest importance but, unfortunately, the necessary conditions of the present experiments prevented its determination with any degree of accuracy, especially in the cases of reactions under pressure. The pressure in each case was "built up" by gas generation due to cracking of original oil and there was therefore in each experiment a considerable period during which pressure was not up to the prescribed mark. In addition it was

TABLE IIA—RESULTS OF EXPERIMENTAL RUNS WITH PENNSYLVANIA, OKLAHOMA AND CALIFORNIA OILS

| Temperature: | 850 | 850 | 800 | 750 | 750 | 750 | 750 | 650 | 600 | 600 | 600 | 600 | 600 | 600 | 550 | 550 | 500 | 500 | 500 | 500 | 500 | 500 | 450 | 450 | Gaso. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pressure—Atmospheres | 1 | Vac | Vac | 12 | 6 | 1 | Vac. | Vac. | 24 | 18 | 12 | 6 | 1 | Vac. | 24 | 18 | 24 | 18 | 12 | 6 | 1 | Vac. | 18 | 12 | on. |
| PENNSYLVANIA OIL: | | | | | | | | | | | | | | | | | | | | | | | | | |
| Oil used (grams) | 731 | ..... | ... | 37.2 | 54.5 | 89.3 | 80.0 | ... | 56.8 | 57.2 | 54.7 | 86.1 | 59.1 | 75.0 | ... | ... | 57.6 | 53.9 | 56.1 | 98.1 | 78.0 | 75.0 | ... | 57.5(a) | ... |
| Oil recovered (per cent) | 9.7 | ..... | ... | 15.9 | 16.9 | 16.5 | 33.9 | ... | 37.3 | 40.5 | 43.6 | 31.4 | 59.9 | 97.4 | ... | ... | 72.5 | 79.7 | 84.2 | 57.8 | 94.5 | (75.8 g.) | ... | 93.1 | ... |
| Carbon (per cent) | 7.4 | ..... | ... | 24.3 | 15.3 | 3.7 | 16.1 | ... | 7.5 | 5.3 | 3.6 | 2.4 | 0.6 | 0.0 | ..... | ... | 1.2 | 0.0 | 0.0 | 0.0 | 0.0 | (0.6 g.) | ... | 5.1 | ... |
| Sp. gr. of oil recovered | 1.026 | ..... | ... | 0.910 | 1.020 | 1.012 | 0.905 | ... | 0.962 | 0.926 | 0.918 | 0.885 | 0.840 | 0.811 | ..... | ... | 0.828 | 0.819 | 0.808 | 0.810 | 0.799 | 0.802 | ... | 0.809 | 0.802 |
| Viscosity | ..... | ..... | ... | ..... | ..... | ..... | 1.04(c) | ... | ..... | ..... | 1.11(c) | 1.00(c) | ..... | 1.04(c) | ..... | ..... | 97(c) | 96(c) | 98(c) | 1.00(c) | 1.00(c) | 1.04 | ... | 1.02(c) | 1.05 |
| First drop | 70° | ..... | ... | 75° | 70° | 60° | ... | ... | 36° | 30° | 33° | ... | 31° | ..... | ... | ... | 32° | 30° | 30° | 40° | 36° | ... | ... | 30° | 120° |
| Temperature | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % |
| 100 | 18.0 | ..... | ... | 30.2 | 31.6 | 16.8 | 3.7 | ... | 19.0 | 19.0 | 18.0 | 14.5 | 8.7 | 0.5 | ... | ... | 13.5 | 9.5 | 9.5 | 5.0 | 1.0 | 0.0 | ... | 3.5 | ..... |
| 150 | 7.0 | ..... | ... | 9.4 | 9.7 | 14.3 | 14.3 | ... | 21.5 | 25.0 | 24.2 | 25.0 | 18.5 | 3.5 | ... | ... | 16.2 | 14.5 | 14.3 | 10.0 | 6.7 | 3.0 | ... | 8.3 | 4.8 |
| 200 | 10.0 | ..... | ... | 17.9 | 8.3 | 8.9 | 9.2 | ... | 9.3 | 12.7 | 15.0 | 21.0 | 36.5 | 44.5 | ... | ... | 27.3 | 32.7 | 34.0 | 38.8 | 42.5 | 46.0 | ... | 34.0 | 46.7 |
| 250 | 30.0 | ..... | ... | 25.5 | 23.2 | 20.7 | 24.7 | ... | 13.5 | 15.3 | 14.0 | 16.5 | 25.5 | 41.0 | ..... | ... | 25.0 | 28.5 | 27.3 | 33.0 | 38.0 | 37.5 | ... | 33.0 | 39.0 |
| 300 | ..... | ..... | ... | ..... | ..... | 8.2 | 6.3 | ... | ..... | ..... | ..... | 7.5 | 5.7 | ..... | ... | ... | ..... | ..... | ..... | 8.0 | ..... | ..... | ... | ..... | ..... |
| 150 | 25.0 | ..... | ... | 39.6 | 41.3 | 31.1 | 18.0 | ... | 40.5 | 44.0 | 42.2 | 39.5 | 27.2 | 4.0 | ... | ... | 29.7 | 24.0 | 23.8 | 15.0 | 7.7 | 3.0 | ... | 11.8 | 4.8 |
| 250 | 40.0 | ..... | ... | 43.4 | 30.5 | 29.6 | 62.9 | ... | 22.8 | 28.0 | 29.0 | 37.5 | 60.0 | 85.5 | ... | ... | 52.3 | 61.2 | 61.3 | 71.8 | 80.5 | 83.5 | ... | 67.0 | 85.7 |
| Temperature | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. |
| 100 | .875 | ..... | ... | .865 | .876 | .876 | .800 | ... | .837 | .816 | .807 | .772 | .759 | ..... | ... | ... | .726 | .714 | .725 | .735 | .718 | ..... | ... | .715 | ..... |
| 150 | .859 | ..... | ... | .834 | .860 | .878 | .832 | ... | .862 | .855 | .851 | .839 | .803 | .770 | ..... | ... | .802 | .790 | .786 | .780 | .761 | .760 | ... | .758 | .763 |
| 200 | .885 | ..... | ... | .824 | .873 | .922 | .848 | ... | .876 | .860 | .857 | .838 | .815 | .791 | ..... | ... | .813 | .806 | .801 | .793 | .787 | .786 | ... | .793 | .784 |
| 250 | Solid | ..... | ... | Solid | Solid | Solid | .904 | ... | Solid | .931 | .930 | .889 | .850 | .818 | ..... | ... | .850 | .839 | .831 | .820 | .814 | .813 | ... | .820 | .811 |
| 300 | ..... | ..... | ... | ..... | ..... | (d) | .956 | ... | ..... | ..... | ..... | .956 | .901 | ..... | ..... | ... | ..... | ..... | ..... | .851 | ..... | ..... | ... | ..... | ..... |
| 150 | .873 | ..... | ... | .858 | .872 | .877 | .826 | ... | .847 | .837 | .833 | .809 | .790 | .769 | ..... | ... | .771 | .765 | .763 | .767 | .758 | .760 | ... | .764 | .763 |
| 250 | ..... | ..... | ... | ..... | ..... | ..... | .858 | ... | ..... | .900 | .893 | .861 | .827 | .804 | ..... | ... | .832 | .819 | .814 | .804 | .800 | .798 | ... | .805 | .797 |
| OKLAHOMA OIL: | | | | | | | | | | | | | | | | | | | | | | | | | |
| Oil used (grams) | ..... | 86.2 | 93.7 | 59.6 | 70.3 | 132.5 | 91.2 | 115.9 | 58.1 | 57.4 | 55.4 | 81.3 | 98.2 | 169.2 | 57.7 | 57.0 | 59.0 | ..... | 51.8 | 60.1 | 70.5 | 53.6 | 55.0 | 54.7 | ..... |
| Oil recovered (per cent) | ... | 23.1 | 29.3 | 20.2 | 22.2 | 17.5 | 51.7 | 88.7 | 33.9 | 35.6 | 62.2 | 37.3 | 50.8 | 100.0 | 38.1 | 55.0 | 63.8 | ... | 88.2 | 91.8 | 99.0 | 99.8 | 76.9 | 87.7 | ... |
| Carbon (per cent) | ... | 5.8 | 4.1 | 24.6 | 20.0 | 11.3 | 4.1 | 2.2 | 17.2 | 13.2 | 6.7 | 9.6 | 3.1 | 0.0 | 9.2 | 7.0 | 4.6 | ..... | 1.4 | 1.2 | 0.0 | 0.0 | 0.0 | 0.0 | ... |
| Sp. gr. of oil recovered | ..... | 0.997 | 0.963 | 0.965 | 1.040 | 1.039 | 0.925 | ... | 1.008 | 0.973 | 0.907 | 0.931 | 0.906 | 0.899 | ... | 0.908 | 0.877 | ..... | 0.870 | 0.867 | 0.872 | 0.901 | 0.882 | 0.873 | 0.894 |
| Viscosity | ..... | ... | 1.64(c) | ... | ... | ... | 1.44 | ... | ... | ... | 1.48 | 1.08 | 1.27 | 7.29(c) | 1.05 | ... | 1.25(c) | ..... | 1.32(c) | 1.54(c) | 2.51(c) | 13.4(c) | 1.50(c) | 1.73 | 35.40 |
| First drop | ..... | 70° | 46° | 50° | ... | 65° | 58° | 60° | 37° | 35° | 30° | 31° | 38° | 66° | 30° | 40° | 30° | ..... | 30° | 33° | 42° | 100° | 30° | 38° | ..... |
| Temperature | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % |
| 100 | ... | 8.9 | 6.5 | 14.4 | 19.6 | 13.7 | 5.3 | 1.2 | 21.0 | 24.0 | 10.0 | 16.5 | 10.3 | 1.0 | 17.5 | 16.3 | 13.0 | ..... | 9.3 | 6.2 | 2.3 | 0.0 | 6.2 | 5.0 | 0.0 |
| 150 | ... | 9.7 | 13.0 | 9.6 | 7.1 | 13.4 | 9.3 | 2.5 | 17.4 | 18.0 | 9.8 | 21.7 | 15.0 | 1.8 | 15.5 | 15.5 | 9.3 | ..... | 6.7 | 6.0 | 2.7 | 0.8 | 6.3 | 5.3 | 0.3 |
| 200 | ... | 6.8 | 7.5 | 8.3 | 5.8 | 5.1 | 9.0 | 4.0 | 4.5 | 5.7 | 5.0 | 12.3 | 10.5 | 3.7 | 9.3 | 7.5 | 9.0 | ..... | 7.5 | 9.8 | 4.2 | 2.7 | 5.8 | 5.3 | 2.0 |
| 250 | ... | 18.9 | 11.2 | 18.7 | 19.2 | 19.1 | 10.7 | 11.0 | 11.8 | 10.8 | 11.2 | 16.0 | 11.2 | 9.5 | 11.0 | 11.0 | 12.5 | ..... | 10.7 | 9.7 | 11.8 | 7.0 | 8.8 | 9.7 | 5.5 |
| 300 | ... | ..... | 10.8 | ... | ... | 6.9 | 12.8 | 15.5 | ... | ..... | 14.0 | 8.0 | 14.0 | 13.0 | ..... | ... | 13.5 | ... | 14.3 | 16.0 | 11.2 | 13.5 | ... | 14.3 | 14.0 |
| 150 | ... | 18.6 | 19.5 | 44.0 | 26.7 | 27.1 | 14.8 | 3.7 | 38.4 | 42.0 | 19.8 | 38.2 | 25.3 | 2.8 | 33.0 | 31.8 | 22.3 | ... | 16.0 | 12.2 | 5.0 | 0.8 | 12.5 | 10.3 | 0.3 |
| 250 | ... | 25.7 | 18.7 | 27.0 | 25.0 | 24.2 | 19.7 | 15.0 | 16.3 | 16.5 | 16.2 | 28.3 | 21.7 | 13.2 | 20.3 | 18.5 | 21.5 | ... | 18.2 | 15.5 | 16.0 | 9.2 | 13.3 | 12.8 | 7.5 |
| Temperature | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. |
| 100 | ... | .873 | .827 | .858 | .879 | .873 | .775 | ... | .845 | .833 | .785 | .805 | .769 | ..... | .758 | .752 | .718 | ..... | .712 | .704 | .724 | ... | .748 | .713 | ..... |
| 150 | ... | .868 | .856 | .853 | .857 | .876 | .827 | .798 | .871 | .867 | .839 | .850 | .817 | .791 | .842 | .833 | .803 | ..... | .790 | .777 | .766 | ... | .813 | .783 | ..... |
| 200 | ... | .921 | .872 | .855 | .850 | .917 | .849 | .826 | .900 | .891 | .848 | .853 | .840 | .817 | .865 | .859 | .827 | ..... | .821 | .810 | .807 | .806 | .827 | .811 | .801 |
| 250 | ... | ..... | .919 | Solid | Solid | Solid | .879 | .848 | .987 | .977 | .873 | .902 | .872 | .839 | .917 | .905 | .863 | ..... | .853 | .840 | .835 | .839 | .856 | .839 | .826 |
| 300 | ... | ..... | .928 | ..... | ..... | .994 | .893 | .855 | ..... | ..... | .885 | .956 | .894 | .850 | ..... | ... | .886 | ..... | .868 | .858 | .848 | .844 | ... | .855 | .841 |
| 150 | ... | .870 | .847 | .857 | .874 | .875 | .811 | .793 | .855 | .860 | .813 | .832 | .798 | .791 | .786 | .792 | .755 | ..... | .752 | .741 | .729 | ... | .782 | .751 | ..... |
| 250 | ... | ..... | .899 | ..... | ..... | ..... | .882 | .842 | .963 | .948 | .866 | ..... | .855 | .827 | .893 | .887 | .847 | ..... | .739 | .828 | .827 | .834 | .847 | .839 | .819 |
| CALIFORNIA OIL | | | | | | | | | | | | | | | | | | | | | | | | | |
| Oil used (grams) | ... | 64.6 | 58.2 | 31.5 | 53.9 | 60.3 | 57.8 | ... | 56.9 | 51.7 | 59.7 | 98.7 | 61.1 | 55.1 | 56.3 | ... | 57.1(a) | ... | 62.1 | 57.1 | 51.1 | 51.0 | ... | 61.3 | ..... |
| Oil recovered (per cent) | ... | 31.2 | 43.7 | 21.1 | 20.9 | 20.9 | 47.4 | ... | 31.6 | 33.7 | 52.5 | 43.9 | 46.6 | 81.8 | 40.6 | ... | 53.6 | ... | 64.8 | 71.8 | 91.3 | 73.6 | ... | 75.4 | ..... |
| Carbon (per cent) | ... | 7.1 | 6.9 | 38.8 | 36.2 | 9.9 | 8.7 | ... | 26.7 | 27.5 | 19.3 | 16.2 | 12.3 | 13.6 | 21.1 | ... | 11.7 | ... | 14.5 | 10.1 | 3.7 | 11.9 | ... | 2.3 | ..... |
| Sp. gr. of oil recovered | ... | 1.025 | 1.017 | 1.022 | 1.025 | 1.092 | 0.963 | ... | 1.030 | 0.997 | 0.996 | 0.984 | 0.966 | 0.960 | 0.991 | ... | 0.942 | ... | 0.925 | 0.928 | 0.939 | 0.950 | ... | 0.924 | 0.950 |
| Viscosity | ... | ... | 3.95 | ... | ... | ... | ... | ... | ... | ... | 1.79(c) | 1.15(c) | 1.08(c) | ..... | ... | ... | 1.35(c) | ... | 1.35(c) | 1.53(c) | 6.16(c) | ... | ... | 2.71 | 35.7(c) |
| First drop | ... | ... | ... | 70° | 67° | 70° | ... | ... | 40° | 33° | 67° | 35° | 33° | ..... | 30° | ... | 33° | ..... | 35° | 38° | 50° | ... | ... | 40 | ..... |
| Temperature | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % | % |
| 100 | ... | 8.0 | 12.8 | 32.8 | 31.1 | 13.4 | 1.7 | ... | 11.3 | 21.3 | 11.0 | 16.8 | 8.3 | 3.3 | 12.5 | ... | 12.8 | ..... | 11.0 | 8.8 | 3.2 | 0.3 | ... | 4.3 | ..... |
| 150 | ... | 6.0 | 7.8 | 14.8 | 8.4 | 10.8 | 6.8 | ... | 22.7 | 17.5 | 11.5 | 19.2 | 14.8 | 3.2 | 17.3 | ... | 12.3 | ..... | 11.0 | 10.7 | 4.8 | 1.3 | ... | 8.2 | ..... |
| 200 | ... | 8.0 | 8.3 | 6.5 | 2.6 | 3.6 | 2.1 | ... | 4.7 | 5.3 | 7.0 | 7.3 | 8.0 | 4.0 | 8.2 | ... | 7.0 | ..... | 8.4 | 7.8 | 5.3 | 1.0 | ... | 5.5 | 1.8 |
| 250 | ... | 14.7 | 14.0 | 22.2 | 11.1 | 17.5 | 10.8 | ..... | 10.6 | 13.1 | 10.5 | 10.8 | 12.0 | 11.3 | 11.0 | ... | 12.3 | ..... | 10.7 | 9.8 | 8.8 | 5.3 | ... | 9.3 | 5.5 |
| 300 | ... | 9.0 | 10.0 | ... | ... | ... | 13.8 | ... | ..... | ..... | 14.0 | 10.0 | 15.5 | 9.7 | ..... | ... | ..... | ..... | 10.5 | 11.0 | 13.2 | 12.0 | ... | 11.8 | 10.0 |
| 150 | ... | 14.0 | 20.0 | 17.6 | 39.5 | 24.2 | 8.5 | ... | 34.0 | 38.8 | 22.5 | 35.7 | 22.8 | 6.5 | 29.8 | ... | 25.1 | ... | 22.0 | 19.2 | 7.7 | 1.8 | ... | 9.5 | ..... |
| 250 | ... | 22.7 | 22.3 | 28.7 | 13.7 | 21.1 | 17.9 | ... | 15.3 | 18.4 | 17.5 | 18.3 | 20.0 | 15.3 | 19.2 | ... | 19.3 | ... | 19.0 | 17.3 | 14.1 | 6.3 | ... | 11.8 | 7.3 |
| Temperature | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. | S. G. |
| 100 | ... | .864 | .849 | .852 | .879 | .870 | ..... | ... | .837 | .847 | .828 | .876 | .767 | .800 | .787 | ... | .736 | ... | .729 | .759 | .727 | ... | ... | .770 | ..... |
| 150 | ... | .861 | .859 | .849 | .864 | .875 | .814 | ... | .871 | .870 | .853 | .863 | .831 | .832 | .862 | ... | .828 | ... | .812 | .818 | .785 | .807 | ... | .793 | ..... |
| 200 | ... | .879 | .874 | .862 | .886 | .917 | .811 | ... | .908 | .893 | .870 | .887 | .861 | .847 | .894 | ... | .863 | ... | .848 | .858 | .824 | ... | ... | .825 | .806 |
| 250 | ... | .953 | .929 | Solid | Solid | Solid | .874 | ... | .990 | .980 | .922 | .952 | .902 | .883 | .966 | ... | .910 | ... | .891 | .893 | .865 | .848 | ... | .867 | .854 |
| 300 | ... | .962 | .963 | ..... | ..... | ..... | .906 | ... | ..... | ..... | .946 | .988 | .947 | .905 | ..... | ... | ..... | ... | .930 | .919 | .891 | .883 | ... | .891 | .886 |
| 150 | ... | .863 | .852 | .848 | .875 | .873 | .814 | ... | .862 | .867 | .842 | .847 | .808 | .817 | .829 | ... | .783 | ... | .776 | .794 | .765 | ... | ... | .764 | ..... |
| 250 | ... | .926 | .908 | ..... | ..... | ..... | .859 | ... | .964 | .953 | .903 | .926 | .884 | .873 | .936 | ... | .893 | ... | .852 | .876 | .848 | .845 | ... | .851 | .841 |

(a) 7 to 9 atmospheres.
(b) Viscous at 21°.
(c) 28 atmospheres.

necessary for the experiments at lower temperatures to have the furnace greatly superheated at the start in order to get the system up to the desired pressure before too large a proportion of the original charge of oil had been run through.

If a run at 500° and 24 atmospheres is taken as an example the following conditions obtained: the furnace was started at 650° and atmospheric pressure and oil run in till the pressure reached the desired height while, at the same time, the temperature was allowed to fall. In such an experiment it was necessary to run through from 150 to 200 grams of the total 600-gram charge of oil before desired conditions were established. It must be understood therefore that the percentage recoveries are invariably low for pressure reactions and that the error is considerable in the case of the lower temperatures.

The first point to be noted in the data is that the differences among original oils seem to have no marked influence over the magnitude of the percentage recoveries. There is an exception in the case of the Mexican crude where a large amount of the liquid product of reaction was held by the carbon deposit. Among the other oils the variations, though of some magnitude, are distributed with perfect impartiality. Thus the Pennsylvania recovered oils are liable to show either a maximum or a minimum percentage recovery.

It is indicated with entire definiteness in the tabulation of averages that percentage recovery decreases with increase of temperature. It appears also that vacuum recoveries are greater than those at atmospheric pressure. Indications for pressures above one atmosphere are not entirely correct on the basis of figures given here. It was noted, for instance, that in the case of a pressure reaction at 500° gas formation was practically nil after the initial period during which conditions were being established. In this case there should have been a recovery of practically 100 per cent as carbon is not formed in the absence of gas and the only possible products must have been liquid. The low yields here indicated were due to the preliminary cracking period during which pressure was low and temperature high. The indications for the effect of pressure at higher temperatures are undoubtedly correct, being in accord with theory and not explainable on the basis of any known experimental error.

TABLE IIB—RESULTS OF EXPERIMENTAL RUNS WITH RUSSIAN AND MEXICAN OILS

| | Russian Oil: | | | Mexican Oil | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature: | 675° | 500° | Orig. | 750 | 600 | 600° | 600° | 500 | 500 | 400 | Orig. |
| Pressure—Atmospheres | 12 atmos. | 12 atmos. | oil | Vac. | 12 | 1 at. | Vac | 12 | 1 | 10–11 | oil |
| Oil used (grams) | 443 | 387 | | 812 | 479 | 628 | 500 | 573 | 591 | 527 | |
| Oil recovered (per cent) | 28.3 | 77.3 | | 37.3 | 47.2 | 40.2 | 66.0 | 54.5 | 72.8 | 73.5 | |
| Carbon (per cent) | 21.7 | 0.0 | | 10.5 | 13.1 | 16.4 | 9.0 | 16.2 | 9.8 | 13.8 | |
| Sp. Gr. of oil recovered | .965 | .880 | .897 | .992 | .941 | .992 | .942 | .918 | .930 | .934 | 986 |
| Viscosity | | 1.44° | 11.92° | 2.70° | | 1.96° | 6.73° | 1.15° | 1.88° | 4.43° | Over 300° |
| First drop | 40° | 30° | | | 30° | 40 | 70° | 30° | 55° | 35° | |
| Temperature | % S. G. | % S. G. | % S. G. | % S. G. | % S. G. | % S. G. | % S. G. | % S. G. | % S. G. | % S. G. | % S. G. |
| 100 | 30.5 .863 | 7.3 .718 | 0.0 .... | 8.3 .822 | 13.3 .765 | 13.0 .802 | 2.3 .751 | 13.5 .721 | 7.0 .739 | 4.8 .729 | 0.0 .... |
| 150 | 16.1 .867 | 7.8 .796 | 0.0 | 5.0 .836 | 12.5 .829 | 8.3 .837 | 3.5 .782 | 13.3 .807 | 8.7 .792 | 6.0 .789 | 1.1 .759 |
| 200 | 4.7 .891 | 5.7 .829 | 1.5 | 7.7 .868 | 8.0 .846 | 9.2 .860 | 8.3 .811 | 11.0 .837 | 8.5 .825 | 7.0 .816 | 2.5 .798 |
| 250 | 13.9 Solid | 13.8 .856 | 10.7 .836 | 10.5 .915 | 11.0 .899 | 13.0 .923 | 10.5 .846 | 13.0 .884 | 12.5 .875 | 11.0 .856 | 8.3 .843 |
| 300 | 5.9 .964 | 16.5 .881 | 16.3 .859 | 14.5 .941 | 11.7 .943 | 12.5 .968 | 15.5 .880 | 12.2 .945 | 11.7 .902 | 13.7 .898 | 25.2 .871 |
| 150 | 46.6 .865 | 15.1 .761 | | 13.3 .827 | 25.8 .877 | 21.3 .816 | 5.8 .771 | 26.8 .766 | 15.7 .770 | 10.8 .762 | 1.1 .759 |
| 250 | 24.5 .... | 19.5 .846 | 12.2 .836 | 18.2 .897 | 19.0 .797 | 22.2 .909 | 18.8 .829 | 24.0 .862 | 21.0 .854 | 18.0 .843 | 10.8 .833 |

TABLE III CARBON FORMATION, PHYSICAL PROPERTIES AND PERCENTAGES OF OILS RECOVERED

| | Percentage of Carbon Formation | | | | | Properties of Oils Recovered | | | | | | | | | | Percentages of Oil Recovered | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Viscosities (Engler degrees) | | | | | Specific gravities | | | | | | | | | |
| Oil: | Pa. | Okla. | Cal. | Mex | Av. | Pa. | Okla. | Cal. | Mex. | Russ | Pa. | Okla. | Cal. | Mex. | Av. | Pa. | Okla. | Cal. | Mex. | Av. |
| Temp. ° C. / Pres. atm. | | | | | | | | | | | | | | | | | | | | |
| 850 1 | 7.4 | .. | .. | .. | 7.4 | .. | .. | | | .. | 1.026 | .... | .... | .... | 1.026 | 9.7 | .... | | | 9.7 |
| Vac. | .. | 5.8 | 7.1 | .. | 6.4 | .. | .... | | | .. | .... | 0.997 | 1.025 | .... | 1.011 | .. | 23.1 | 34.2 | | 28.6 |
| 800 Vac. | .. | 4.1 | 6.9 | .. | 5.5 | | 1.64 | 3.98 | | .. | .... | 0.963 | 1.017 | .... | 0.990 | .... | 29.3 | 43.7 | .. | 36.5 |
| 750 12 | 24.3 | 24.6 | 38.8 | .. | 29.2 | .. | .. | | | .... | 0.910 | 0.965 | 1.022 | .... | 0.965 | 15.9 | 20.2 | 21.1 | .. | 19.1 |
| 6 | 15.3 | 20.0 | 36.2 | .. | 23.8 | .. | .. | | | .... | 1.020 | 1.040 | 1.025 | .... | 1.028 | 16.9 | 22.2 | 20.9 | .. | 20.0 |
| 1 | 3.7 | 11.3 | 9.9 | | 8.3 | .. | .. | .... | .. | .. | 1.012 | 1.039 | 1.092 | .... | 1.048 | 16.5 | 17.5 | 20.9 | | 18.3 |
| Vac. | 16.1 | 4.1 | 8.7 | 10.5 | 13.1 | 1.04 | 1.44 | .... | 2.70 | .... | 0.905 | 0.925 | 0.963 | 0.992 | 0.946 | 33.9 | 51.7 | 47.4 | 37.3 | 42.6 |
| 650 Vac. | .. | 2.2 | .. | .. | 2.2 | .. | .. | .. | .. | .. | .... | .... | .... | .... | .... | .. | 88.7 | .. | .. | 88.7 |
| 600 24 | 7.5 | 17.2 | 26.7 | .. | 17.1 | .. | .. | .... | .. | .. | 0.962 | 1.008 | 1.030 | .... | 1.000 | 37.3 | 33.9 | 31.6 | | 34.2 |
| 18 | 5.3 | 13.2 | 27.5 | .. | 15.3 | 1.11 | 1.48 | 1.79 | | .. | 0.926 | 0.973 | 0.997 | .... | 0.965 | 40.5 | 35.6 | 33.7 | .. | 36.6 |
| 12 | 3.6 | 6.7 | 19.3 | 13.1 | 10.7 | 1.00 | 1.08 | 1.15 | .. | .... | 0.918 | 0.907 | 0.996 | 0.941 | 0.940 | 43.6 | 62.2 | 52.5 | 47.2 | 51.4 |
| 6 | 2.4 | 9.6 | 16.2 | .. | 9.4 | .. | 1.27 | 1.98 | 1.96 | .. | 0.885 | 0.931 | 0.984 | .... | 0.933 | 31.4 | 37.3 | 43.9 | .. | 37.5 |
| 1 | 0.6 | 3.1 | 12.3 | 16.4 | 8.1 | 1.04 | 7.29 | .... | 6.73 | .. | 0.840 | 0.906 | 0.966 | 0.992 | 0.926 | 59.9 | 50.8 | 46.6 | 40.2 | 49.4 |
| Vac. | 0.0 | .. | 13.6 | 9.0 | 7.5 | | | | | | 0.811 | 0.899 | 0.960 | 0.942 | 0.903 | 97.4 | 100.0 | 81.8 | 66.0 | 85.0 |
| 550 24 | .. | 9.2 | 21.1 | .. | 15.1 | | 1.05 | | | | .... | .... | 0.991 | .... | 0.991 | .... | 38.1 | 40.6 | .. | 39.3 |
| 18 | .. | 7.0 | .. | .. | 7.0 | .. | .. | .. | .. | .. | .... | 0.908 | .... | .... | 0.908 | .... | 55.0 | .. | .. | 55.0 |
| 500 24 | 1.2 | 4.6 | 11.7 | .. | 5.8 | 0.97 | 1.28 | 1.38 | | .. | 0.828 | 0.877 | 0.942 | .... | 0.882 | 72.5 | 63.8 | 53.6 | .. | 63.3 |
| 18 | 0.0 | .. | .. | .. | 0.0 | 0.96 | .. | .. | .. | .. | 0.819 | .... | .... | .... | 0.819 | 79.4 | .. | .. | .. | 79.4 |
| 12 | 0.0 | 1.4 | 14.5 | 16.2 | 8.0 | 0.98 | 1.32 | 1.35 | 1.15 | 1.44 | 0.808 | 0.870 | 0.925 | 0.918 | 0.880 | 84.2 | 88.2 | 64.8 | 54.5 | 72.9 |
| 6 | 0.0 | 1.2 | 10.1 | .. | 3.8 | 1.00 | 1.54 | 1.52 | | .. | 0.810 | 0.867 | 0.928 | .... | 0.868 | 57.8 | 91.8 | 71.5 | .. | 73.7 |
| 1 | 0.0 | 0.0 | 3.7 | 9.8 | 3.6 | 1.00 | 2.51 | 6.16 | 1.88 | .. | 0.799 | 0.872 | 0.939 | 0.930 | 0.885 | 94.5 | 99.0 | 91.3 | 72.8 | 89.4 |
| Vac. | 6.0 | 0.0 | 11.9 | | 5.9 | 1.04 | 13.42 | .. | .. | .. | 0.802 | 0.901 | 0.950 | .... | 0.884 | 100.0 | 99.8 | 73.6 | .. | 91.1 |
| 450 18 | .. | 0.0 | .. | .. | 0.0 | .. | 1.50 | 2.71 | .. | .. | .... | 0.882 | .. | .. | 0.882 | .. | 76.9 | .. | 73.5 | 75.2 |
| 12 | .. | .. | .. | .. | .. | 1.02 | 1.73 | .... | 4.43 | .. | .... | .. | .. | .. | .... | .... | .. | .. | .. | .. |
| Original | .. | .. | .. | .. | .. | 1.05 | 35.40 | 35.7 | Over 350 | 11.92 | .... | .. | .. | .. | .... | .... | .. | .. | .. | .. |

| Average Percentages Carbon Formation | | | | | | Viscosities for Oklahoma Series | | | | | | Average Specific Gravities of Recovered Oils | | | | | | Average Percentages of Oil Recovered | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pres. atm. / Temp. | Vac. | 1 | 6 | 12 | 18 | 24 | Vac. | 1 | 6 | 12 | 18 | 24 | Vac | 1 | 6 | 12 | 18 | 24 | Vac. | 1 | 6 | 12 | 18 | 24 |
| 450° | .. | .. | .. | 2.5 | 0.0 | | | | | 1.73 | 1.50 | | | | | 0.868 | 0.882 | .... | | | | 85.4 | | |
| 500° | 5.9 | 3.6 | 3.8 | 8.0 | 0.0 | 4.8 | 13.42 | 2.51 | 1.54 | 1.32 | .. | 1.25 | 0.884 | 0.885 | 0.868 | 0.880 | 0.819 | 0.882 | 91.1 | 89.4 | 73.7 | 72.9 | 79.4 | 63.3 |
| 550° | .. | .. | .. | 7.0 | 15.1 | | .. | .. | .. | .. | .. | 1.05 | .. | .. | .. | 0.908 | 0.991 | | .. | .. | .. | .. | .. | 39.5 |
| 600° | 7.5 | 8.1 | 9.4 | 10.7 | 15.3 | 17.1 | 7.29 | 1.27 | 1.08 | 14.8 | | | 0.903 | 0.926 | 0.933 | 0.940 | 0.965 | 1.000 | 85.0 | 49.4 | 37.5 | 51.4 | 36.6 | 34.2 |
| 650° | 2.2 | .. | .. | .. | .. | | .. | .. | .. | .. | .. | | .... | .... | .... | .... | .... | | 88.7 | .. | .. | .. | .. | |
| 750° | 13.1 | 8.3 | 23.8 | 29.2 | .. | .. | 1.44 | | | | | | 0.946 | 1.048 | 1.028 | 0.965 | .... | | 42.6 | 18.3 | 20.0 | 19.1 | | |
| 800° | 5.5 | .. | .. | .. | .. | .. | 1.64 | | | | | | 0.990 | .... | .. | .. | .. | .. | 36.5 | .. | .. | .. | | |
| 850° | 6.4 | 7.4 | | | | | | | | | | | 1.011 | 1.026 | | | | | 28.6 | 9.7 | | | | |

### FORMATION OF GASOLINE AND AROMATIC HYDROCARBONS

GASOLINE FORMATION—From both a scientific and a commercial point of view the most important factors to be considered in the cracking reaction are the physical and chemical relations between original and recovered oils. The chief commercial interest in the cracking reaction has of late centered on the problem of gasoline production. It is rather a difficult matter to establish a satisfactory definition of gasoline and for present purposes it is unnecessary, as the differences obtained among reaction products have been so great that no fine distinctions are necessary. In the present connection the magnitude of the distillation cut up to 150° C. has been considered a measure of the "naphtha" or "gasoline." On this basis the amount of gasoline production has been figured for the different runs and results listed in Table IV. The calculations from experimental figures were conducted as follows. The amount of oil in the original sample distilling below

TABLE IV—FORMATION OF GASOLINE AND AROMATICS

| Temp. °C. | Pressure | Percentage Gasoline Formation Pa. | Okla. | Cal. | Mex. | Av. | Formation of Low Boiling Aromatic Hydrocarbons Pa. | Okla. | Cal. | Mex. | Av. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 850 | 1 | 2.3 | .. | .. | .. | 2.3 | 2.4 | . | . | ... | 2.4 |
| | Vac. | . | 4.2 | 4.8 | .. | 4.5 | . | 4.1 | 4.4 | . | 4.3 |
| 800 | Vac. | . | 5.6 | 8.8 | . | 7.2 | . | 4.6 | 7.1 | . | 5.9 |
| 750 | 12 | 5.5 | 8.8 | 10.0 | .. | 8.1 | 5.6 | 7.7 | 8.0 | .. | 7.1 |
| | 6 | 6.2 | 5.8 | 8.2 | .. | 6.7 | 6.8 | 5.9 | 7.9 | .. | 6.9 |
| | 1 | 4.3 | 4.7 | 5.1 | . | 4.7 | 5.1 | 4.7 | 5.0 | . | 4.9 |
| | Vac. | 4.5 | 7.5 | 4.0 | 4.6 | 5.1 | 4.1 | 4.2 | 2.2 | 2.9 | 3.4 |
| 650 | Vac. | . | 3.0 | . | .. | 3.0 | . | 1.4 | . | . | 1.4 |
| 600 | 24 | 13.3 | 12.9 | 10.7 | .. | 12.3 | 12.4 | 11.2 | 9.7 | . | 11.1 |
| | 18 | 15.8 | 16.6 | 13.0 | . | 15.1 | 13.4 | 14.0 | 12.3 | ... | 13.1 |
| | 12 | 16.3 | 12.1 | 11.8 | 11.6 | 12.9 | 13.4 | 6.9 | 8.8 | 4.1 | 8.3 |
| | 6 | 10.0 | 14.1 | 15.7 | . | 13.3 | 7.1 | 9.8 | 12.2 | . | 9.7 |
| | 1 | 13.4 | 12.7 | 10.6 | 8.1 | 11.2 | 7.3 | 5.8 | 5.1 | 4.3 | 5.6 |
| | Vac | 0.0 | 2.5 | 5.3 | 3.1 | 3.6 | 1.0 | 1.1 | 3.0 | 0.4 | 1.4 |
| 550 | 24 | . | 12.4 | 12.1 | .. | 12.3 | . | 4.7 | 7.7 | . | 6.2 |
| | 18 | | 17.3 | | .. | 17.3 | | 7.3 | | . | 7.3 |
| 500 | 24 | 18.1 | 14.0 | 13.5 | .. | 15.2 | 7.0 | 2.1 | 4.2 | . | 4.4 |
| | 18 | 15.3 | 13.8 | .. | .. | 14.6 | 5.6 | . | . | . | 5.6 |
| | 12 | 16.0 | 10.9 | 14.3 | 14.6 | 13.7 | 5.6 | 1.8 | 3.7 | 0.9 | 3.0 |
| | 6 | 5.9 | 4.7 | 13.7 | 10.6 | 8.7 | 2.6 | . | 5.4 | ... | 4.0 |
| | 1 | 2.7 | 0.0 | 7.0 | .. | 4.9 | 1.8 | 0.6 | 1.2 | 1.1 | 1.2 |
| | Vac. | 0.0 | | 1.1 | .. | 1.1 | 0.7 | . | | | 0.7 |
| 450 | 18 | . | 9.4 | | .. | 9.4 | | 3.3 | .. | | 3.3 |
| | 12 | 6.5 | 8.8 | 7.2 | . | 7.5 | 2.9 | 1.3 | 1.1 | | 1.8 |
| 400 | 10 | .. | .. | .. | 7.1 | 7.1 | .. | . | . | 0.2 | 0.2 |

| Pres. atm. Temp. | Average Percentages Gasoline Formation Vac. | 1 | 6 | 12 | 18 | 24 | Average Low-Boiling Aromatic Hydrocarbons Vac. | 1 | 6 | 12 | 18 | 24 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 450° | | | | 7.5 | 9.4 | .. | . | ... | ... | 1.8 | 3.3 | |
| 500° | 1.1 | 4.9 | 8.7 | 13.7 | 14.6 | 15.2 | 0.7 | 1.2 | 4.0 | 3.0 | 5.6 | 4.4 |
| 550° | . | ... | ... | . | 17.3 | 12.3 | . | . | . | . | 7.3 | 6.2 |
| 600° | 3.6 | 11.2 | 13.3 | 12.9 | 15.1 | 12.3 | 1.4 | 5.6 | 9.7 | 8.3 | 13.1 | 11.1 |
| 650° | 3.0 | . | . | . | . | .. | 1.4 | . | . | . | . | . |
| 750° | 5.1 | 4.7 | 6.7 | 8.1 | . | . | 3.4 | 4.9 | 6.9 | 7.1 | . | . |
| 800° | 7.2 | .. | | | | | 5.9 | ... | . | . | | |
| 850° | 4.5 | 2.3 | | | | | 4.3 | 2.4 | . | . | | |

the 150° mark was deducted from the distillation figure for the recovered oil. This last corrected percentage was reduced to terms of the original oil, giving a percentage which represents its degree of transformation into hydrocarbons boiling below 150° C.

Thus for example, in the case of an experiment at 500° and 12 atmospheres with Pennsylvania oil the distillation cut given in Table I is 23.8 per cent up to 150°. The original oil distilled 4.8 per cent up to the same temperature. The increase is therefore 19.0 per cent. But of the original oil only 84.2 per cent was recovered and the gasoline formation was therefore 84.2 per cent of 19.0, or 16.0 per cent.

An examination of the results shows first of all a remarkable agreement among the effects of the same conditions of temperature and pressure on the different original oils. The comparison of the average percentages indicates that the formation of a large percentage of hydrocarbons boiling below 150° C. is favored by pressure and that the optimum temperatures are in the neighborhoods of 500° and 600°. It is not, however, sufficient to limit our considerations to the data appearing in Table IV. There are vast physical and chemical differences between cuts of approximately the same magnitude formed respectively at 500 and 600° as will be noted when a comparison is made of the figures for specific gravities.

DIFFERENCES IN SPECIFIC GRAVITY OF CUTS TO 150° FROM RUNS AT LIKE PRESSURES AND TEMPERATURES 600 AND 500°

| Pressure | Pennsylvania | Oklahoma | California | Mexican |
|---|---|---|---|---|
| Vac. | 0.009 | | | |
| 1 | 0.032 | 0.046 | 0.043 | 0.046 |
| 6 | 0.042 | 0.081 | 0.051 | |
| 12 | 0.070 | 0.061 | 0.056 | 0.032 |
| 18 | 0.086 | | | |
| 24 | 0.088 | 0.111 | 0.053 | |

The above is a list of these density differences between distillates obtained from runs at the same pressures and at temperatures respectively of 600 and 500°. The gravities of the 600° products are invariably the higher. It will be noted also that the 600° products represent a large percentage of a small recovery while the reverse is the case for 500° products. *In addition it must be remembered that the inherent error of operation made low the amounts of gasoline recovered for pressure runs.*

The obvious conclusion is that the favorable conditions for producing gasoline, as determined by the comparison of results of the present series of experiments, involve a moderate temperature and a high pressure.

FORMATION OF AROMATIC HYDROCARBONS—It has long been known that aromatic hydrocarbons may result from the cracking of petroleum. A recent study[1] of the properties of gas oils and derived tars has demonstrated this fact again with entire definiteness, and the present experiments have served to determine only what are the most favorable conditions for this type of transformation.

As was indicated in the preceding section the characteristic property of aromatic hydrocarbons is their great density. Benzene, which boils at 80.5°, has a specific gravity of 0.883 and toluene, with a boiling point of 111°, has a gravity of 0.872. Paraffin or olefin hydrocarbons of equivalent boiling points possess much lower gravities. This is indicated by the following figures for straight chain hydrocarbons boiling at temperatures slightly higher than those required for benzene and toluene.

| Hydrocarbon | Boiling point | Specific gravity |
|---|---|---|
| Heptane | 98.0 | 0.712 |
| Octane | 125.5 | 0.708 |
| Heptylene | 98.0 | 0.703 |
| Octylene | 123.0 | 0.721 |

The quantitative separation of the different groups of hydrocarbons is not a process which can be conducted with ease and accuracy. There are chemical methods which have been recommended and these have been tried with results which have appeared in another communication. For present purposes the indications furnished by specific gravity measurements have been found sufficiently clear-cut to differentiate results with a satisfactory degree of accuracy.

[1] Rittman and Egloff, THIS JOURNAL, 7 (1915), 481.

A scheme has been devised for the approximate calculation of the percentage formation of hydrocarbons of the aromatic series, boiling below 150°. The assumption has been made that the average gravity of the mixed aromatics benzene, toluene and the three xylenes is 0.875. This figure is undoubtedly very near the true value and is justified by the results obtained through its use. By studying some results of a previous paper[1] it was learned that with the methods of distillation here employed the average specific gravities of 150° distillation cuts of uncracked oils are as follows:

| Pennsylvania | Oklahoma | California | Mexican |
|---|---|---|---|
| 0.721 | 0.734 | 0.742 | 0.759 |

Using these figures in connection with a value of 0.875 for the mixed aromatics a series of calculations was conducted and values obtained for the percentage formation of low-boiling aromatic hydrocarbons.

The following example is typical of one of the less favorable runs. For a California (Kern River) oil, cracked at 600° and 12 atmospheres the percentage recovery was 52.5 per cent and this oil gave be'ow 150° a 22.5 per cent distillation cut of gravity 0.842. The last figure, according to the scheme indicated above represents a mixture containing 75 per cent of the aromatics. The total aromatic formation was therefore $75 \times 22.5 \times 52.5$ per cent or 8.3 per cent on the basis of the original oil.

Figures obtained in this way are shown in Table IV and again there appears an excellent agreement among the different original oils. The variations are moderate and are not characteristic. In consideration of the several approximations and the inherent experimental errors the agreement may be considered as striking. Again there is proof that the conditions of treatment are of such importance that any original tendencies on the parts of the oils used are rendered of negligible importance.

It will be noted from the average figures for low-boiling aromatics in Table IV, that most favorable conditions for the formation of benzene, toluene and xylenes seem to be 600° and above and at pressures greater than 4 atmospheres.

SUMMARY

Results of experiments here described have indicated the following conclusions:

I—Equilibrium products of the cracking reaction seem to be independent of the influence of chemical and physical properties of the original oils or at most are affected only in minor degree by such tendencies. The matter of carbon formation is the one clear-cut exception. Carbon is a residual product and its formation is proportional to the amount originally contained in the oil. Viscosities and specific gravities seem to show in slight degree the influence of properties of original oils but the differences are so slight that they may well be explained on the basis of failure to reach complete equilibrium.

II—The formation of aromatic hydrocarbons occurs best at moderate to high temperatures and under high pressure.

III—The formation of gasoline (low-boiling, low gravity hydrocarbons) is favored by moderate to low temperatures and by high pressure.

IV—The results obtained by the series of laboratory experiments indicate striking commercial possibilities.

The experimental work connected with this paper was carried out in the laboratories of the Department of Industrial Chemistry of Columbia University, New York.

CHEMICAL SECTION OF PETROLEUM DIVISION
U. S. BUREAU OF MINES, PITTSBURGH

[1] Rittman and Egloff, THIS JOURNAL, **7** (1915), 578.

## A QUANTITATIVE METHOD FOR THE DETERMINATION OF THE ADULTERATION IN CHINESE WOOD OIL[1]

By J. C. BRIER

Received October 5, 1915

Examination of a large number of shipments of Chinese wood oil extending over a period of several years, each shipment being checked against its behavior in the varnish kettle, has convinced the writer that the advocated methods of testing Chinese wood oil, while affording valuable indications in certain cases, can be used with any degree of accuracy only on grossly adulterated oils.

Hoffman[2] reports that the adulteration of wood oil with foreign oils was very common in China in former years and that the oils, pressed in China, hardly ever reached the market in a pure state. According to him, oil from the kernel of the vegetable tallow seed, especially, was employed for the fraudulent blending of wood oil. Boughton[3] states that Chinese wood oil is frequently adulterated with soya bean oil. From numerous inquiries the writer believes that the larger amount of intentional adulteration is confined to the use of these two oils, but that frequent accidental adulteration happens with ground nut oil, sesame oil, and occasionally, with tea seed and perilla oils. Importers, who are familiar with the production of Chinese wood oil and the various stages and methods of its transportation until barreled ready for export, have informed the writer that adulteration, although not nearly as prevalent as at the time at which Hoffman wrote, is still exceedingly common.

It is well known that the oil is obtained from a large number of small producers by the middlemen or merchants, who transport it in baskets made of bamboo lined with oiled paper (the average capacity of these baskets being approximately 17 gallons). The native boats, which transport the oil to the export markets, frequently carry mixed cargoes of the oils occurring in that section of China where Chinese wood oil is produced. The frail baskets being piled on top of each other often become leaky, thus allowing the oils from the upper baskets to contaminate the contents in the others. Then, too, the oils that drip on the floor are collected and distributed among the various baskets throughout the cargo. Such cases as those just cited make it difficult for the Chinese wood oil importers to be sure as to the purity of the oil they are buying,

[1] This method was developed in collaboration with Dr. C. D. Holley in the Research Laboratory of the Acme White Lead and Color Works.

[2] *Seifensieder Zeit.*, **35** (1908), 169.

[3] *Drugs, Oils and Paints*, **29**, 252–256

since the methods of detecting adulteration are so unsatisfactory.

The demand for Chinese wood oil for the manufacture of varnishes has increased very rapidly during recent years owing to the fact that with certain gums, as well as rosin, this oil, when properly manipulated, gives a very high-grade product for certain uses. Since slight variations in the purity of the oil affect the finished product it is necessary that the varnish maker have a uniform grade of oil, otherwise every shipment will mean an experimental batch.

### METHODS OF EXAMINATION

The oldest method for testing Chinese wood oil is the practical kettle test. This, however, is hardly feasible when one considers that large plants use from 100 to 300 or more barrels per month.

The methods of Bacon, Worstall, Potsdammer, Browne and others,[1] are based on the well-known characteristic that Chinese wood oil has of polymerizing when heated to 280° C.

Other methods of testing Chinese wood oil are the McIlhiney,[2] the iodine jelly[3] and the Ware Schumann.[4]

The urgent need for standardizing the methods of testing Chinese wood oil, led Sub-committee D1 of the American Society for Testing Materials to take up the problem. Their work has covered a period of several years and the various methods have been tried out. However, specifications for raw Chinese wood oil were not proposed until the report of the committee was given at the meeting of the society held June 22, 1915. These specifications were based on the analytical constants which had been determined in previous years along with the modified Browne's method and the modified iodine jelly test, which were reported on at this time. The work for this year was done on the following five samples:

| Oils | Per Cent Present in Sample No. 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Pure China wood oil | 100 | 95 | 90 | 95 | 90 |
| Soya bean oil | | 5 | 10 | | |
| Linseed oil | | | | 5 | 10 |

From the results obtained by the various operators on these samples the time limit at or under which pure oil should polymerize was specified as 12 minutes when using the Browne test, while a time limit of four minutes was specified for the setting period in the iodine jelly test.

The wide variations in the results obtained by the different members of the committee indicate the necessity of working both the tests against standards, and not to a time limit as proposed in the specifications. A brief résumé of the results obtained show the large personal equation involved:

(*a*)—Accepting the 12-minute time limit in the case of the Browne test, at or under which the oil is to be considered acceptable, and above which it is to be rejected, the pure sample should be rejected by one operator, the sample adulterated with 5 per cent soya bean oil should be accepted by 5 operators and the sample adulterated with 10 per cent soya bean oil should be accepted by one operator. The sample adulterated with 5 per cent linseed oil is acceptable by the reports of 3 operators.

(*b*)—Accepting the time limit of 4 minutes, as is specified in the case of the iodine jelly test, 6 out of the 9 operators reporting gave figures below the time limit on sample No. 2. With sample No. 4, the same 6 operators gave in their reports figures which were below the accepted time limit for pure Chinese wood oil.

The contention that all tests on shipments of wood oil should be made against standards is further supported by the supplementary report of Boughton (meeting held June 22, 1915), which shows that variations in temperature of the bath, the weight of oil used, the amount of chloroform taken, and the strength of the iodine solution, cause large differences in the results obtained.

The index of refraction has been reported as giving valuable information as to the purity of Chinese wood oil by Wise,[1] Chapman,[2] Hoepfner and Burmeister,[3] and Boughton.[4] Dr. Holton[5] noticed, while working with the Abbey instrument on the index of refraction, that it was necessary to set the compensator at an abnormal point when taking readings on Chinese wood oil.

Shook,[6] while working on the dispersion of various oils with the Pulfrich refractometer, noticed that Chinese wood oil showed anomalous dispersion; *i. e.*, while the spectrum of all the other oils appeared with the red on the upper side and the green and blue on the lower side (Fig. 1), Chinese wood oil completely reversed this condition, showing the blue and green on top with the red on the lower side of the spectrum (Fig. 2). This phenomena probably accounts for the observations made by Holton.

FIG. 1 SPECTRUM SHOWING NORMAL DISPERSION

FIG. 2 SPECTRUM SHOWING ANOMALOUS DISPERSION (CHINESE WOOD OIL)

FIG. 3 APPEARANCE OF SPECTRUM AT TURNING POINT.

### APPARATUS

The principle used is that of the Pulfrich refractometer. The essential features of the apparatus are as follows: Referring to Fig. 4, *X* is the source of light and in this work was a tungsten light. *L* is a condensing lens. The prism *P*, the most essential part of the apparatus, is a 90° prism having an index of refraction of 1.62. The cell *C*, in which the oils were placed, is so mounted on the prism that the upper surface of the prism is above the joining of the cell and prism. The telescope *T*, which picks up

[1] Boughton, "Testing of Chinese Wood Oil," *Proc. Am. Soc. Test. Materials*, **13** (1913), 923.

[2] THIS JOURNAL, **4** (1913), 496-497.

[3] *Proc. Am. Soc. Testing Materials*, **1914**, 242.

[4] THIS JOURNAL, **6** (1914), 806.

[1] *J. Soc. Chem. Ind.*, **4** (1912), 497.

[2] *Analyst*, **37** (1912), 543.

[3] *Chem. Zeit.* (**1913**), No. 2, 18.

[4] *Drugs, Oils and Paints*, **29**, 252–256.

[5] Private communication to Dr. C. D. Holley, Chief of this Laboratory.

[6] *Met. and Chem. Eng.*, Oct., 1915, and also private communication.

the spectrum, is bent at a right angle of 90° between the objective *O* and the eyepiece *e* for convenience in observing the spectrum.

EFFECT OF DIFFERENT OILS ON THE SPECTRUM OF CHINESE WOOD OIL

Additions of linseed oil to Chinese wood oil up to about 8 per cent show very little change in the spectrum. Beginning with 9 per cent adulteration, the yellow becomes more pronounced while the red begins to disappear. However, when the adulteration reaches 10 per cent, the green takes the form of a more distinct band with the red slowly decreasing in intensity. With 11 per cent adulteration, the green band becomes more marked and the line of demarcation from the yellow is much sharper than with 10 per cent adulteration. The red shows now only to a very limited degree. The addition of 12 per cent linseed oil to the Chinese wood oil shows a spectrum consisting of only two colors, green and yellow, which appear as very distinct bands of about the same width, the green still remaining upon the upper side. The appearance of the bands with 13 per cent adulteration is very little different from that with 12 per cent, the green, however, being a trifle less distinct. With 13.5 per cent the conditions remain practically the same, while with 14 per cent and 14.5 per cent the green shows very indistinctly, and when 15 per cent linseed oil has been added, only a distinct yellow band can be seen. The next change noted, occurring with 15.5 per cent adulteration, is the red beginning to appear in a distinct narrow band on the upper side of the spectrum. This is the most noticeable change and the one most readily observed, and in the work which follows this point is called the "turning point" (Fig. 3). Further additions of linseed oil increase first the distinctness of the red, and when about 16 to 16.5 per cent has been added, the green begins to appear. From this point on the colors gradually develop until finally the spectrum has been completely and distinctly reversed.

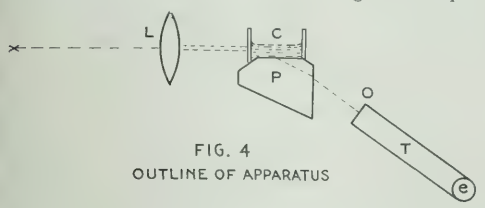


FIG. 4
OUTLINE OF APPARATUS

All other oils used as adulterants of Chinese wood oil affected its spectrum in the same manner, the changing point varying over a range of 2.5 per cent depending on the particular oil used. To illustrate: light tallow seed oil and perilla oil begin to affect the spectrum of Chinese wood oil at about 9 per cent, while the "turning point" is at 17 per cent adulteration. On the other hand, with ground nut, cotton seed, sesame and rape oils this effect is first noticed at a little below 7 per cent and the "turning point" takes place with 14.5 per cent adulteration. Candle nut, linseed, poppy seed, dark tallow seed, and soya bean oils affect the spectrum of Chinese wood oil at a point about midway between the cases just cited, the "turning point" taking place with 15.5 per cent adulteration in the case of poppy seed, linseed, and candle nut oils, with 16 per cent of dark tallow seed, and with 15 per cent adulteration of soya bean oil.

TABLE I APPEARANCE OF THE SPECTRA OF ADULTERATED CHINESE WOOD OIL AT 25° C.

| Adulterant Present Per cent by weight | Tallow Oil (Light) | Seed Oil (Dark) | Perilla Oil | Candle Nut Oil | Linseed Oil (Raw) | Linseed Oil (Refined) | Poppy Seed Oil | Soya Bean Oil | Sesame Oil | Ground Nut Oil | Cotton-Seed Oil | Rape Oil |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 13.5 | | | | | | | | Green Yellow | Green Yellow | Green Yellow | Green Yellow | Green Yellow |
| 14.0 | | | | Green Yellow | Green Yellow | Green Yellow | Green Yellow | Green Yellow | | | | Yellow |
| 14.5 | | | | Green Yellow | Green Yellow | Green Yellow | Green Yellow | | Red Yellow | Red Yellow | Red Yellow | Red Yellow |
| 15.0 | | Green Yellow | | Yellow | Yellow | Yellow | Yellow | Red Yellow | | | | |
| 15.5 | Green Yellow | Green Yellow | Green Yellow | Red Yellow | Red Yellow | Red Yellow | Red Yellow | | | | | |
| 16.0 | Green Yellow | | Green Yellow | | | | | | | | | |
| 16.5 | | Red Yellow | | | | | | | | | | |
| 17.0 | Red Yellow | | Red Yellow | | | | | | | | | |

Table I shows the effect of the individual adulterants on the spectrum of Chinese wood oil at varying percentages just below and at the "turning point."

Reading from top to bottom, it will be noticed that at 0.5 per cent below the "turning point" the spectrum showed, in each case, only a yellow band, while, with an adulteration of one per cent less than this, the spectrum showed two bands, namely, green and yellow. In all cases these bands were very definitely divided and not blended one with the other.

TABLE II—APPEARANCE OF SPECTRA OF ADULTERATED CHINESE WOOD OIL

| Adulterant Per cent by weight 20° C. | 30° C. | Tallow Seed Oil (Dark) | Linseed Oil (Raw) | Soya Bean Oil | Cotton-Seed Oil | Ground Nut Oil | Sesame Oil |
|---|---|---|---|---|---|---|---|
| 13.75 | 12.25 | | | | Green Yellow | Green Yellow | Green Yellow |
| 14.25 | 12.75 | | | Green Yellow | Green Yellow | Green Yellow | Green Yellow |
| 14.75 | 13.25 | | Green Yellow | Green Yellow | Yellow | Yellow | Yellow |
| 15.25 | 13.75 | | Green Yellow | Yellow | Red Yellow | Red Yellow | Red Yellow |
| 15.75 | 14.25 | Green Yellow | Yellow | Red Yellow | | | |
| 16.25 | 14.75 | Green Yellow | Red Yellow | | | | |
| 16.75 | 15.25 | Yellow | | | | | |
| 17.25 | 15.75 | Red Yellow | | | | | |

Temperature influences the effect of the adulteration on the spectrum of Chinese wood oil to a very marked degree. However, this factor seems to be the same for each of the oils used. For example:

the "turning point" with soya bean oil at 25° C. takes place with 15 per cent adulteration, at 20° C. with 15.75 per cent adulteration, and at 30° with 14.25 per cent adulteration. With linseed oil the "turning point" at 25° C. takes place with 15.5 per cent, at 20° C. with 16.25 per cent, and at 30° C. with 14.75 per cent adulteration. A comparison of Tables I and II clearly shows the influence of temperature on the spectrum at the different adulterations.

It is obvious from these results that either a correction for temperature should be made when making a determination, or, better, all readings should be made at one temperature. In the remainder of the work this latter plan has been adopted.

Up to this point in the investigation the work has been carried on using only one sample of Chinese wood oil. This oil is No. 1 in Table III, which shows the effect on the spectra of different Chinese wood oils when the same soya bean oil is used as an adulterant. It will be noticed that the "turning point"

TABLE III

| Soya Bean Oil Per cent by weight | Appearance of the Spectra of different Chinese Wood Oils Adulterated with Soya Bean Oils | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 13.0 | ..... | ..... | ..... | Green | ..... | Green | Green |
| | ..... | ..... | ..... | Yellow | Yellow | Yellow | Yellow |
| 13.5 | Green | Green | Green | Green | Red | Green | Green |
| | Yellow | Yellow | Yellow | Yellow | Yellow | Yellow | Yellow |
| 14.0 | Green | Green | Green | ..... | ..... | ..... | ..... |
| | Yellow | Yellow | Yellow | Yellow | ..... | Yellow | Yellow |
| 14.5 | ..... | ..... | ..... | Red | ..... | Red | Red |
| | Yellow | Yellow | Yellow | Yellow | ..... | Yellow | Yellow |
| 15.0 | Red | Red | Red | ..... | ..... | ..... | |
| | Yellow | Yellow | Yellow | ..... | ..... | ..... | |

in the cases of oils 1, 2 and 3 takes place at the same point, that is, with an adulteration of 15.0 per cent, in the cases of oils 4, 6 and 7 with 14.5 per cent, and with oil 5, the poorest one given in the table, with 13.5 per cent.

Samples 1, 2, 3, 5, 6 and 7 were taken from shipments covering a period of two years and from different importers. Sample No. 4 was furnished to Dr. C. D. Holley by Mr. E. W. Boughton and is the *Aleurites fordii* used by him in his investigations on the various oils from the Orient. In actual use, oil No. 5 proved to be inferior to oils 1, 2, 3, 6 and 7.

Of the oils mentioned above, the ones generally supposed to be used as adulterants are soya bean, tallow seed, sesame, and occasionally ground nut and candle nut oils. It has been pointed out that the effect on the spectrum of Chinese wood oil when adulterated with these oils is to cause the "turning point" to take place at adulterations varying between the limits of 14.5 to 17.0 per cent. As a working basis for an analytical method, the writer assumes an arbitrary adulteration of 15.5 per cent, at which the "turning point" will take place, *i. e.*, when the red first appears on the upper side of the spectrum.

## ANALYTICAL METHOD

Since 15.5 per cent of linseed oil in Chinese wood oil causes the "turning point" to take place, it is used as the oil to be added when necessary to bring about the "turning point."

The author's procedure is as follows: First a sample of the oil in question is placed in the cell and its spectrum examined. If the oil is pure, or contains less than 8 per cent of adulteration, the spectrum will be inverted and appear practically the same in all cases. If the percentage of adulteration is over 8 per cent and under the "turning point" (15.5 per cent), the spectrum will appear as previously described for the various adulterations within these limits. By this means one may get a clue as to about what the adulteration is. If the first observation indicates that the oil is pure, or contains less than 8 per cent adulteration, 15 per cent of linseed oil is added. Then, if the oil in question is pure, only the yellow band will be visible in the spectrum, and as a check, the writer at this point then makes another observation on a sample of the oil adulterated with 15.5 per cent of linseed oil, and if the red now appears on the upper side of the spectrum, the sample of Chinese wood oil may be considered pure beyond question. If, on the other hand, the spectrum has reversed to the normal it is evident that the oil is adulterated, since more than 15 per cent of foreign oil is required to bring this reversal about. The amount of adulteration will, however, not exceed 8 per cent, as shown by the preliminary examination. The depth of the colors of the spectrum will give some idea as to whether or not the adulteration is very small or quite large. If the green is very indistinct the adulteration will probably not be over two per cent. However, if more than two per cent of adulteration is present, the colors will be more intense, since the intensity of both the green and the red vary directly with the adulteration when over 15.5 per cent foreign oil is present. In order to determine the percentage it is necessary to find out how much adulterant must be added before the "turning point" is reached, then, by subtracting the amount added from 15.5, the amount present in the oil may be obtained.

If the preliminary examination shows the adulteration to be between the limits of 8 per cent and 15.5 per cent, successive additions of the adulterating oil are added to the sample in question until the "turning point" has been reached. Then by subtracting the amount added from the arbitrary figure, 15.5 per cent, the amount of adulteration in the Chinese wood oil is obtained, as in the case when the foreign oil present is less than 8 per cent. This procedure is best illustrated by concrete examples.

1—A sample of oil which was rejected on the kettle test during the past year, was examined as follows: the oil when placed in the cell for preliminary examination showed the characteristic spectrum of pure Chinese wood oil, or of an oil not adulterated over 8 per cent. Upon adding 15 per cent of linseed oil the spectrum was observed to have been completely reversed, showing the colors red, yellow and green comparatively strong, thus indicating that the oil contained about 5 to 8 per cent adulteration. Seven per cent of linseed oil was then added to the original sample. The spectrum of the oil thus adulterated showed a distinct green band on top with a yellow band on the bottom, indicating that sufficient adulterant had not

been added. When a sample of the original oil to which 8 per cent of linseed oil had been added was examined, its spectrum showed only a yellow band; 8.5 per cent of linseed oil was then added to the original sample and the observation made; the "turning point" was now reached, shown by the characteristic red band appearing on the upper side of the spectrum. Subtracting the amount added, 8.5 per cent, from the arbitrary figure 15.5 per cent, it is evident that the sample in question contained 7 per cent adulteration.

2—Another sample taken from a rejected shipment, when first observed in the cell, showed a spectrum which was deficient in the red. It was therefore thought to contain about 10 per cent adulteration. When 6 per cent of linseed oil was added to this sample, the spectrum appeared only as a yellow band, and when 6.5 per cent of adulterant was added to the sample in question the red appeared on the upper side of the spectrum. Subtracting 6.5 from 15.5 the adulteration was shown to be 9 per cent.

3—Another sample, taken from a rejected shipment, when examined by this method, showed an adulteration of 7.5 per cent, and a sample marked questionable by the chemist of a large varnish works, showed an adulteration of 4.5 per cent.

The sample of pure Chinese wood oil used by the American Society for Testing Materials, and reported on as an exceptional oil, required an addition of 17.0 per cent linseed oil before the "turning point" occurred; hence in examining the four adulterated samples of this oil, which were used by the society in the work for 1915, it was deemed advisable, for sake of comparison, to use the figure 17.0 as well as the arbitrary figure of 15.5. Table IV gives the results in both cases:

TABLE IV

| Sample No. | Per cent adulteration found by using as "turning point" | |
|---|---|---|
| | 17.0 per cent | 15.5 per cent |
| 2 | 5.25 | 3.75 |
| 3 | 10.50 | 9.00 |
| 4 | 5.0 | 3.5 |
| 5 | 10.0 | 8.5 |

If these samples had been examined without having the pure oil the last column would have been considered as the percentage to which the Chinese wood oil had been adulterated.

SUMMARY OF RESULTS

If the adulterating oil is known, very accurate results can be obtained by this method, otherwise the accuracy is limited to 1.25 per cent either way from the true value, owing to the fact that the turning point varies between the limits of 14.5 to 17.0 per cent and the arbitrary value of 15.5 is not correct.

If, however, the oil with which the Chinese wood oil is adulterated can be determined, the accuracy is thereby increased. Lewkowitsch,[1] in commenting on tallow seed oil, says: "The most characteristic property of this oil is that it rotates the plane of polarized light to the left, *viz.*, 6° 45′ in a 200 mm. tube in a Laurent polarimeter, corresponding to —29.9 saccharimeter degrees. The optical activity is confirmed by Nash." This is being investigated as a means of detection in Chinese wood oil at the present time in this laboratory. If the attempt is successful the accuracy for adulterations with other oils will be increased, since the only other oil which causes the "turning point" to take place as high as 17.0 per cent adulteration is perilla oil, which is used only occasionally as an adulterant of wood oil.

The detection of sesame by the Baudouin test and the detection of cottonseed oil by the various methods as described in Lewkowitsch, would eliminate most of the oils which affect the turning point as low as 14.5 per cent. The remaining oils affect the turning point within such a close range of each other that the arbitrary figure assumed as the turning point would be very close to the true value.

The writer believes that concentration of the adulterating oils by the light break method described by Ware and Schumann[1] may facilitate the detection of those oils readily identified.

Another factor which must be taken into consideration is the fact that the prism itself has a dispersive power and if its dispersion is too large the anomalous dispersion of Chinese wood oil will be counteracted. Also, prisms, though having a dispersion low enough to be used in this method, may vary from each other, so that in using an instrument of this type one must first calibrate his prism before making determinations. This is readily done by finding the "turning points" brought about by the addition of different oils to Chinese wood oil.

The fatty acids of Chinese wood oil also show anomalous dispersion. This fact gives promise of interesting information when studied in connection with other fatty acids.

RESEARCH LABORATORY
ACME WHITE LEAD AND COLOR WORKS
DETROIT, MICHIGAN

[1] "Chemical Technology and Analysis of Oils, Fats and Waxes," Vol. II, p. 70.

## COMPOSITION OF WOOD TURPENTINE[2]

By MAXWELL ADAMS

Received June 14, 1915

Because of the shortage in the supply of "gum" turpentine, and the enormous wood waste of our lumber mills during the past ten years, many methods for the extraction of turpentine from wood have been proposed. The economics of steam, solvent, alkali digestion, oil bath, destructive distillation, under both increased and diminished pressure processes have been given thorough consideration, but very little attention has been accorded the composition of the turpentine obtained by these different procedures. Although the products obtained by these various methods differ widely as to color, odor and physical constants, without any attempt at standardization, they have all been classed together. The result has been that a strong prejudice has arisen against any product sold under the name of wood turpentine.

The physical properties of wood turpentine obtained, presumably, from long leaf or Cuban pine, have been

[1] THIS JOURNAL, 6 (1914), 806.

[2] This work was in part done in Prof. Wallach's laboratory at Göttingen, Germany, and supported by the Adams Fund of the Nevada Agricultural Experiment Station.

worked out by Hawley,[1] F. W. Richardson and J. E. F. Whitaker,[2] Marcille,[3] Parry.[4] Others have published methods for the analysis of different kinds of turpentine, but for the most part these workers have been concerned with the identification of adulterants, or with physical constants; little attempt has been made to identify or separate the different terpenes present, and in no case observed has wood turpentine obtained from any variety of Western pine been investigated.

The present investigation was undertaken for the purpose of determining the physical properties and identifying the various terpenes present in the wood turpentine prepared from pine growing in the western part of the United States. The "gum" turpentines of the varieties chosen have previously been examined by Schorger.[5]

Samples of wood from Western yellow pine (*Pinus ponderosa*), obtained from trees growing in the neighborhood of Independence Lake, Cal., Jeffrey pine (*Pinus jefreyi*) from trees growing on the Eastern slope of Mount Rose and near Galena Creek, Nev., and from single leaf nut pine (*Pinus monophylla*) growing on the western slope of the mountains between Steamboat Springs and Virginia City, Nevada, were collected. Each sample was distilled under diminished pressure in a retort, around which circulated hot oil, according to the method described by Adams and Hilton.[6] The distillate from the wood was separated roughly into three fractions: (1) that which comes over below 160°, (2) the distillate between 160 and 220, and (3) that driven over above 220°. In most of the following experiments only the first fraction was used. The second fraction contained considerable quantities of decomposition products, which could be removed only by alternate treatments with sulfuric acid and caustic soda, together with steam distillation. Since treatment with these chemicals might affect the chemical composition of the oil, the second and third fractions were discarded. This procedure has doubtless slightly increased the percentage of the lower boiling terpenes over that which would be found in ordinary crude wood turpentine.

### SINGLE LEAF NUT PINE

A sample of wood turpentine obtained from the distillation of the wood of single leaf nut pine, according to the above method, when redistilled with steam, had the following physical constants: $d_{15°}$ 0.9702, $n_{D15°}$ 1.4771, $\alpha_{D20°}$ +21.15. The oil was colorless and had a very characteristic aromatic odor. A sample of the oil was dried over fused potassium carbonate, distilled at a pressure of 15 mm. and separated into three portions:

I—B. p. 50–60°, consisted of 77.9 per cent of the original oil and had the following properties: $d_{15}$ 0.8691, $n_{D15}$ 1.4693, $\alpha_{D20°}$ +20.76

II—B. p. 60–80°, consisted of 7.6 per cent of the original oil and had the following constants: $d_{15}$ 0.8721, $n_{D15°}$ 1.4777, $\alpha_{D20°}$ +11.78

III—B. p. 80–135°, consisted of 9.2 per cent of the original oil and had the following constants: $d_{15}$ 0.8982, $n_{D15°}$ 1.4856

There was a residue left in the distilling flask consisting of 5 per cent of the original oil. Each fraction decolorized an alkaline solution of permanganate and absorbed bromine readily, but none gave a test with sodium bisulfite or semicarbizide for aldehydes or ketones.

α-PINENE—From Fraction I. when distilled over sodium, there was obtained a material with a boiling point of 155–156°, which when dissolved in acetic acid and treated with amyl nitrite and hydrochloric acid gave crystals of pinene nitrosochloride. After dissolving in chloroform and reprecipitating with methyl alcohol the crystals melted at 103°. The nitrol piperidene, prepared in the usual manner[1] from the nitrosochloride melted at 118°. The above results prove the presence of *d*-α-pinene.

β-PINENE—Fraction II, after several redistillations over sodium, yielded 15 per cent, or about one per cent of the original oil, which boiled at 167°; 3.7 grams of this oil were added to 4.9 grams of potassium permanganate, and 1.8 grams of sodium hydroxide dissolved in 11 grams of water and crushed ice. The mixture was agitated on a shaking machine for 6 hours, according to the method of Wallach.[1] As the ice melted the temperature was allowed to rise to that of the room. The hydrocarbons not acted upon were driven off with steam and the solution remaining in the retort was filtered from the oxide of manganese and the filtrate evaporated, while a constant stream of carbon dioxide was conducted through the solution. Crystals of sodium nopinate separated when the solution cooled. The yield, however, was so small that an attempt to prepare the nopinic acid in sufficient quantity for complete identification failed.

CADINENE—The third fraction, which was light yellow in color, when heated at atmospheric pressure began to boil at 170° but turned brown, indicating some decomposition. A second portion was therefore distilled at 15 mm. pressure and separated into two portions. The lower boiling fraction was tested for limonene and phellandrene without positive results. The higher boiling fraction, after distilling over sodium, thereby removing considerable tar, boiled without any apparent decomposition at 205–215°. This fraction, thus purified, was dissolved in four parts of glacial acetic acid, cooled in brine and ice, and saturated with dry hydrogen chloride. A heavy brown liquid separated, which when placed in an open dish evolved considerable gas and quickly solidified. This solid was dissolved in acetic acid and allowed to stand for 12 hours. A good yield of white crystals separated, which melted at 117°, thus establishing the presence of cadinene.

These results, when compared with those of Schorger[2] on the volatile oil obtained from the oleoresin, indicate that wood turpentine obtained from this species is almost identical in both physical properties and chemical composition with the pure "gum" spirits.

[1] *Eighth Int. Congr. Applied Chem.*, **1912**, and Forest Service, *Bull.* **105.**
[2] *J. Soc. Chem. Ind.*, **30**, 115.
[3] *Bull. soc. chim.*, **2**, 762.
[4] *Chem. and Drugg.*, **81**, 52.
[5] THIS JOURNAL, **5** (1913), 971, and U. S. Forest Service, *Bull.* **119.**
[6] *Ibid.*, **6** (1914), 378.

[1] *Ann.*, **356**, 288. [2] *Loc. cit.*

JEFFREY PINE

In the following experiments on the volatile oil from Jeffrey pine especial care was taken to identify the wood used, because the differentiation between *Pinus jefreyi* and *Pinus ponderosa* is very close, and some confusion has arisen on this account. Sadtler[1] reports having obtained heptane from *Pinus ponderosa*. This error probably arose from a confusion of Yellow pine with Jeffrey pine.

Sudwirth[2] says in writing of Jeffrey pine: "Some specialists consider it a variety of *Pinus ponderosa*, which it resembles so closely in its habits and soil and climate requirements that from the foresters' point of view there appears to be no practical reason for distinguishing the two."

Jepson[3] says, "The Jeffrey pine which merges insensibly into the Yellow pine is in its typical form found at high elevations ranging from 6000 to 9000 feet. By some writers this variety is regarded as a species. While the typical form is clearly to be recognized it is to be said, on the contrary, that Jeffrey pine not only passes over into Yellow pine, but that the transition forms in the intermediate region are quite as numerous and occupy as extensive an area as the true Jeffrey pine itself."

In the publications of the United States Forest Service[4] similar ideas are expressed as follows: "The Jeffrey pine bears very close resemblance to western yellow pine and some authorities regard it simply as a variety."

Because of the distinct chemical difference in the volatile oils obtained from the woods of these trees, as shown by the following analyses, there is good evidence for the contention that Yellow and Jeffrey pine are distinct species; at least there is a definite chemical method for distinguishing between them. It would be interesting in this connection to examine chemically the volatile oil from a specimen which the botanist considers a transition form.

A sample of wood turpentine obtained from distilling carefully selected wood from a well identified Jeffrey pine tree, was distilled under diminished pressure. The distillate thus obtained was steam-distilled, the resulting volatile oil dried over potassium carbonate and separated into four fractions by distilling at a pressure of 15 mm.:

| Fraction | I | II | III | IV | Residue |
|---|---|---|---|---|---|
| Boiling point | 25–30° | 30–35° | 35–65° | 65–125° | |
| Per cent obtained | 74 | 13 | 6 | 4 | 3 |

The first three fractions distil without decomposition at ordinary pressure. They were combined and distilled over sodium and a portion, consisting of about 90 per cent of the entire volatile oil, was obtained which distilled between 99 and 100.5°. This distillate gave no test for the double bond with von Beyer's reagent, neither would it absorb bromine. When added to amyl nitrite in acetic hydrochloric acid solution it gave no test for pinene. The physical properties were $d_{15°}$ 0.6877, $n_{D20°}$, 1.3890, optically inactive. These tests prove that the volatile oil from Jeffrey pine wood contains from 90 to 95 per cent of normal heptane.

The fourth fraction was redistilled at diminished pressure and separated into two parts. The lower boiling fraction was distilled over sodium and tested for limonene and dipentene. It absorbed the calculated amount of bromine to form the tetrabromide, butr cystals were not obtained from the oil. The higher boiling fraction gave a precipitate with sodium bisulfite, which would indicate the presence of citronellal, but the small amount of the material available prevented making confirmatory tests.

YELLOW PINE

A sample of volatile oil obtained from Yellow pine, according to the method already described, was clear, water-white, and had the odor which is characteristic of Yellow pine wood. Its specific gravity at 15° was 0.8626, index of refraction 1.4727, specific rotation —13.15.

On distilling 500 grams of the oil, using a Norton and Otto distilling tube, and at a barometric pressure of 642 mm., the following results were obtained:

FRACTIONAL DISTILLATION OF THE VOLATILE OIL OBTAINED FROM THE WOOD OF *Pinus ponderosa*

| Temp. °C. | Distillate Observed | Distillate Cumulative | Specific gravity, 15° | Index of refraction, 15° | Specific rotation, 20° |
|---|---|---|---|---|---|
| 156–158 | 4.72 | 4.72 | 0.8467 | 1.4621 | —15.14 |
| 159.9 | 9.39 | 14.11 | 0.8525 | 1.4710 | —14.48 |
| 161.2 | 9.20 | 25.32 | 0.8546 | 1.4731 | —14.57 |
| 162.1 | 9.99 | 33.32 | 0.8552 | 1.4732 | —13.68 |
| 163.0 | 10.08 | 43.40 | 0.8559 | 1.4738 | —12.15 |
| 163.9 | 9.51 | 52.91 | 0.8562 | 1.4740 | —11.89 |
| 164.9 | 9.65 | 62.56 | 0.8590 | 1.4744 | —11.04 |
| 176.7 | 9.95 | 72.51 | 0.8603 | 1.4745 | —10.56 |
| 169.8 | 6.958 | 79.47 | 0.8633 | 1.4752 | —10.97 |
| 173.4 | 7.86 | 87.35 | 0.8733 | 1.4913 | —14.12 |
| 180.3 | 9.36 | 97.71 | 0.9246 | 1.5038 | —17.22 |
| Residue | 2.3 | | | | |

When the above table is compared with a similar one prepared by Schorger[1] on "gum" spirits, it will be noted that the wood turpentine contains more of the low boiling and less of the high boiling fractions than that obtained from the oleoresin of western pine. This difference is perhaps due to the fact that wood turpentine was obtained from the first fraction of the wood distillate and that the barometric pressure was abnormally low.

A second analysis, which was made upon a smaller but a more representative sample of Yellow pine wood distillate, and which contained all the volatile oil given off up to the temperature at which the wood began to decompose, gave the following results:

| Fraction | I | II | III | Residue |
|---|---|---|---|---|
| Distilling temperature | 156–164° | 164–172 | 172–180 | |
| Per cent distillate | 8.7 | 72.5 | 16.4 | 2.4 |

Fraction I of the oil when tested for $\alpha$-pinene readily yielded nitropiperidine which melted at 118°. Fraction II, when oxidized with potassium permanganate according to the method previously described, gave an abundant yield of crystals of nopinic acid, which melted at 125°. Fraction III gave crystals of limonene tetrabromide when treated with bromine.

CONCLUSIONS

The presence of practically every constituent of the

[1] *Am. Jour. Pharm.*, **51**, 176.
[2] "Trees of the Pacific Slope."
[3] "The Silva of California," p. 80.
[4] Silvica Leaflet, p. 21.

[1] U. S. Forest Service, *Bull.* **119**, 12.

volatile oil of the oleoresin has been identified in the wood turpentine of the three varieties of wood under examination. The physical properties and the percentage composition do not always agree, yet they coincide as closely as could be reasonably expected, when we consider the inaccuracies of some of the methods available. The results thus far obtained justify the conclusion that the volatile oil obtained from distilling wood under diminished pressure is similar to that obtained from the oleoresin of the same species of tree.

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# LABORATORY AND PLANT

## SOME IMPROVED ELECTRICAL LABORATORY APPARATUS

By CHAS. MORRIS JOHNSON
Received July 23, 1915

### I—QUICK HEATING ELECTRIC FURNACE FOR THE DETERMINATION OF CARBON IN STEEL, ETC., WITH TRAIN

The train (Fig. I) consists of: (1) a mercury tube to detect leaks and stoppages; (2) a safety jar containing a 1 : 1 solution of KOH; (3) a tower filled loosely with a plug of glass wool followed with anhydrous calcium chloride, a layer of soda lime and another plug of the wool; (4) a jar of short pieces of stick caustic potash with a plug of glass wool at the top and at the bottom; (5) a clay and rubber connector doing away with rubber stoppers at the charging end; (6) the vitrified clay combustion tube with the tapered outlet doing away with the rubber stopper at this point also; (8) is the jar of granulated zinc to stop acid and sulfur; (9) is a jar of phosphoric acid powder and (10) is the bulb for absorbing and weighing the $CO_2$. This train was designed by the writer, being a simplification of his train described in *J. Am. Chem. Soc.*, May, 1908.

The writer has now used the tapered clay combustion tubes for over two years for the determination of carbon in steel, etc., and has been using them for some months for oxygen determinations also.

The new split muffle type of furnace was designed about a year ago. It is of most simple construction, consisting of a split muffle of kieselguhr, a coil of nichrome wire embedded in alundum cement as a replaceable heating element, and a supporting stand. The furnace will heat from the cold to 1000° C. in 20 to 25 minutes with a current consumption of 3 to 4 amperes. It can be cooled rapidly, if desired, by lifting off the top half of the split muffle. The writer has supplanted for some time in this laboratory, and in another laboratory under his direction, all of the type introduced by him in 1908[1] with this new type shown in Fig. I.

This type of electric furnace can be built in any length of heating surface with coils connected in parallel. The type shown in Fig. I is 13 inches long by $3^5/_{32}$ inches O. D. and $1^{15}/_{16}$ I. D. The writer built the same type for organic work 18 inches long. By using three rheostats a long furnace can be made to heat to three different temperatures at once or it can be heated in one part if desired.

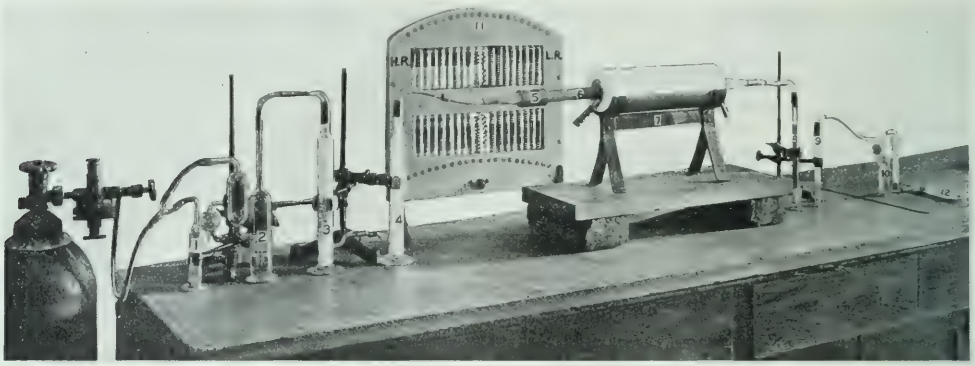


FIG. I

The furnace presents a bright neat appearance with its white muffle; new heating elements can be kept in stock and quickly put in place in case of a burn-out as there are no screws or powdered heat insulation to bother with. In case the muffle becomes soiled it can be put in a muffle furnace and heated to a red heat for about 20 minutes when it becomes as white as new. The simple construction makes the furnace a very inexpensive one.

By using a split insulation muffle of $5^5/_8$ inches O. D. and $2^5/_{32}$ I. D., the writer obtained a furnace of this type which is developing 1020° C. with a current consumption of only 2.7 amperes. This furnace has been in daily service in this laboratory for several months.

[1] *J. Am. Chem. Soc.*, **30** (1908), 773.

II—A NEW TYPE OF PORTABLE LABORATORY RHEOSTAT

Fig. II shows the rheostat designed by the writer with a view to making repairs more easy and to have a piece of apparatus with sufficient capacity to fill the needs of most laboratories. It consists of 21 coils of nichrome wire giving a total resistance of 30 ohms and a maximum capacity of 14 amperes. It can be used either on the furnace shown in Fig. I or with the large one given in Fig. III. It holds the large furnace in Fig. III for any length of time at any temperature from 200° C. up to 1000° C.

The rheostat occupies but a few inches of table width and can be set behind the other apparatus as illustrated in Fig. I. Repairs are easily made and the white board of hard asbestos board gives a cheerful effect. If desired, two such rheostats can be bolted together making a double instrument. The rheostat is practically indestructible so long as its capacity is not exceeded as there is nothing about its design to get out of repair. In Fig. II, 11 is the front and 13 the back view showing details of construction.

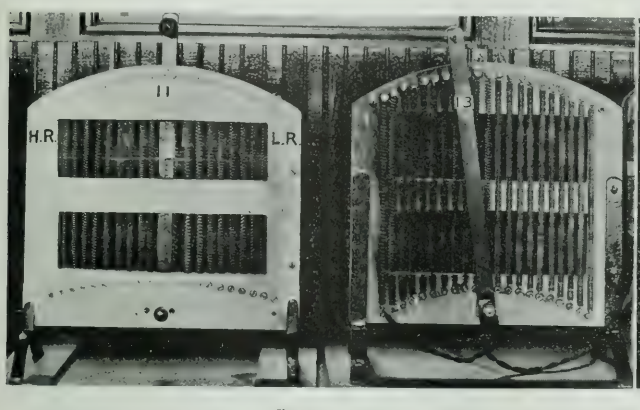


FIG. II

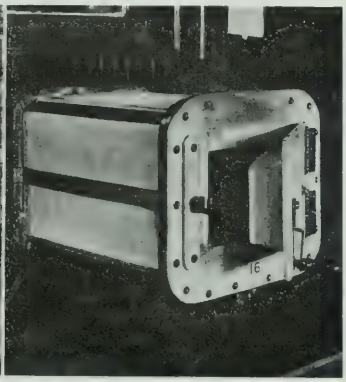


FIG. III

III—A NEW RECTANGULAR LABORATORY ELECTRIC MUFFLE FURNACE WITH SOLID HEAT INSULATION CASE

The furnace shown in Fig. III is in principle just the same as the cylindrical furnace described in Fig. I. A white solid case of kieselguhr surrounds the heating element and working muffle which has an available working space of $11^1/_2 \times 5 \times 7$ in. This is ample for most laboratories. To control the temperature of the furnace the rheostat shown in Fig. II is used and by means of it any desired temperature can be maintained for hours at a time up to 1000° C. The author keeps three furnaces of this size in constant service.

On account of the simplicity of construction, the repairs can be easily made and, as no insulating powder is used, the furnace is free from powder falling out into the working chamber. With the absence of the heat insulating powder the repairs are much simplified. The whole furnace is supported and enclosed in a stout, soft steel frame which makes it very rigid.

The white casing makes an attractive looking piece of apparatus. The interior muffle on which the wire is wound is of a special composition which is now being tested out. This same composition used in combustion boats made the remarkable run of 525 steel combustions per boat with the test boats still in commission but considerably worse for wear. It is highly probable that the muffle will be equally superior to the old mixture for heating core muffles.

The scheme is to keep these working muffles already prepared with the heating wire cemented on them ready for use so that repairs can be quickly made. As the furnace consists of three parts its construction it is considerably cheaper than that of the old types, besides having the advantages already mentioned.

The door opens horizontally: the author has found this arrangement to be much more desirable than the vertically opening door used in some of the old types.

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## A NEW DIRECT-READING VISCOSIMETER

By R F. MacMichael

Received September 8, 1915

Viscosimeters are instruments for measuring the viscosities of fluids. They operate on two general principles:

I—The *time* required to produce a definite relative movement of the fluid particles under a given force.

II—The *force* required to produce a definite relative movement of the fluid particles in a given time.

Familiar examples of the application of the *first* principle are:

*a*—Long capillary tube, used by scientists.

*b*—Short-tube commercial instruments, *e. g.*, Saybolt, Engler and Redwood.

*c*—Falling bodies within the fluid, *e. g.*, Arnold, Ladenburg and Flowers.

*d*—Rising bubble.

*e*—Retarded surface, *e. g.*, Doolittle and Stormer.

In each of these instruments the time required for a

definite movement of the fluid particles to take place is noted. The acting force in each case, except that of Doolittle, is gravity. This may be the weight of the fluid itself, or the weight of a foreign body acting within or upon the fluid, or bouyancy of an air bubble. In the case of Doolittle, energy is stored up in a steel spring, and allowed to expend itself in rotating a disk.

In well designed instruments of this class the control of the acting force is almost absolute. However, the time required to make a test is frequently a drawback, and the difficulties of maintaining an exact temperature during the test are often very serious. The fluid must usually be strained before testing; with very viscous fluids, this necessitates heating; Small particles of foreign matter within the instrument may interfere with proper action, and at times will introduce very large errors. It is only rarely that colloidal or glue-like substances, or suspensions of finely divided solids, such as clay slips, can be handled successfully in these instruments.

Results are usually expressed in seconds of time. Even in the simplest forms of instruments, elaborate and involved calculations are required to reduce the readings to scientific units, while most of the instruments noted above are not even susceptible to such calculations. In the latter case the results are expressed in an arbitrary manner in empirical units. The personal equation is large, and considerable care and skill are required if accurate results are to be obtained. The difficulties and annoyances attending the constant use of a stop-watch are too well known to require comment.

Viscosimeters of each of the above types have been before the public for many years. Up to the present it has not been found possible to combine in any one instrument based on the first principle all of the essential features required in a viscosimeter for general scientific and commercial use. It is not to be asserted that this cannot be done, but merely that after many years of effort, it has not been done.

The most prominent examples of instruments based on the *second* principle are those of Couette, Clark and MacMichael. In each of these instruments a cylinder or disk is suspended in a cup of fluid; then either the disk or the cup is revolved, and the torsional force noted. Couette's experiments were conducted at an early date, and though the principles involved were sound, mechanical difficulties were encountered which proved insurmountable at that time. In the more recent Clark machine, the tangential force applied to the rotating member is measured: this instrument under proper conditions gives excellent results, but the construction introduces mechanical complications which render it unsuitable for general use.

In the author's viscosimeter, the force exerted by the rotation of the fluid itself on the stationary member is measured. This force is equal and opposite to that applied to the rotating member. A description of this instrument follows.

APPARATUS—Fig. 1 shows the machine assembled and ready for a test. A disk is suspended in the cup of fluid by a torsion wire about 10 in. long, running down through the stem of the plunger, and fastened near the bottom. The head of the torsion wire is triangular, and is held between two grooved pins at the top of the standard. The cup and plunger may be removed and replaced without manipulating any catches or fastenings.

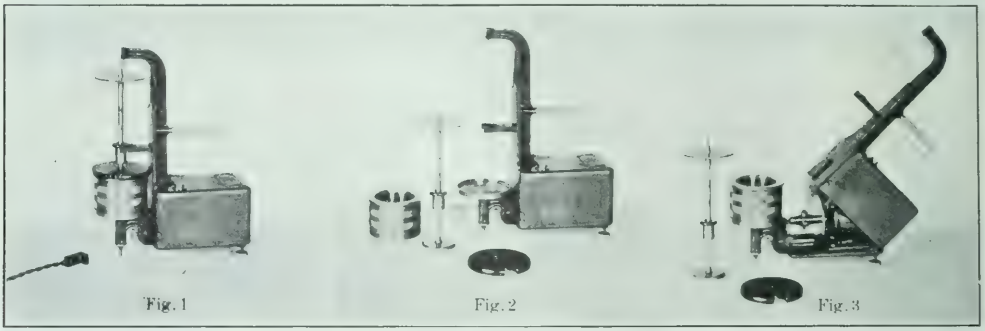

Fig. 1 Fig. 2 Fig. 3

Fig. 2 shows the cup and plunger removed for cleaning. All surfaces are smooth and rounded and may be cleaned with the greatest ease. The cup is oil-jacketed, being formed of two pieces of heavy spun brass. Within the oil jacket is immersed an electric heating coil. This coil draws current from the same line as the motor, only one connection being necessary.

The fluid to be tested is heated in place, no other heating device being required. The operation is very rapid. Stirring is effected by a slight vertical movement of the plunger. A bent thermometer inserted through an opening in the cover indicates the temperature, the bulb being immersed in the fluid. The temperature during test may be controlled to within a small fraction of 1° F. For low temperature work, the fluid and the adjacent parts are chilled in an ice bath or brine solution.

The graduated dial at the top of the plunger is secured to the stem by a friction disk, permitting the adjustment of the zero mark to its proper location.

The fine adjustment is effected by means of the steel wire pointer at the head of the standard.

The same figure shows the dash pot on the stem of the plunger. This device is frictionless and automatic in action, and requires no attention from the operator. Its function is to check incipient vibrations and to permit quicker readings by damping the action.

In Fig. 3 the standard and hood are thrown back, showing the driving mechanism. The speed control is of the familiar phonograph type and gives excellent results. The motor is specially wound for this service and is furnished either in a. c. or d. c. for use on ordinary lighting circuits. Variations in voltage do not affect the accuracy of the determination.

OPERATION—In operation, the cup is filled to the mark on the side with the fluid to be tested. This requires about 100 cc. The cover is put on and the thermometer inserted. By means of the heating coils the temperature is raised to nearly the desired point. As expansion of the fluid will probably have taken place, the excess fluid is removed by means of a pipette furnished with the machine. This automatically fixes the proper level, without further attention from the operator. The temperature is brought exactly to the desired point, the thermometer removed and the motor started. Within a few seconds the dial will have come to rest, and will remain steadily at one point. The deflection noted is the viscosity of the fluid. This entire operation is very rapid, so that the drop in temperature on ordinary work is entirely negligible.

For extreme accuracy, the temperature may be raised slightly above the desired point, and an allowance made for the drop up to the moment of reading. This will seldom be found necessary in actual practice.

READINGS—The readings are in degrees of angular deflection, 300° to the circle, designated as °M. The practical working unit is 1/1000 of the absolute unit. As water at 20° C., or 68° F., has exactly 1/100 of the absolute unit of viscosity, water at this temperature reads 10° M. Thus, by shifting the decimal point, practical units, absolute units, and specific viscosity may be obtained at one reading. Readings are taken directly from the dial, no intermediate calculations being required.

Torsion wires ordinarily give water as 10° M., and may be used up to 500° M. This covers the range of most liquids ordinarily to be tested. For extremely thin and extremely thick liquids, lighter and heavier wires giving readings for water of 100° and 1°, respectively, are supplied. This covers every range of viscosity up to about 5000° M., or 500 times that of water.

CALIBRATION of the instrument is effected by testing with a standard fluid of known viscosity. Sugar syrup is used for this purpose. Water may be used for calibrating, but this is not advisable as it is too thin for the best results. Should the reading of the dial, on test, be found to vary slightly from the correct value, the speed of rotation of the cup is altered by means of the speed control screw at the lower front of the machine. The deflection of the dial will vary directly as the speed, other factors being constant, and the correct indication may be obtained. When calibrated accurately for one value, the readings will be correct for any other value.

The accuracy of the instrument under ordinary working conditions should be well within an error of 1/2 per cent above or below the true value. For extremely accurate work, extra precautions should insure results within a small fraction of this error.

As the time required for a reading is extremely short, determinations may be made on suspensions, such as clay slips, which settle rapidly.

Colloidal solutions such as glues, gums, starch solutions, gelatine, and other similar materials can be handled successfully. Likewise, the viscosity of complicated mixtures such as catsup, or other food materials or chemical substances may be readily determined. Straining is unnecessary as small particles of foreign material do not in any way affect the accuracy of the determination.

It is believed that this instrument offers an accurate, rapid, convenient and thoroughly satisfactory means for determining the viscosity of fluids.

SEATTLE, WASHINGTON

# ADDRESSES

## COAL-TAR DYES AND THE PAIGE BILL[1]

By BERNHARD C. HESSE

The Paige Bill is the latest of a number of attempts to saddle compulsory working of patents upon American inventors in the United States. Its text is as follows:

A BILL

To amend Sections Forty-Eight Hundred and Eighty-Six and Forty-Eight Hundred and Eighty-Seven of the Revised Statutes, relating to patents.

*Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled*, That Section Forty-Eight Hundred and Eighty-Six of the Revised Statutes, as amended by Act of Congress approved March Third, Eighteen Hundred and Ninety-Seven, be, and the same is hereby, amended so as to read as follows:

"SEC. 4886. Any person who has invented or discovered any new and useful art, machine, manufacture, or composition of matter, or any new and useful improvement thereof, not known or used by others in this country before his invention or discovery thereof, and not patented or described in any printed publication in this or in any foreign country before his invention or discovery thereof or more than two years prior to his application, and not in public use or on sale in this country for more than two years priors to his application, unless the same is proved to have been abandoned, may, upon payment of the fees required by law and other due proceedings had obtain a patent therefor: *Provided, That no patent shall be granted on any application filed subsequent to the passage of this Act upon any drug, medicine, medicinal chemical, coal-tar dyes or colors,*

[1] Address before the Rochester Section of the American Chemical Society, Rochester, New York, October 4, 1915.

*or dyes obtained from alizarin, anthracene, carbazol, and indigo, except in so far as the same relates to a definite process for the preparation of said drug, medicine, medicinal chemical, coal-tar dyes or colors, or dyes obtained from alizarin, anthracene, carbazol, and indigo.*"

SEC. 2. That Section Forty-Eight Hundred and Eighty-Seven of the Revised Statutes, as amended by Act of Congress approved March Third, Eighteen Hundred and Ninety-Seven, and as further amended by Act of Congress approved March Third, Nineteen Hundred and Three, be, and the same is hereby, amended so as to read as follows:

"SEC. 4887. No person otherwise entitled thereto shall be debarred from receiving a patent for his invention or discovery, nor shall any patent be declared invalid, by reason of its having been first patented or caused to be patented by the inventor or his legal representatives or assigns in a foreign country, unless the application for said foreign patent was filed more than twelve months in cases within the provisions of Section Forty-Eight Hundred and Eighty-Six of the Revised Statutes, and four months in cases of designs, prior to the filing of the application in this country, in which case no patent shall be granted in this country.

"An application for patent for an invention or discovery or for a design, filed in this country by any person who has previously regularly filed an application for a patent for the same invention, discovery, or design in a foreign country, which, by treaty, convention, or law, affords similar privileges to citizens of the United States, shall have the same force and effect as the same application would have if filed in this country on the date on which the application for patent for the same invention, discovery, or design was first filed in such foreign country: *Provided*, That the application in this country is filed within twelve months in cases within the provisions of Section Forty-Eight Hundred and Eighty-Six of the Revised Statutes, and within four months in cases of designs, from the earliest date on which any such foreign application was filed. But no patent shall be granted on an application for patent for an invention or discovery or a design which had been patented or described in a printed publication in this or any foreign country more than two years before the date of the actual filing of the application in this country, or which had been in public use or on sale in this country, for more than two years prior to such filing: *Provided, however, That in case any drug, medicine, medicinal chemical, coal-tar dyes or colors, or dyes obtained from alizarin, anthracene, carbazol, and indigo, on which a patent for a definite process for the preparation thereof had been granted on any application filed subsequent to the passage of this Act, is not manufactured in the United States by or under authority of the patentee, within two years of the granting of said patent, and after the commencement of said manufacture the same is not continuously carried on in the United States in such a manner that any persons desiring to use the article may obtain it from a manufacturing establishment in the United States, then said patentee shall have no rights under the patent laws of the United States as against any citizen of the United States who may import such drug, medicine, medicinal chemical, coal-tar dyes or colors, or dyes obtained from alizarin, anthracene, carbazol, and indigo, into the United States or who may produce or manufacture the same in the United States or who may handle for sale or use such article so imported or manufactured.*"

NOTE: Italicized matter is the new matter introduced by this Bill.

The Paige Bill was introduced for the purpose of forcing European dye and medicinal makers to the United States: it is utterly incompetent and unable to do anything of the sort.

The compulsory working of patents is a legislative device which appeals very strongly and persistently to the very great majority of lay minds as a most efficient, equitable, just and effective mode of introducing the industry relating to the subject matter of the patent into the country in which the patent runs. There seems to be nothing on its surface nor immediately beneath its surface to suggest difficulties in enforcement and inequalities, injustices and economic errors in such an enactment.

However, the legislative experience of 57 countries, extending over a period certainly for the past 83 years, has taught that the compulsory working of patents, if it is to be just, economically profitable and enforceable, is a thing almost impossible of achievement and presents obstacles which, to the most astute minds and the most experienced persons, seem unsolvable.

Contrary to all expectations, manufacture within the country is not so stimulated but dumping from without is thereby increased.

### GENERAL NATURE OF RESULTS

To go no further back than 1832, when the United States enacted its compulsory working clause,[1] a study of that enactment shows compulsory working as absolute and as bare as any enactment could be, yet it was repealed within four years and no similar statute has ever been placed upon our statute books.

Coming next to the attempts of the French Government in 1844 and the modifications that it has from time to time added thereto, it is correct to say that the legislative measures of that country have been a series of compromises and modifications, all of them aimed at reducing the harm that was being done to France through this legislation, and at the same time retaining, in some measure, the benefits that were supposed to have accrued to France thereby.

The experience of other countries is very much the same and the latest efforts in that direction have been the conclusion of treaties between various countries, which amount in effect to an abrogation of these laws, so far as the citizens or subjects of the two countries involved are concerned. That is, two countries get together and say to each other: "If you will not enforce your working clause against my citizens, I will not enforce my working clause against your citizens."[2]

To put it in a few words: Experience has shown that this seemingly innocent legislative device is possessed not only of a "punch" but also of a "kick" (*i. e.*, it hurt and oppressed domestic inventors); that the "kick" in most cases is more powerful than the "punch" and no legislative efforts have been directed towards removing the "kick" without, at the same time, interfering with the "punch." At the end of about 80 years of legislative experimentation these 57 countries have drifted into the position of removing the "kick" by removing the "punch" at the same time. In other words, having a compulsory working law which is a dead letter towards some peoples and, at any rate, a sleeping letter towards other peoples and when enforced doing quite as much, if not more, harm than good.

### THE BRITISH WORKING CLAUSE

When the British compulsory working clause was adopted in 1907, the world had a right to expect that that Act would contain the very best legislative devices that could be constructed in the light of the past experience of the world. The present European war, however, has shown how futile this British working clause was; that it failed utterly in introducing within the British realm those industries which it was the particular aim and object of that enactment to bring into Great Britain from without. Instead of the $500,000,000 of fresh capital that were lavishly promised to be introduced into Great Britain because of this enactment, and in place of the thousands, if not hundreds of thousands, of fresh labor to be employed there-

[1] THIS JOURNAL, **7** (1915), 504.

[2] Transactions International Association for the Protection of Industrial Property, **16** (1912), 183.

through, the best obtainable information[1] is that not to exceed fifty different firms came to England from without, that not to exceed $5,000,000 of fresh capital has found its way into Great Britain, and not to exceed 8,000 additional people have been employed in Great Britain. No new self-contained industries of any kind were thereby brought to Great Britain; on the contrary, dumping from without grew apace by virtue of revoked patents.[2]

### WHY BRITAIN FAILED

Without attempting to go into the refinements of the various reasons that have been given for the failure of the British working clause, it can be fairly stated that the main reason why it failed of efficient enforcement is that it called for an encroachment upon or an abrogation of personal and private rights which in all civilized countries are regarded as inalienable, namely: that the burden of proof of a charge lies upon him who makes it. In order to make the British working clause efficient, it was necessary to reverse that principle and hold every charged person guilty until he proved himself innocent. In other words, in order to make the British working clause effective it is necessary to regard every patentee as dishonest and to regard everybody else as thoroughly honest and to put every patentee in a position where he must establish his innocence[3] by full disclosure to the public of all of his business dealings on the subject matter of the patent.

### GERMAN WORKING CLAUSE AND DYE PATENTS

It has been asserted[4] that the presence of a compulsory working clause in the German patent law is *the* cause of the existence of a coal-tar chemical industry in Germany, because unless patents were worked efficiently in Germany they could be revoked and would revert to the German public and that is why non-Germans do not take out German coal-tar process patents. Nothing could be further from the truth than that assertion. So far as I have been able conveniently to ascertain, not one single German coal-tar patent, whether held by a foreigner or by a German subject, has ever been revoked for non-working, and yet I personally know of any number of German patents for processes for making coal-tar products, which are not worked, never have been and probably never will be, worked in Germany. Americans, British, Swiss and French have taken out patents in Germany for coal-tar products and dyes.

The rate of revoking patents in Germany for non-working is probably not in excess of four patents per year;[5] non-Germans and Germans as well owned the patents so revoked. The British rate of revoking patents for non-working is about 5 per year.[6]

Germany herself is very willing to repeal her working clause if the other countries will do the same.[7]

### COMPULSORY WORKING DOES NOT CREATE A DYE INDUSTRY

If a compulsory working clause necessarily gives birth to a coal-tar chemical industry, then it necessarily follows that France should dominate the world, because the French working clause dates back to 1844, or 12 years *before* the first coal-tar dye (apart from picric acid) was invented, and the German compulsory clause dates from 1877 only, or 21 years *after* the first coal-tar dye was invented and 17 years after the German coal-tar dye industry started; Germany had *no* patent laws prior to 1877. Switzerland had no compulsory working until 1907, or 48 years *after* its coal-tar dye industry started; on this reasoning of the supporters of compulsory working, Switzerland, which has for 40 years at least been second to Germany in the coal-tar dye business, should not have had any coal-tar dye industry at all. Furthermore, a French patent is invalidated if the subject of that patent or materials similar to the subject of that patent are imported into France or French territory from without. Theoretically, this certainly is a very effective way of insuring that the consumption within the country would be produced within the country. However, France, either in 1844 or shortly thereafter, proceeded to remove the "kick" by inserting a modification that partly manufactured materials for use in a process patented in France could be imported into France without invalidating the patent. That is the milk in the cocoanut: France has had for a great number of years, certainly since 1873, within her borders, branches of practically all of the German coal-tar dye factories, but they were merely, or, almost merely, assembling plants and Germany shipped into France its partly manufactured materials, carried out the patented steps in France, complied with the French working law, but absolutely nullified the hope for favorable economic effect. In short, when France could no longer trade with Germany, France was left holding the empty bag; she had "assembling" plants but she had nothing to "assemble." Russia and England were in precisely the same fix, while Switzerland was not much better off.

The following letter (in translation), dated Sept. 13, 1915, and addressed to me by the French branch factory, established in 1873, of a very large German coal-tar dye plant, reinforces this statement:

"We are purchasers of beta-naphthol, beta-naphthylamine, diphenylamine, dimethylaniline.

"Will you please tell us whether you sell these products, and in case you do, please inform us of your conditions and the quantities which you can offer us.

"At the same time, we beg you to inform us of other raw materials of interest for the manufacture of dyestuffs which you may have to offer us, aside from those mentioned above.

"In case your answer should be negative, we should be obliged to you if you would kindly indicate to us the addresses of firms to whom we could address ourselves with prospect of success."

### GENERAL SURVEY OF COMPULSORY WORKING

Without going into all of these enactments in detail, it will be enough to say that some 15 years ago it became my specific duty to examine the working clauses of all countries and to report to my principals, who were then in Germany, as to the possibility or feasibility of the enactment of a compulsory working law in the United States that could force them to come to the United States. After giving more than six months to a study of this subject, my report was in substance that I could not draft up any legislative enactment which would force an industry into the United States without doing the domestic industry of the United States in that and in other directions an amount of harm far in excess of any possible good that could flow from it and therefore that, in my judgment, a compulsory working act which would force the transplantation of the complete coal-tar dye industry into the United States would work more damage to the country at large than it could possibly do it good,[1] and that therefore in my opinion such legislation would not be enacted.

When the British working clause of 1907 was passed, I frankly confess I felt for a while that I had skipped a cog in my judgment; it seemed on the surface as though they had worked out something that I had overlooked. Be that as it may, my conclusion as to the ultimate effect of this sort of legislation was and is correct.

### BELGIUM'S EXPERIENCE

How compulsory working operates in smaller countries, such as Belgium, is described as follows by Jacques Gevers, Patent Agent of Antwerp, in Vol. XVI of *Transactions of the International Association for the Protection of Industrial Property*, pp. 168–169:

[1] See also THIS JOURNAL, **7** (1915), 311.

[1] THIS JOURNAL, **7** (1915), 306.
[2] *Ibid.*, **7** (1915), 306, 311, 315.
[3] *Ibid.*, **7** (1915), 313, 315, 316.
[4] *Textile World Record*, **1906** (Nov.), p. 65 and **1914** (Sept.), p. 56.
[5] *Trans. Int. Soc. Protection Indust. Property*, **16**, 177; see also *Textile World Record*, May, 1915, p. 92.
[6] THIS JOURNAL, **7** (1915), 311.
[7] *Ibid.*, **7** (1915), 305; *7th Int. Congr. Appl. Chem.* (London, 1909), Sec. XI, p. 9.

"The general interest that there is in abolishing reciprocally the requirement of working has been abundantly proved by the numerous papers written on this question. It is, however, of interest to consider exactly why small countries such as Belgium have still greater interest than other countries in the abolition of this requirement.

"At present the Belgian inventor or manufacturer who is the proprietor of patents is obliged to manufacture the patented article separately in Great Britain, Germany, France, Austria, Hungary, Italy, Spain, Portugal, Denmark, etc.

"Instead of being able to extend the manufacture in Belgium and export to these other countries, he is obliged, under risk of having his patent annulled, to manufacture in each country the patented articles which he sells there. This splitting up of manufacture increases the cost in a manner which is prejudicial to the success of his enterprise. Existing laws, therefore, militate against manufacture for exportation. It will be seen that exporting countries are those which suffer most from the present law. Belgium, which exports about three-quarters of its total industrial production, is obliged, in the case of patented articles, to manufacture these for the most part elsewhere, in order to maintain the validity of the patents. On the other hand, the principal argument of those who are in favor of maintaining the law as at present, is that, Belgium being a small country, foreign inventors must be prevented from importing into Belgium, notwithstanding that in return Belgium manufacturers are still to be obliged to manufacture in all foreign countries.

"But do the existing laws prevent importation into Belgium and does the foreigner really manufacture in our country the patented articles which he sells there? Facts show that he does not.

"There are used in Belgium large quantities of sewing machines, typewriting machines, cash registers, and photographic apparatus for which thousands of patents have been granted by the Belgium Government (the number, according to the Dictionnaire des Brevets, is 4,687). So that, although each Letters Patent granted says 'you are obliged by law to manufacture the patented articles in Belgium,' not 1 per cent of these articles are in fact manufactured there.

"Let us take the case of Van Berckel's patent which was annulled in 1911. These are the facts: A meat-cutting machine which is to be found in every meat salesman's establishment, was patented by Van Berckel. The inventor and his legal representatives brought successfully a number of infringement actions. The reports of these actions prove the extensive use of the machine. In Belgium alone more than 2,000,000 francs worth were sold, and as many could be furnished as required. Van Breckel's patent was subsequently attacked for non-manufacture. Notwithstanding the steps usually taken by interested parties, the Government annulled the patent, once more interpreting the law in the sense that 'exploiter' meant 'fabriquer.'

"A more attentive examination of the operation of economic laws shows also how it happens that the requirement to manufacture is nothing more or less than an obstacle to the establishment of the prosperous manufacture in Belgium of patented articles. An invention of value is never patented in Belgium alone. If, therefore, an inventor is to maintain his patents he must either manufacture in each country, or he must compromise by manufacturing only in certain countries and importing into others. If he takes the first course he must establish a factory in each country, which is impracticable. The multiplication of factories entails too large costs, raises the price of the article and prevents manufacture on a large scale and upon uniform lines.

"If he chooses between the countries, where shall he manufacture? In a small country where the consumption is small, or in a large country where the consumption is considerable? Which is the patent to be safeguarded, the patent with a limited value in a small country, or the patent granted in a large country where it is of ten times the value? The answer is obvious. Manufacture of patented articles is perhaps established in the larger countries to ensure the validity of the patent there. The establishment of manufacture in smaller countries is omitted in order to avoid multiplication of factories. That is why small countries, which have a limited domestic market and export by far the largest part of their manufactured products, have the greatest possible interest in abolishing upon reciprocal terms this requirement of manufacture under patents which is so prejudicial to export trade."

No one should attempt to pass upon this subject without first having given careful thought to the Symposium of the Imperial Industries Club of Great Britain printed in full in THIS JOURNAL, **7** (1915), 307–317 and to the facts collected in the paper published in THIS JOURNAL, **7** (1915), 304–307.

### NO BENEFITS FROM COMPULSORY WORKING

The supporters of the compulsory working of patents have not yet come forward with any specific or concrete instance of advantage arising therefrom and to the enacting country; as much as they have done is to indulge in glittering generalizations, vague promises and hypothetical assurances; both sides were ably represented at the Symposium of the British Industries Club just above referred to, yet the supporters failed utterly to make out any reasonable case in their favor.

### COMPULSORY WORKING A DELUSION

Personally, I would most heartily welcome a compulsory working law that would force industries from without into the United States and at the same time would do no harm to the United States in other directions, or at any rate, not enough to counterbalance any benefits that might flow from such introduction of extra-territorial industries. My own view is that any attempt to solve a legislative problem of that kind is of the same order, not merely as to attractiveness and desirability, but as to absolute unsolvability as is the problem of perpetual motion. The reason seems to be that you cannot treat domestic and foreign inventors each and all alike *and at the same time* "play favorites" toward the domestic inventors; it is most frequently *not* to the best interests of domestic inventors to be compelled to work their patents; therefore the makeshifts, compromises and the like that have everywhere been introduced in the hope of helping domestic inventors but in fact and at the same time benefitting foreign inventors to the same extent; hence, the inoperativeness of all such enactments.

Therefore, believing as I do, and for the reasons given, I am convinced that if we embark upon a policy of compulsory working of patents, we shall simply be living in a fool's paradise; we shall be leaning on a broken reed and we shall be fooling ourselves thoroughly and from the ground up. In the language of the day: "It can't be done."[1]

In the past 20 years, numerous attempts have been made in the Congress at Washington to pass some such legislation. However, and fortunately as I firmly believe, such legislation has not been passed. The judgment of the American Bar Association and of the American Patent Law Association is almost unanimously against any such legislation. As a result of a study of the various hearings held in Congress, I have come to the conclusion that those who favor compulsory working do not take anything but a very personal, that is, a very narrow view of such legislation. The most any legislation can hope to accomplish is the greatest good to the greatest number; to condemn legislation because in individual or isolated cases it does not work quite right, is visiting condemnation upon practically all of our legislation and an indictment of all law.

[1] THIS JOURNAL, **7** (1915), 311.

I believe that those who take the entire interests of the entire United States into consideration and balance benefit against disadvantage, are of the opinion that such an enactment will do us more harm than it can possibly do us good (even though it might rectify certain abuses to-day existent) because, as a result thereof, other abuses and inequalities of far greater extent and of greater economic effect would necessarily arise at once.

### PAIGE BILL SHOULD BE KILLED

What I have particularly in mind is that if we enact the pending so-called Paige Bill we would meet retaliatory legislation from other countries. That Bill picks out a certain branch of chemical industry in which compulsory working of patents is to be introduced, and exempts the rest of the chemical industry, and in fact all the other industrial activities of the United States. It is unreasonable to expect that other countries would not at once pass similar laws and, instead of limiting them to that particular branch of chemistry that this Bill has selected, would select some industrial branch in which we are supreme and would shut our products out of their markets or would force our industries to go to those countries and establish plants there for the manufacture of their patented products.

When Great Britain passed its compulsory working act, Germany made her compulsory working act sharper against Great Britain, and so did France; then Great Britain raised the barrier. Germany and France did the same. Each was hurting the other as well as itself, and in view of the very best information that I can get, not only by consultation of public documents but by correspondence with most competent men abroad, it is certain that these laws have not been effective in the direction in which they were expected to be. Judging from the reams upon reams of discussion appearing in the various *Proceedings of the International Association for the Protection of Industrial Property*, every one of the countries that has a working clause would be willing to drop it if everybody else would drop it; one is afraid to drop it and the other dare not. Some countries have made mutual treaties abrogating those laws with respect to each other. There you are! Should we commit ourselves to a policy of legislation which we adopted 83 years ago, rejected 79 years ago, and have since not put on our statute books and with which 56 other nations have been tinkering for over 70 years with an amount of success far less than the effort put forth and the damage incurred?

### TEXTILE INTERESTS AND THE PAIGE BILL

The chemists of this country are, or ought to be, particularly interested in the so-called Paige Bill, officially known as H. R. 19187, 63rd Congress, 2nd Session, which was introduced into Congress by Hon. Calvin D. Paige, of the Third District of Massachusetts, October 8, 1914, to force European dye and medicinal makers to come to the U. S. This Bill came up for endorsement on the part of the National Association of Cotton Manufacturers at its meeting in Boston on April 28, 1915, but was not so endorsed. What cotton manufacturers know about the chemical business it is difficult to understand. They have constantly opposed the enactment of suitable tariff provisions so that the dye industry could thrive in this country, on the ground, among others, that it would raise the price of a dozen red flannel undershirts by 25 cents[1] and that dyes were their raw materials, that increase in the cost of dyes would increase the cost of goods to the United States consumer and would interfere with their ability to do export business; that a protective tariff on dyes would simply mean an increased cost in goods with no added public benefit.

The facts seem to be that prior to the tariff of 1882 the cost to the textile people of at least two colors *did* drop,[1] *i. e.*, magenta dropped from $6.50 to 1860 to $2.50 in 1882, and rosaniline blues, which commanded $4.00 in 1881, were sold in this country at $2.50 in 1882. The cause of this drop in prices of these two products is ascribed, by trustworthy sources, to the internal

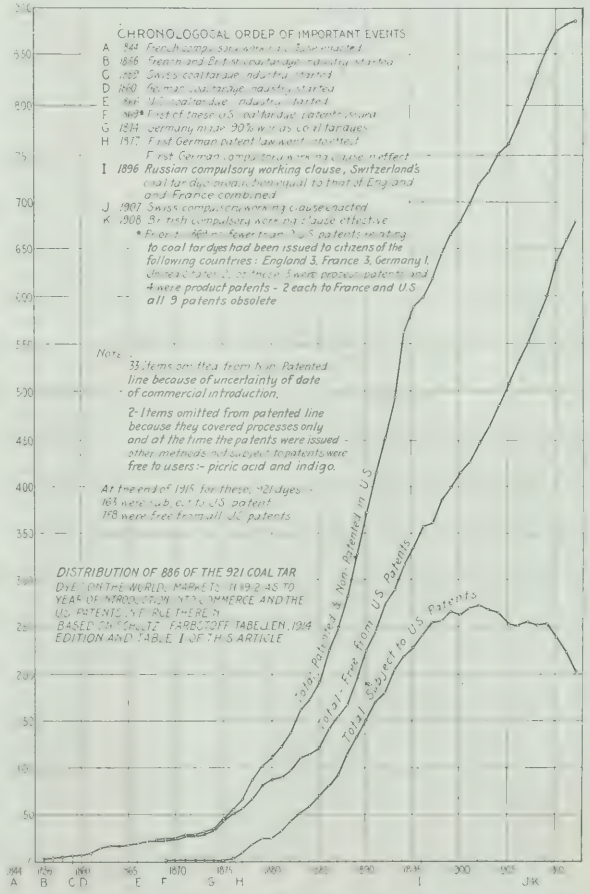


FIG. 1

competition within this country between the nine coal-tar dye factories then operating. The textile men have conclusively proven that they guessed things absolutely wrong on the tariff for dyes and that certainly is no qualification for them to offer themselves as infallible or desirable guides or as even probably good guides in so complicated a question as patents. The answer to them is that they have in the past been swayed altogether too much by self-interest; they have disregarded the rights of others and their duties to others; they have run the steam-roller of tariff legislation over our chemical indus-

[1] THIS JOURNAL, 7 (1915), 694

[1] THIS JOURNAL, 7 (1915), 695, 696, 697.

tries and now propose to run the patent-law steam-roller over them as well, and in those circumstances, the chemists of this country must wake up and see to it that their interests in Congress are not further jeopardized by the selfish and short-sighted activities of the textile people.

PAIGE BILL NO HELP TO AMERICAN COAL-TAR DYE INDUSTRY

Can the Paige Bill help the coal-tar chemists? The answer is: it cannot. The reasons are:

I—At no time in the history of the development of the coal-tar dye industry did the number of commercial coal-tar dyes subject to United States patents equal the number of commercial coal-tar dyes *not* patented in the United States.

II—In all but a very few instances dyes free from U. S. patent-restraint could at all times be made which could be and were offered as successful substitutes for dyes subject to U. S. patents.

III—At no time was the American industry throttled or

TABLE I—COMMERCIAL DYES PATENTED AND NOT-PATENTED IN U. S. YEAR BY YEAR (EXPIRED PATENTS ALLOWED FOR)

| Year | Pat. | Free to all | Excess of free to all over patented | No. of patented per 100 free to all |
|---|---|---|---|---|
| 1856 | | 4 | 4 | 0 |
| 1858 | | 5 | 5 | 0 |
| 1859 | | 7 | 7 | 0 |
| 1861 | | 9 | 9 | 0 |
| 1862 | | 15 | 15 | 0 |
| 1863 | | 18 | 18 | 0 |
| 1866 | | 20 | 20 | 0 |
| 1867 | | 22 | 22 | 0 |
| 1868 | | 23 | 23 | 0 |
| 1869 | 1 | 23 | 22 | 4.8 |
| 1871 | 1 | 27 | 26 | 3.7 |
| 1873 | 1 | 30 | 29 | 3.3 |
| 1874 | 1 | 34 | 33 | 2.9 |
| 1875 | 1 | 44 | 43 | 2.3 |
| 1876 | 3 | 52 | 49 | 5.8 |
| 1877 | 9 | 58 | 49 | 15.5 |
| 1878 | 19 | 68 | 49 | 27.9 |
| 1879 | 24 | 82 | 58 | 29.3 |
| 1880 | 24 | 89 | 65 | 27.0 |
| 1881 | 33 | 90 | 57 | 36.1 |
| 1882 | 41 | 98 | 57 | 41.8 |
| 1883 | 52 | 111 | 59 | 46.8 |
| 1884 | 59 | 115 | 56 | 51.3 |
| 1885 | 71 | 121 | 50 | 58.7 |
| 1886 | 82 | 143 | 61 | 57.3 |
| 1887 | 94 | 155 | 61 | 60.7 |
| 1888 | 116 | 168 | 52 | 69.1 |
| 1889 | 133 | 196 | 63 | 67.9 |
| 1890 | 150 | 224 | 74 | 67.0 |
| 1891 | 170 | 246 | 76 | 69.1 |
| 1892 | 180 | 273 | 93 | 65.9 |
| 1893 | 205 | 289 | 84 | 70.9 |
| 1894 | 218 | 316 | 98 | 69.0 |
| 1895 | 228 | 336 | 108 | 67.9 |
| 1896 | 242 | 358 | 116 | 68.9 |
| 1897 | 256 | 364 | 108 | 70.3 |
| 1898 | 258 | 387 | 131 | 66.7 |
| 1899 | 267 | 400 | 133 | 66.8 |
| 1900 | 263 | 416 | 153 | 63.2 |
| 1901 | 270 | 427 | 157 | 63.2 |
| 1902 | 272 | 448 | 176 | 60.7 |
| 1903 | 268 | 465 | 197 | 57.6 |
| 1904 | 265 | 485 | 223 | 54.6 |
| 1905 | 252 | 509 | 257 | 49.5 |
| 1906 | 251 | 531 | 280 | 47.3 |
| 1907 | 257 | 551 | 294 | 46.6 |
| 1908 | 252 | 579 | 327 | 43.5 |
| 1909 | 254 | 603 | 349 | 42.1 |
| 1910 | 259 | 637 | 398 | 37.5 |
| 1911 | 223 | 660 | 437 | 33.8 |
| 1912 | 206 | 680 | 474 | 30.3 |
| 1912(a) | 207 | 714 | 507 | 29.1 |

(a) For all 921 dyes.

even handicapped by U. S. patents held by foreigners to such an extent that it could not offer successful substitutes for the great majority of patented articles; the American industry always had at its disposal means of getting into the market and which were free from U. S. patent-restraint, *provided* that industry was strong enough to get into the market.

These statements are conclusively proven by the data in Table I based upon the 1914 edition of Schultz's "Farbstofftabellen" for 886 of the 921 commercial dyes there listed and for which dates of appearance on the world's markets could be fixed with any approach to reasonable accuracy; of the 35 entries not considered, 33 never were subject to U. S. patents and 2 were subject to U. S. patents, namely, picric acid (expired) and indigo (some still alive).

At the end of 1912, 206 dyes were subject to U. S patents (or 207 adding indigo) and 680 (or 714 adding picric acid and the 33 others above referred to) were then free from all U. S. patent-restraint to U. S. makers.

Limiting further discussion now to these 886 dyes out of those 921, the Table I speaks for itself; under the column "Pat." are given the numbers of dyes subject to U. S. patents for the year given (all patents 17 years old being counted as lapsed); under the column "Free to all" are given the number of dyes not subject to U. S. patents for the year given *inclusive* of all dyes whose U. S. patents had then lapsed.

It must be remembered that the intermediates used in the non-patented dyes were not patented in the U. S. and that very few, if any, of the intermediates used in the patented dyes were patented in the U. S.

This 1912 situation is visualized in part in Fig. I, which needs no elucidation. It shows the rapid growth of the business and emphasizes that whatever brought the coal-tar dye industry to Germany, it was not the U. S. patent system. Something else was at work—the market was being developed and the industry being created. Both these things were being done by a number of nations—Swiss, British, French, Germans, Austrians, Italians, Dutch and Americans, but the Germans succeeded better than any or all of their competitors. There is no blinking that fact. As far back as 1887, Otto N. Witt[1] wrote as follows:

"The success of a coal-tar dye factory is to-day no longer dependent upon the careful guarding of factory secrets as in the past, but upon a systematically arranged plant and the proper distribution therein of the work to be performed and above all upon skillful commercial management, both within and without the factory."

In considering this diagram, however, the following chronological order of events must not be lost sight of:

| | |
|---|---|
| 1844 | French compulsory working clause enacted. |
| 1856 | French and British coal-tar dye industry started. |
| 1859 | Swiss coal-tar dye industry started. |
| 1860 | German coal-tar dye industry started. |
| 1866(*a*) | U. S. coal-tar dye industry started. |
| 1869(*b*) | First of these U. S. coal-tar dye patents issued. |
| 1873 | French branch factories of German dye-works erected. |
| 1874 | Germany made 90 per cent of world's coal-tar dyes. |
| 1877 | German compulsory working clause enacted; first German patent law |
| 1896 | Russian compulsory working clause enacted; Swiss coal-tar dye production equal to that of France and England combined. |
| 1907 | Swiss compulsory working clause enacted. |
| 1908 | British compulsory working clause effective. |

(*a*) THIS JOURNAL, **7** (1915), 695.

(*b*) Prior to 1869 no fewer than 9 U. S. patents relating to coal-tar dyes had been issued. Classified according to citizenship of owners: England 3, France 3, Germany 1, U. S. 2; five were specific process patents only; 4 were product patents, 2 each to France and to the U. S.; all of these have since become obsolete.

Further, in 1912, Germany exported $51,545,326 of coal-tar dyes, intermediates and crudes in excess of her imports thereof; Switzerland had a corresponding excess of $3,794,898, while Great Britain had the reverse, an excess of imports over exports, of $6,275,775.[2]

A most liberal estimate of the production in 1912[3] of all coal-tar dyes for those five countries is as follows:

| | |
|---|---|
| Germany | $68,222,846 |
| Switzerland | 6,452,651 |
| England | 5,982,676 |
| France | 5,000,000 |
| United States | 3,750,000 |

In 1896 Switzerland (eleven years *before* it had a compulsory working clause and 37 years *after* it started its coal-tar dye industry) produced $3,200,000 worth of coal-tar dyes,[4] *i. e.*, as much as France and England together in that year. French

[1] *Chemische Industrie*, **1887**, p. 215.
[2] THIS JOURNAL, **6** (1914), 1015.
[3] *Ibid.*, **6** (1914), 1017.
[4] *Ibid.*, **6** (1914), 1026.

figures for 1897 and later are not accessible, but France's production is smaller than that of Switzerland.

Finally, Germany produced:[1]

| Year | Alizarin | All other coal-tar dyes |
|---|---|---|
| 1874 | $3,000,000 | $ 3,000,000 |
| 1878 | $6,250,000 | $ 3,750,000 |
| 1882 | $8,750,000 | $ 3,750,000 |
| 1890 | $6,250,000 | $10,000,000 |

The cause of this slow increase of values is the great price-reduction per unit of dyestuff; the 1890 unit-values are barely 40 per cent of the 1879 unit values. Germany's excess of exports over imports[1] is as follows:

| Year | Anilin oil and salt | Anilin, etc., dyes | Alizarin 10 per cent waste |
|---|---|---|---|
| 1876 | 175 tons | 175 tons | Not known |
| 1880 | 345 tons | 1640 tons | 5871 tons |
| 1885 | 1241 tons | 4213 tons | 4145 tons |
| 1890 | { 3411 tons, $1,706,000 | 6695 tons, $8,656,000 | 7892 tons, $3,157,000 |

The 1890 German export excess totals $13,519,000; the corresponding figure for 1912 is $51,545,326, or very nearly four-fold.

The above productions are 90 per cent of the world's production[2] for the years shown. Therefore, Germany in 1874—three years before she had a patent law or a compulsory working clause, fourteen years after she started the coal-tar dye industry, and 18 years after this industry started in France and England—had even then outstripped all of her competitors combined, by 9 to 1, and that in spite of France having a compulsory working clause from 1844 (12 years *before* this industry started) down to the present.

This state of affairs certainly cannot be charged up to compulsory working laws, and, therefore, those who attempt to force compulsory working in the U. S. will have to find a better excuse than have the advocates of the Paige Bill.

It is perfectly obvious and self-evident that the value of the markets in the 207 dyes still patented in the U. S. in 1912 is very much smaller than the value of the markets in the 714 dyes then free from any and all U. S. patent-restraint. Since 1912 U. S. patents on 44 further dyes out of the above 207 have expired, leaving 163 dyes of these 921 subject to U. S. patents, or about 4.5 free dyes for each dye subject to U. S. patents.

Under this state of facts it is clear that the French working clause did not keep the coal-tar dye industry in France and that the German working clause did not create or retain the coal-tar dye industry for Germany, nor did it create the coal-tar dye industry for Switzerland; neither can the U. S. patent system be charged with Germany's present-day success because in 1868 (12 years after this business started) the U. S. had the advantage over Germany in this respect (see foot-note (*b*), page 968 and Table V).

For the purpose of this discussion, the time from 1856 to 1912 (both inclusive) has been divided into three periods:

| | |
|---|---|
| I | 1856–1882 |
| II | 1883–1896 |
| III | 1897–1912 |

The first period corresponds to the time when the U. S. industry had a protective tariff high enough to enable it to compete with Europe.

The third period was chosen to show approximately the course of events during the past 17 years and represents the conditions during the life of those patents now (1915) about to expire and issued from 1897 onward; overlapping earlier patents are not considered, and no account of dyes introduced in 1913, 1914 and 1915 could be taken since that information is not accessible except at prohibitive labor.

The commercial products whose patents issued in each of these three periods and those non-patented commercial products of each of these three periods is given in Table II (no allowance for expired patents).

TABLE II

| | Patented | Not-patented | Totals |
|---|---|---|---|
| 1856–1882 | 41 | 98 | 139 |
| 1883–1896 | 225 | 236 | 461 |
| 1897–1912 | 187 | 99 | 286 |
| Totals | 453 | 433 | 886 |

In Table III is shown the number of patents taken out in these three periods by the different countries and also the number of non-patented dyes invented and exploited by these countries together with their respective totals as shown.

TABLE III—SHOWING PATENTED AND NON-PATENTED DYES FOR EACH OF THE THREE PERIODS AS STATED

Total 886 dyes—no allowance for expired patents

| Country | 1856–1882 Pat. | 1856–1882 Not-pat. | 1883–1896 Pat. | 1883–1896 Not-pat. | 1897–1912 Pat. | 1897–1912 Not-pat. | Totals Pat. | Totals Not-pat. | Grand Totals |
|---|---|---|---|---|---|---|---|---|---|
| Germany | 38 | 53(*a*) | 159 | 202 | 122 | 74 | 319 | 329(*a*) | 648(*a*) |
| Switzerland | 0 | 9(*b*) | 48 | 11 | 56 | 19 | 104 | 39(*b*) | 143(*b*) |
| England | 1 | 18(*c*) | 11 | 12 | 2 | 2 | 14 | 32(*c*) | 46(*c*) |
| France | 2 | 27(*d*) | 4 | 3 | 3 | 1 | 9 | 31(*d*) | 40(*d*) |
| Italy | 0 | 0 | 0 | 1 | 0 | 2 | 0 | 3 | 3 |
| Holland | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 2 | 2 |
| Austria | 0 | 0 | 1 | 3 | 0 | 0 | 1 | 3 | 4 |
| U. S. | 0 | 0 | 2 | 3 | 4 | 0 | 6 | 3 | 9 |
| | 41 | 107(*e*) | 225 | 236 | 187 | 99 | 453 | 442(*e*) | 895(*e*) |

(*a*) 7 simultaneously with 2 or 3 other countries.
(*b*) 2 simultaneously with 2 or 3 other countries.
(*c*) 2 simultaneously with 2 or 3 other countries.
(*d*) 6 simultaneously with 2 or 3 other countries.
(*e*) Less 9 for simultaneous invention by 2 or more countries.
NOTE—Differences in totals are accounted for by the above foot-notes.

In Table IV are given the distribution of the patented and non-patented 886 dyes over the 17 chemical classes, no allowance being made for expired patents. This table shows at a glance that except for two, namely, auramines and indophenols, each chemical classification had at all times members free from U. S. patent-restraint; in the majority of the other classifications the non-patented dyes were very well provided for as against the patented dyes.

TABLE IV—CHEMICAL DISTRIBUTION OF PATENTED AND NON PATENTED DYES

No Allowance for Expired Patents. (Total 886 Dyes)

| Dye class | 1856–82 Pat. | 1856–82 Not-pat. | 1883–96 Pat. | 1883–96 Not-pat. | 1897–1912 Pat. | 1897–1912 Not-pat. | Totals Pat. | Totals Not-pat. | 1912 Totals |
|---|---|---|---|---|---|---|---|---|---|
| Nitroso | .. | 2 | 1 | 1 | ... | .. | 1 | 3 | 4 |
| Nitro | 1 | 1 | . | . | 1 | . | 2(*a*) | 1 | 4 |
| Stilbene | . | . | 2 | 5 | 3 | . | 5 | 5 | 10 |
| Pyrazolone | . | . | 1 | 1 | 6 | 4 | 7 | 5 | 12 |
| Azo | 24 | 43 | 137 | 165 | 43 | 37 | 204 | 245(*b*) | 462 |
| Auramines | .. | .. | 2 | ... | ... | .. | 2 | ... | 2 |
| Triphenyl- and diphenylnaphthylmethane | 3 | 17 | 20 | 16 | 9 | 4 | 32 | 37(*c*) | 72 |
| Xanthone | . | 18 | 8 | 8 | 3 | 1 | 11 | 24 | 35 |
| Acridine | . | 1 | 3 | 2 | . | 2 | 3 | 5 | 8 |
| Quinoline | 3 | 1 | . | . | . | . | 3 | 1 | 4 |
| Thiobenzenyl | .. | .. | 3 | 2 | ... | .. | 3 | 2 | 5 |
| Indophenols | 1 | .. | ... | ... | ... | .. | 1 | ... | 1 |
| Oxazine and thiazin | 2 | 1 | 16 | 12 | 13 | 3 | 31 | 16(*d*) | 48 |
| Azine | 2 | 8 | 11 | 15 | . | . | 13 | 23(*e*) | 38 |
| Sulfur | . | 1 | 8 | 2 | 21 | 19 | 29 | 22(*d*) | 52 |
| Anthraquinone and related dyes | 5 | 5 | 13 | 9 | 52 | 23 | 70 | 37(*f*) | 116 |
| Indigos | . | . | . | 1 | 36 | 6 | 36(*a*) | 7(*g*) | 48 |
| Totals | 41 | 98 | 225 | 236 | 187 | 99 | 453(*a*) | 433(*h*) | 921 |

(*a*) Add 1 for patented but uncertain date of introduction.
(*b* to *h*) Add for non-patented but uncertain date of introduction: (*b*) 13, (*c*) 3; (*d*) 1, (*e*) 2, (*f*) 9, (*g*) 5, (*h*) add 33.

## U. S. COAL TAR DYE PATENTS PRIOR TO 1883

Before the end of 1882, 138 U. S. patents for coal-tar dyes had issued. Table V gives details, as shown, for them.

[1] Wichelhaus, "Wirthschaftliche Bedeutung Chemischer Arbeit," pp. 33 and 34.

[2] "Guide Book for the Exhibition of the Chemical Industry of Germany at the World's Fair, Chicago, 1893," p. 68.

TABLE V—DETAILS OF 138 PATENTS ISSUED PRIOR TO 1883

P = Product patent M = Method or process patent

| Year | France P | France M | England P | England M | Germany P | Germany M | U. S. P | U. S. M | Totals |
|---|---|---|---|---|---|---|---|---|---|
| 1861 | | 1 | | | | | | | 1 |
| 1863 | | | | 1 | | | | | 1 |
| 1864 | | | | 1 | | | | | 1 |
| 1865 | | | | 1 | | 1 | | | 2 |
| 1866 | 1 | | | | | | | | 1 |
| 1868 | 1 | | | | | | 2 | | 3 |
| 1869 | | 1 | | | 2 | | | | 3 |
| 1870 | | | | | | | | | 0 |
| 1871 | | | | | | | | | 0 |
| 1872 | | | | 1 | | | | | 1 |
| 1873 | | | | | | | | | 0 |
| 1874 | | | | | 2 | | | | 2 |
| 1875 | | | | | | | | | 0 |
| 1876 | | | 1 | | | | | | 1 |
| 1877 | | 1 | | 2 | | 1 | | | 4 |
| 1878 | 1 | | | | 5 | | | | 6 |
| 1879 | 3 | | | | 3 | | 7 | | 13 |
| 1880 | 1 | | | | 11(*a*) | | | | 12 |
| 1881 | 1 | | 2 | | 23(*b*) | 2 | 1 | | 29 |
| 1882 | 2 | | 3 | | 31(*c*) | 9 | 13 | | 58 |
| Totals | 8 | 5 | 3 | 9 | 73 | 17 | 23 | | 138 |
| Per cent of total | 5 8 | 3 6 | 2 2 | 6 6 | 52 9 | 12 3 | 16 7 | | ... |
| Total per cent by countries | 9 4 | | 8 8 | | 65.2 | | 16.7 | | |
| Stayed until 1912 | 0 | 0 | 1 | 0 | 28 | 2 | 0 | | 31(*d*) |
| Efficiency—per cent | 0 | | 8 3 | | 33 3 | | 0 | | |

(*a*) 7 for synthetic indigo all obsolete.
(*b*) 11 for synthetic indigo never commercially useful.
(*c*) 7 for synthetic indigo.
(*d*) Covering 33 different dyes still commercial in 1912; for 8 of the 41 dyes on the markets in 1882 the U. S. patents did not issue until *after* 1882.

UNITED STATES A POOR SCORER

In the language of the baseball score, at the close of 1882:

| | At bat | Runs |
|---|---|---|
| France | 13 | 0 |
| England | 12 | 1 |
| Germany | 90 | 30 |
| U. S. | 23 | 0 |
| Total | 138 | 31 |

UMPIRES—World's Markets and Dye Users

Therefore, it appears that each of these four countries made many wrong guesses as to the dyes suitable for exploitation and which stayed on the markets until 1912. On that basis France and the U. S. each made no score, England made 1 score, Germany made 30 scores. In percentages, the efficiency of "guessing the market" is, France and U. S. each zero; England 8.3 per cent; Germany 33.3 per cent.

Everybody knows the multitude of different reasons that are generally given for the failure of the home-team to win the pennant; and after it is all over the real sportsman says: "The best team won." Why should this case be an exception?

Whatever may have been the reason why "our team" did not win, the Paige Bill could not have helped it win. Many a ball-team has played poor ball for lack of proper home-support.

From Table IV it follows that the U. S. received outright and as a free gift and free from any and all U. S. patent-restraint 466 (433 and 33) dyes out of 921 products on the world's market in 1912; from Table I it follows that of the 455 dyes once patented in the U. S., 247 had become free from all patent-restraint by the end of 1912. By the end of 1915, 44 more patented dyes will have become free, making 291, or 64.2 per cent, of the 455 commercial and once patented dyes of 1912 free from all U. S. patent-restraint. Therefore, at the end of 1915 the condition for these 921 is:

| | | |
|---|---|---|
| Free to all | 758 or | 82.3 per cent |
| Patented | 163 or | 17.7 per cent |
| Total | 921 | 100.0 per cent |

The condition at any year is shown in the diagram. From Table III it follows:

For 886 of the 921 dyes on the markets in 1912:

I—The U. S. originated but 9, patenting 6 and not-patenting 3.

II—Germany patented 319 and did not patent 329.

III—Switzerland patented 104 and did not patent 39.

IV—England patented 14 and did not patent 32.

V—France patented 9 and did not patent 31.

The 35 dyes not contained in Table III, distributed as to originating countries, are as follows:

| | Germany | Switzerland | England |
|---|---|---|---|
| Patented | 2 | | |
| Not-patented | 26 | 6 | 1 |

Therefore, Germany, France and England each treated Switzerland and the U. S. with greater liberality than the latter did the former.

For the 921 commercial dyes of the Schultz "Farbstofftabellen" the total number of patents taken out in the four principal countries is as follows:

| | | | |
|---|---|---|---|
| Germany | 810 | United States | 487 |
| England | 524 | France | 399 |

From Table V it follows that while the U. S. did take out some patents it did not succeed in "picking any winners" that lasted till 1912.

From all this it irresistibly follows that there is nothing in the history of the development of the coal-tar dyes industry that could have been cured at all by compulsory working, which failed so utterly in France, Russia and in England.

This is reinforced by the history of this industry as follows:

GERMANY'S FIGHT FOR SUPREMACY

The following (in translation) from the pen of Otto N. Witt, of Berlin, in the Introductory Chapter to the "Sammel-Ausstellung der Deutschen Chemischen Industrie" for the Paris Exposition of 1900 (pp. 5 and 6) bears on this point:

"The almost simultaneous discovery of the first two aniline dyes, Mauvein by Perkin and Anilin-red by Natanson, occurred in 1856; the first practicable manufacturing process for Anilin-red was worked out by Verguin in 1859. Immediately and almost simultaneously the new chemical industry of artificial dyestuffs arose in both France and England. Seldom has any new industry come into being with such brilliancy and such immediate success as has this industry. To none as to this industry has been spared the reaction, after the first access of enthusiasm has died out. Its development is a series of triumphs which continue even to-day after an existence of more than 40 years.

"Germany contributed to the rise of this industry since one of its greatest chemists, August Wilhelm Hofmann, helpfully participated at the time of its introduction and development. But only with hesitation did Germany decide to take up this new industry. And yet Germany was particularly well prepared for such an industry; for only one step was needed to pass from the manufacture of fine chemicals, which had steadily progressed since its early introduction into Germany, to the dyestuff industry. Experience gained in the one could very profitably be translated to the other field; Germany's surplus of well-trained help could not find better employment than in an industry which was to flourish upon a foundation so complicated and theoretical.

"If Germany, nevertheless, allowed years to pass before she turned to the production of artificial dyestuffs the reason was probably that here likewise the fundamental economic conditions for the industry were more favorable abroad, and particularly in England, than at home. Not only were the necessary auxiliary substances, such as fuel and the products of the industries of acids and alkalis much cheaper in England, but Germany lacked also particularly the raw material—tar and its distillation products—because the gas industry was here not nearly so well developed as in England and in France."

So does the following from Heinrich Caro's lecture on the development of the coal-tar dye industry[1] (in translation):

"This industry, which arose in England and France, has finally and after a mighty struggle found its principal home in Germany, and that in spite of our being in an unfavorable geographical location and far removed from the source of raw materials and the consumers of the products of this industry and hampered

[1] *Berichte*, **1892** (3), p. 956; see also *Jour. Soc. Chem. Ind.* **1885**, p. 436; *Jour. Soc. Arts*, **1886**, p. 759; *Jour. Soc. Chem. Ind.*, **1886**, p. 351 for more reasons

as we are on many sides through unfavorable foreign tariff and patent laws."

Finally, the following from Sir William Henry Perkin,[1] the founder of the coal-tar dye industry, is suggestive:

"And, moreover, who could have formed any idea of the wonderful development of the coal-tar color industry that exists to-day, started from such small beginnings, but which through the researches of an army of scientific men, is now of such colossal magnitude."

In view of all this it is clear that the Paige Bill is no relief whatever for the condition it seeks to cure. On the contrary, it is full of harm to us as a nation and can do us no good.

### PAIGE BILL BROADLY EXAMINED

Before proceeding to any detailed discussion of the Paige Bill, I want to say that I consider it to represent an attack upon the best interests of this country, as ill-advised as it is full of pernicious potentialities. We in this country believe that class legislation is intolerable; that being so, what must we think of *sub*-class legislation? The textile people believe that compulsory working is good—for a few of us chemists; in other words, the Paige Bill selects a few of us upon which to experiment with this compulsory working of patents. If compulsory working of patents is a good thing for the chemists, or a few of us, we are certainly willing to share our good fortune with the rest of the country. If it is a doubtful thing or a bad thing, then there is no reason why some of us should be selected for the purpose of "trying it on the dog;" under these circumstances, the whole country ought to step in and make every man take his just share of the risk, and not as this Bill contemplates, enable the textile and other people to stand from under and simply shove us chemists, or some of us, out where we are exposed to injury.

Congressman Paige himself is reported[2] as saying of this Bill at the banquet given in Boston by the National Association of Cotton Manufacturers on April 28, 1915:

"There were those who feared that the Bill I introduced would be applied to all patents, and they were naturally lukewarm, if not actually opposed to it, but the Bill contemplated nothing of the kind. It was introduced solely for the purpose of relieving American manufacturers from the deplorable conditions which existed in September last.

"I think the textile manufacturers of the country should have investigated the merits of the Bill, even if they did not feel warranted in urging its passage. But the manufacturers who ought to have been so deeply interested in this problem in New England got cold feet because it was represented to them that the Bill would be of no avail."

Since compulsory working of textile patents is regarded as bad by our textile interests why should compulsory working of chemical patents be considered good for our chemical interests? If compulsory working is as good as represented by our textile interests why should our textile makers "fear" that the Paige Bill would apply to *their* patents? If *they* "fear" under those circumstances why should chemical manufacturers not do the same? Since some of our textile interests are "naturally lukewarm" or "actually opposed" to any effort to enforce compulsory working of textile patents why should our chemical interests do otherwise with respect to the compulsory working of chemical patents? Why should our chemical manufacturers be so recklessly sacrificed for the benefit of our textile interests? The above quotation throws a convincing light upon the mental attitude of the supporters of this Bill and proves beyond question that compulsory working is in itself a bad thing and as such is instinctively dreaded by those likely to be affected thereby.

Not only is the Paige Bill badly constructed from the point of view of the needs of the chemists, but it is the very poorest kind of law-building; it attempts to inject into a Patent Act the language of a Tariff Act; in other words, it has selected, from a law-building point of view, the entirely wrong tool with which to do its work.

The Paige Bill is bare and unequivocal compulsory working, absolutely devoid of any of the legislative and administrative compromises which the experience of the world has unqualifiedly proven to be absolutely essential; it absolutely ignores the legislative experience of 57 countries for the past 80 years.

### PAIGE BILL REVERSES TWO LONG-ESTABLISHED U. S. POLICIES

The U. S. Patent Act of April 10, 1790, did not specify "composition of matter" which is the basis of our product claims, among the patentable subject-matter; this Act was repealed February 21, 1793, and "composition of matter" was then made patentable and has remained so ever since, or for 122 years.

The U. S. Patent Act of July 12, 1832 (repealed July 4, 1836, 79 years ago) provided for compulsory working of all U. S. patents to be held by foreigners;[1] no such legislation has since been passed.

Those who wish to bring about such fundamental reversals in our policies of such long standing surely must sustain the burden of showing positive advantages and the sponsors of compulsory working have utterly failed to do so.[2]

The past has taught nothing to the advocates of this Bill.

### SIXTEEN CRITICISMS OF PAIGE BILL

Without attempting a minute and exhaustive analysis of this Paige Bill, it is sufficient to point out in sketchy fashion the following 16 directions in which it is open to serious criticism:

1—The things to be affected by this Paige Bill are "any drug, medicine, medicinal chemical, coal-tar dyes or colors, or dyes obtained from alizarine, anthracene, carbazol and indigo." These things are to be deprived of the right to a product patent, to a generic process patent and are to be limited to *the* process of manufacture specifically described and no other; all other products to continue to enjoy the rights thus taken away from these enumerated products.

2—Process patents relating to these designated things must be worked within this country by the patentee or by a licensee inside two years from the issue date of the patent, and the product must be continuously manufactured within this country thereafter throughout the life of the patent.

3—The products of these patents must be for sale at the plant where they are made; they must be sold to all comers without exception.

4—A *citizen* of the United States escapes infringement if he uses the process of the product of a patent covering any of these things, if the patentee fails to observe any of the aforementioned requirements; a *resident* of the United States and *not* a citizen thereof does not so escape infringement.

5—A person who deals in the products of such processes of patents so invalidated is free from suit for infringement; a person who uses that material is not at all exempt from such pursuit and by implication is open to such pursuit.

6—A person using benzol which has been produced from coal tar is put on an entirely different footing from a person who uses benzol recovered from the gas of a by-product coke oven or benzol that may be made by the Rittman process.

To show how these things may work out, it is enough to call your attention to the fact that if Inventor A makes a so-called coal-tar dye from coke-oven benzol he can get a product patent, a generic process patent, and he can do as he pleases with his product and his process; if, however, Inventor B uses coal-tar benzol he *cannot* get a product patent for his new dye therefrom; he cannot get a generic process claim; he can merely have a specific process claim and he *must* operate that process *con-*

[1] *Jour. Soc. Chem. Ind.*, **1906**, p. 785.

[2] *Textile Manufacturer's Journal*, May 1, 1915, p. 50; *Textile World Record*, May, 1915, p. 126.

[1] THIS JOURNAL, **7** (1915), 304.

[2] *Ibid.*, **7** (1915), 307–317.

*tinuously* for the last fifteen years of the statutory life of the patent and he *must* sell at his plant to all comers. It is not only novel but pernicious to attempt to define patentable invention by the *source of the material* employed in carrying out that invention.

7—A man may take coal-tar benzol and therewith invent a new photographic developer or a non-medicinal material or a non-dyeing material which is useful in the arts, obtain a product patent on it, a generic process patent on it, and do absolutely as he pleases with both.

8—If it be contended that the expression "coal tar" as used in the Paige Bill means things that are contained in coal tar, then where do we draw the line? Ammonia is a constituent of coal tar and is obtained from it. Would a dye-product, made with the aid of ammonia, be a coal-tar product *because* of that ammonia? Water is a component of coal tar. Is every dye in whose manufacture water is used a coal-tar dye? These illustrations are enough to show the pernicious effect of the loose, vague, ambiguous and indefinite language of this Bill.

9—Is there any reason why a man who invents a dye from coal-tar benzol should be compelled to have a selling outfit at his manufacturing plant, and a man who makes a photographic developer from coal-tar benzol should *not* have a selling outfit at his plant?

10—Suppose a man invents a new member of the products affected by this Paige Bill, and, in order to protect himself, he proceeds to invent, let us say, five different processes of making that particular new thing; suppose he is operating one of those processes in such a manner that with ten days' production he can supply the needs of the entire United States for the whole year; suppose that only one of these processes is for him a commercially profitable process. Must that man operate his plant 355 days in the year when he cannot sell the output? Must he operate each and every one of those processes throughout the entire year and every day or moment of that year? Must he sell to anybody any amount of a product produced by any one of these processes that a whimsical buyer may specify? If so, it simply opens the door to sandbagging—an unfair attack that certainly cannot appeal to the American people. It takes no great imagination to figure out the pernicious combinations that are possible under this state of affairs. For example, suppose a man decided that A must deliver to him 10,000 lbs. of his product made by his least profitable process; A decides upon a price, which the prospective buyer declines to pay. This Bill says, in effect, that A must sell to B; they cannot agree on the price. Who decides? Or shall B be in a position to browbeat A into selling him the product of a process at a loss?

11—Suppose A and B are competitors. B needs the product in his business that A has invented, just as does A. Suppose B goes to A and insists on buying that product. At what price shall A deliver these goods to B? There is no provision whatever in this Bill for the determination of any such disputes and they are bound to arise. If A's product were not patented he would *not* have to sell to B.

12—Further, suppose A invents a new process of producing a so-called coal-tar dye, by itself, as a pigment and upon fiber. Must he embark not only in the venture of making the coal-tar dye itself, but also of the pigment and of the colored fiber? If A fails to embark in either of these ventures or is unable to obtain a licensee, does he lose his entire patent, and if not, how much and what part does he lose?

13—Suppose A, during the first two years, cannot embark upon the enterprise or is not able to find a licensee. *Must* he lose his patent? If so, this Bill merely puts a prize on prospective licensees to band together, string the inventor along, and when the two years are up, jump in and take for nothing that which they did not create.

14—Suppose an American invents a new and very useful drug derived from animal sources entirely, and a foreigner discovers a way of making that same drug from so-called coal-tar materials. Is this foreigner to be placed in a position to drive the American out of his own market? That is precisely what the Paige Bill makes possible and enthusiastically invites and encourages.

15—Suppose that the inventor does not succeed before the expiration of the twenty-fourth month, in getting his plant in shape, but does during the twenty-fifth month. Is he to be deprived of his patent? If that be so, why should we trouble at all to invent and would it not be easier to let the other fellow do all the work while his time is running against him, interfere with delivery of machinery and the like to him, and when the twenty-fourth month is up, simply rob him of what he has? If this is not putting a premium on piracy, underhanded dealing and double-crossing, there never could be any such inducement. Suppose his plant and stock burn up during the third year and it takes him a week to rebuild, does he lose his patent? If not, why not?

16—This Bill attempts to do away with product patents and substitute specific process patents therefor and abolishes generic process patents. Everybody knows that under the American system, chemical process patents are almost impossible of defense; infringement is difficult to detect and to prove; orders of inspection are very rarely given. If we are to substitute process patents for product patents on the ground that that is the German practice, then we should also incorporate into our system of jurisprudence the German judicial point of view of process patents. While the German claims are in form process claims, yet judicial interpretations have given them the effect of product claims; furthermore, the patentee, upon a reasonable *prima facie* showing, forces the defendant to disclose to three men skilled in the art and acceptable to the Court that which he actually does and the Court then decides whether the thus disclosed matter is or is not an infringement of the patent. For how long does any one suppose the American public would stand for a judicial procedure of this kind? I have yet to see the American chemist who, after fully appreciating this German procedure, was for one instant in favor of abandoning our product claims and product patents for process claims and patents.

### PROCESS AND PRODUCT CLAIMS

The difference between our present practice, now 122 years old, and the practice proposed by this Paige Bill may be fairly illustrated as follows: A prospector locates a valuable gold mine after much wandering and traveling; he stakes and registers his claim; that gold mine is his and all are trespassers who enter upon his claim by whatever route. The Paige Bill proposal would have it that a person reaching that staked and registered mine by a route different from the trail taken by the first locater has equal rights upon the property with the first locater; this Bill wants to try this departure, new to the U. S., upon a few of us chemists, while the textile people continue to live and work under the old plan. In other words, the Paige Bill ranks a finder of a second trail to a gold mine, that he did not discover, as of equal importance with the man who had the grit to go out and find that unknown gold mine; "claim-jumping" is not regarded as particularly honorable and clean dealing and why should the Paige Bill encourage it? To bring it nearer home: suppose you buy a lot and build a house on it; everybody is a trespasser who enters that lot by any route whatever. The Paige Bill says that any one is *entitled* to full and free use of that lot and house and all its contents equally with you, *provided* he enters the lot by any means other than the front gate which happens to be your customary way of entering your grounds Can you imagine the disturbance that this sort of a proposition would make among householders? Then why should the chemists of this country tolerate any such treatment?

### PAIGE BILL INCURABLY BAD

In short, this Bill opens the way to innumerable avoidable

disputes without providing any judicial means of settling them, but leaves it to the individual to work out a set of conclusive judicial interpretations through costly, time-consuming court proceedings. We now have a large body of such decisions based upon our present policy of patent-protection now over 122 years old. To my mind, it is worse than useless to throw away such positive results and send some of us out on another expedition for the same purpose which might require fifty years to accomplish and with every reasonable prospect of not hitting the mark at all, and all at the cost of a selected few of us.

There is no question that many of the above specified objections to this Bill can readily be cured by suitable alterations in its language. But what an indubitable index such imperfections are as to the seemingly haphazard and thoughtless manner in which this legislation was conceived and proposed! With so many on-the-surface faults and shortcomings why is there not just ground for well-founded distrust of the more hidden effects of such proposed legislation, so-called "jokers?" No matter what changes may be made in this Bill as to details like those enumerated, the three insurmountable and irremovable objections to it still remain:

1—Class and subclass legislation.

2—Abandonment of a settled judicial policy and substitution therefor of an effort to create a new judicial policy which the world's experience to date shows conclusively will lead to failure.

3—Introduction of a new system of judicial procedure which cannot be otherwise than obnoxious to American principles and thought.

Experience is said to have shown that manufacture within the country is not stimulated but that dumping is. Shall the Paige Bill stimulate dumping? If so, for whose benefit? Any one else than the dye-*users?*

### COMPULSORY WORKING IN OTHER COUNTRIES

With the aid of the book entitled "Foreign and Colonial Patent Laws," by W. C. Fairweather (published London, 1910) and other publications, I have compiled the following list of countries having compulsory working clauses and have given the date of enactment thereof, so far as it could be ascertained with any approach to accuracy; as to dates this compilation needs checking up.

| Date | Country | Date | Country | Date | Country |
|---|---|---|---|---|---|
| 1832[1] | United States | 1887 | Sweden | 1902 | Nigeria (Northern) |
| 1844 | France | 1888 | India | 1902 | Spain |
| (1856 | Coal-tar dye industry founded) | 1894 | Portugal | 1902 | Transvaal |
| | | 1896 | Costa Rica | 1903 | Barbados |
| 1864 | Liberia | 1896 | Negri Sembilan | 1904 | Rhodesia (Southern) |
| 1869 | Peru | 1896 | Russia | 1905 | Trinidad and Tobago |
| 1877 | Germany | 1897 | Guatemala | 1906 | Ceylon |
| 1880 | Ecuador | 1898 | Finland | 1906 | Leeward Islands |
| 1880 | Luxemburg | 1898 | Granada | 1906 | Roumania |
| 1880 | Turkey | 1899 | Nicaragua | 1907 | Switzerland |
| 1882 | Brazil | 1901 | Seychelles | 1908 | Great Britain |
| 1885 | Norway | 1902 | Bermudas | 1908 | New Zealand |
| 1885 | Uruguay | 1902 | British Guiana | 1908 | Panama |
| | | | | 1909 | Japan |

[1] Repealed 1836.

Those countries whose enactment-dates have not been determined:

| | | | |
|---|---|---|---|
| Argentine | Bolivia | Denmark | Newfoundland |
| Australia | Canada | Hungary | Nigeria (Southern) |
| Austria | Chile | Italy | Orange River Colony |
| Bahamas | Colombia | Iceland | Venezuela |
| Belgium | Cuba | Malta | |

Why do not *all* these countries have coal-tar dye industries? They all have compulsory working laws!

A half-dozen hours' casual reading of the working clauses as set out in this Fairweather publication will convince any one of the futility of the Paige Bill.

### COMPULSORY WORKING AN ABSOLUTE FAILURE

In conclusion, the following from Lord Moulton, the foremost patent-counsel of Great Britain and one of Great Britain's highest law officers of the present day with regard to the British Compulsory Working Act of 1907 and uttered by Lord Moulton in 1914[1] after more than 6 years of enforcement of that Act, is pertinent and suggestive:

"Well, gentlemen, so far as the legislation, as it stands, about compulsory working is concerned, I am afraid I am going to use adjectives. I think it is not only mischievous, it is also idiotic. It is one of those cases which are growing to be common, where the layman rushes into legislation with little or no acquaintance with the subject on which he is legislating. Knowledge has gone so far that the layman cannot keep up with the technical knowledge of a subject, even in politics. In my opinion, it would have been impossible for any man who understood this matter to devise the present legislation.

"Now let us take one example, and remember when you are testing whether a thing is right or wrong by an example, you must never take an extreme example; you must take one which fairly represents it. Let me suppose that a man makes an invention and contents himself by taking out an English patent. The invention turns out to be of world-wide utility; it is adopted, we will say, by every civilized nation in the world; but the inventor has no rights abroad: he has rights in England only. Then comes some person and says, 'Your patent is worked mainly abroad!' Of course it is. Big as England is, the world outside is bigger. Then he appeals to this legislation, and claims that the patent must be revoked because it is worked mainly abroad. In this he is justified and the consequence is that an invention that is universally valuable and universally appreciated stands in the eye of the legislation of England, as it at present exists, as condemned to death, and it will be revoked unless the poor inventor can explain how it is that a useful thing is used more abroad than it is in England.

"It is no use arguing about legislation of that kind. It is self-condemned.

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"The mischief that has stirred up people to pass this legislation is that manufacturers, not inventors, stop the use of inventions in this country. Just think of the cases. Do you think that a man who invents a new dye would not like it to be made by Mr. Levinstein as well as everybody else? But it is a different question when a great foreign firm gets it. They do not want to protect the inventor's rights. They want to protect the manufacturer's rights. The consequence is that the whole cause of the outcry is the manufacturer who wants to get a monopoly by means of the rights which we have given to the inventor as a reward for his original thought, and you never find any mischief of the kind that it is supposed we must guard against as long as the patent remains in the inventor's hands. I smile when I hear those who take the opposite side in this controversy talk about the advantage of compulsory working because it brings trade into England and gives work to our working class. Mr. Levinstein is an old friend and an old client of mine, but do you think he conducts his campaign in order to bring the Badische Anilin and Soda Fabrik into England? No, no, no. If you strip the cases of the formal language in which they are put, you will always find that the man who wants to revoke a patent is a manufacturer who wants to prevent the inventor proper from getting the return of his invention. I have said that I never knew any inventor who kept the interest in his invention in his own hands, who was ever unwilling that it should be worked as largely as possible in every country in the world. Occasionally you may find a crank who puts too high a value on his invention, and will let the few years of the patent pass and his invention remain unused, simply because he thinks that the royalties offered are too low, but those cases are so rare that they may be neglected. No, the applications to revoke patents are not for the purpose of increasing the manufacture in England; they are for the purpose of increasing the importation into England. It is this which makes it so important to give to people clear ideas on the

[1] This Journal, **7** (1915), 314, 315.

subject. As you know, it is quite possible that the specious appearance of a movement in favor of English manufacturers (and it can be clad in those words) may bring some attempt to increase the severity of the law. This can be resisted only by showing to the world, first of all, that the movement is always from the manufacturer—the inventor has no interest in limiting the use of his patent—and, secondly, that the aim of all these attempts is to increase importation into England, and not manufacture in England.

"So much for the real substance of the case. What then is the true remedy? The true remedy is that you ought to protect the monopoly of every inventor who behaves reasonably and punish those only who act unreasonably. If an inventor sells his rights to a foreign manufacturer, and that foreign manufacturer uses the English patent to prevent manufacture in England, a manufacturer who is willing to make the article in England ought to be able to get a license to do it. No patent ought to be used for the purpose of checking work in the country itself. But let me point out the dangers that there are in taking a principle like that and using it without knowledge and without caution. There are many things that are best manufactured by one or two firms. The demand is small for them, and one or two firms can well satisfy it. If you threw it open to hundreds of firms you would get no greater benefit to the country. (A voice: 'Less.') Therefore, we have adopted the rule, and I think it a wise one, that the inventor should be left to manage his own patent, fix his own royalties, and get as much from it as he can with his own personal knowledge of the matter. But if he acts so unreasonably that the patent is having the effect of seriously checking working in England, then give the power to the Courts to grant a compulsory license. That is remedy enough, and I should counsel you not to do anything else whatever. If you do you will find that all you are doing is to help people to take the ideas of the inventor without giving any fair return, and to help people who manufacture abroad to import their goods into this country without remunerating the inventor. We do not want to see that, because we desire to see English manufactures increase, for we feel that we have a growing working population. We are glad to welcome new industries to develop in our midst; but, if we try to bring that about by unjust laws, you may be perfectly certain you will do more harm than good, and ultimately you will regret it."

## CONCLUSIONS

I—Compulsory working has nowhere been successful, is a gross economic error, increases dumping and does not increase home-production, and all other countries are anxious to find some way of dropping it.

II—The Paige Bill takes no notice whatever of the experience of the world for the past 80 years, proposes to start where the rest of the world, including the U. S., began 80 years ago, and wants to re-prove at the expense of a few of us chemists what six hours' reading of past legislation in other countries would teach, to any one, was and is a colossal mistake.

III—The U. S. rejected one of the Paige Bill proposals in 1793 and the other in 1836; no reasonable proof of advantage for such a reversal as now proposed has been promised, much less offered by the supporters of the Paige Bill.

IV—The Paige Bill was devised for the purpose of forcing European dye-makers to the U. S.; compulsory working had nothing whatever to do with the dye industry development.

V—The Paige Bill as it stands puts a premium on dishonest practices and unfair methods of dealing and invites and encourages such conduct.

VI—Compulsory working should not be adopted by the U. S. and the Paige Bill and all Bills like it should be killed for good and all.

50 William Street, New York City

## DISCUSSION

By H. E. Stonebraker

Gentlemen of the Chemical Society:

The request of your committee to have placed before you the other side of the question which Doctor Hesse has so ably presented, places me in an anomalous position, but with your assurance that the following remarks will not be construed as my personal views, or the views of the patent bar generally, I will endeavor to explain the causes for the proposed Bill, and the advantages to be derived, as drawn from my impressions after a study of the Bill in connection with similar acts in foreign countries and the conditions surrounding the much recently proposed patent legislation in the United States.

Before entering into a detailed discussion I want to call attention to several points brought out by Dr. Hesse: *First*, I do not understand that the Bill excludes "generic process patents." It states that patents may be obtained on applications relating to "a definite process," as distinguished from a product, and there is nothing in this to indicate that the Bill contemplates the refusal of a patent on a generic process, since a definite process may be either generic or specific. *Secondly*, the patented product does not necessarily have to be sold at the place where manufactured, as the Bill merely provides that the product shall be "manufactured in the United States by or under authority of the patentee within two years of the granting of said patent, and after the commencement of said manufacture" it is to be continuously carried on in the United States "in such a manner that any persons desiring to use the article may obtain it from a manufacturing establishment in the United States." Under this provision, I do not understand that the patentee shall be compelled to sell at *any* price, but merely that he shall offer it for sale so that it may be obtained by anyone who is willing to pay the required price.

The Paige Bill is divided into two sections, one of which deals with the exclusion of certain patents, except in so far as they relate to a definite process, or, in other words, product patents, whereas the latter part of the Bill deals with the compulsory working feature, which is the more important consideration of the two.

The elimination of product patents will not work any serious injury to an inventor and, in fact, will be of considerable assistance in connection with litigation involving chemical patents, where it is very difficult, and sometimes impossible, to identify a particular product with a patent. It is hard to conceive of a case where an inventor would not be protected as to his product, if a patent is granted to him covering the process employed in making that product, so that the inventor would not suffer except in the unusual case where the product could be manufactured by more than one process. Under such a condition, a generic process patent would afford complete protection, and if the inventor is not entitled to cover a generic process there is no reason why he should be granted a patent covering the specific process which he has developed for producing a certain formula, and every other process that might be developed by others after him, but of which he had no conception. It has been held, as instanced in the case of Downes *vs.* Teter-Heany Development Company, 150 Fed. 122, that where a patent includes claims both for a process and a product of the process, the claims for the product are to be construed in connection with and are limited in scope by the claims for the process and are not infringed unless the process claims are also infringed. In the case of Kuehmsted *vs.* Farbenfabriken, 179 Fed. 701, Hoffman patent No. 644,077, for Acetyl Salicylic Acid, known medically as Aspirin, was involved, and covered the product of a new process. The Court experienced great difficulty in finding any difference between the patented product, old products, and the infringing product and held that "a prior known compound having the same formula is not conclusive

evidence of the lack of patentable novelty in a chemical compound," and the patent was sustained on the ground that the product claimed was produced by a new process. So that in reality the invention was for a process and not for a product, and if the patent had been based on the process instead of the product, much labor and expense would have been eliminated in litigating it. In commenting on the invention and the patent the Court said:

"The fact that the formulae are identical cuts little figure. A chemical formula is simply the symbolical expression of the composition or constitution of a substance; as the formula for water is $H_2O$. Customarily, chemists who intend to produce a combination of two substances write the formula of the product in advance of making it. And, assuming that the formula actually expresses the constitution of the substance chemically, the substance physically, and in consequence, therapeutically, may be widely different, as, for instance, the water of the seas differs in its physical body from the water of certain springs though the chemical formula for water, whether of sea or spring, is $H_2O$. That is to say, two substances having the same chemical formula may differ widely as to impurities upon qualitative analysis."

The net result seems to be that the real invention in every instance of this class of patents resides in the process and not in the product, and to eliminate product patents would be of no serious consequence to the inventor, and, on the other hand, the requirement that he define his invention in terms of the process might be of great help in cutting down litigation and in enabling him to prove infringement with greater certainty.

Turning now to the compulsory working phase of the bill, a great deal has been said in the numerous discussions of compulsory license and working-laws about what the respective laws fail to accomplish, but nowhere has there been pointed out a specific instance of harm having been done as a result of such laws. The disadvantages claimed seem to be in the nature of generalizations, and the hypothetical cases which are cited to show the bad effects of the laws in operation are usually most exceptional instances. In the talk to which you have listened this evening, three reasons have been assigned as a basis for the statement that the Paige Bill cannot help the chemists. These I will take up in the order given.

(1) Commercial coal tar dyes subject to United States patents have never equaled the number of commercial dyes not-patented in the United States. In answer to this, it can be said that the Paige Bill will not affect in any way the unpatented dyes, and it will insure the manufacture of patented dyes or, as an alternative, the lapsing of the patents.

(2) The second point advanced was that in all but a very few instances, dyes free from United States patent-restraint could be made and were offered as successful substitutes for dyes subject to United States patents. This admits the existence of cases where United States patents stood in the way of open competition, and if any of these patents were pigeonholed, it would certainly be a disadvantage to the public in general, and the Paige Bill would cure just such an evil.

(3) At no time was the American industry throttled or even handicapped by U. S. patents held by foreigners to such an extent that it could not offer successful substitutes for the great majority of patented articles. If this condition continues to prevail there may arise no cases that will require operation of the Paige Bill, but if the Bill did nothing more than to insure the continuance of such a happy industrial condition, it would be worth putting into effect for this purpose, in the absence of proof of any actual harm that might be done by it.

The Bill before us is one of several that have been presented to Congress as a result of a combination of conditions that have arisen in recent years, due in part, as claimed by many, to our patent system, and partly to some of the unfortunate business policies that have grown up with our trusts and larger combinations, and it may be of interest to digress for a moment and look at some of the causes for the general state of unrest surrounding our patent institutions.

A patent monopoly in an invention for a limited period is beneficial so long as the patent is not employed for illegitimate purposes, and the patent evils complained of arise only from the perversion of patent monopolies to illegitimate uses. Such illegitimate use has consisted in securing a monopoly more extensive than that covered by the patent, and by accumulating a number of patents and suppressing part of them. Our present-day trusts have come into existence *after* the enactment of our patent laws, at a time when competition was universally accepted in business and combinations for restraining trade were not dreamed of. Under such conditions a patent monopoly was a healthful stimulation for competition, but as soon as competing concerns attempted to combine for dominating any branch of industry, the patent monopoly was put to a use for which it was not originally intended and resulted in extortionate prices and an arrest of progress.

The inventors' guild, which includes in its membership such inventors as Thomas A. Edison, Peter Cooper Hewitt, Michael I. Pupin and H. Ward Leonard, define in the following language the danger that the country faces:

"It is a well-known fact that modern trade combinations tend strongly toward constancy of processes and products and by their very nature are opposed to new processes and products originated by independent inventors, and hence tend to restrain competition in the development and sale of patents and patent rights; and consequently tend to discourage independent inventive thought to the great detriment of the nation, and with injustice to inventors whom the constitution especially intended to encourage and protect in their rights."

It has been clearly demonstrated from experience that certain patent practices, when pursued in a competitive business way are harmless, and sometimes beneficent, whereas the same practices are attended with serious evils when pursued for the purpose of restraining trade, and it has been a world-wide practice to buy up patents for precluding competition, the harm of which has been recognized and dealt with in almost every nation except the United States. Great Britain, Canada, Germany, France and many other nations provide the government with power to liberate the manufacture, sale or use of all patented articles after a fixed period, which affords the patentee sufficient time for supplying the patented product to the public. In case of his failure to do so, in some countries the patent right is forfeited and the privilege of making and selling becomes common to everyone, while in other countries the owner of the patent by his inactivity brings himself within the terms of a compulsory license law.

There is no question but that patents have been bought up in large numbers in the United States for suppressing competition, and instances can be found in the reports of decisions of Federal Courts. Thus in Columbia Wire Co. *vs.* Freeman Wire Co., 71 Fed. 302, the Court, in referring to one of the parties stated that:

"It has become possessed of many if not all of the valuable patents for the manufacture of barbed wire and machines for so doing."

In the case of Indiana Manufacturing Co. *vs.* J. I. Case Threshing Machine Co., 148 Fed. 21, the Court found that one of the parties had acquired over a hundred patents pertaining to straw stackers.

The National Harrow Company was charged with having acquired eighty-five patents on spring-tooth harrows in National Harrow Co. *vs.* Bement, 21 Appellate Division, New York, 290.

And in the so-called Locks case, 166 Fed. 560, the Court said:

"It is a fact familiar in commercial history that patent rights

have a commercial value for purposes of extinction; that many patents are purchased in order to prevent the competition of new inventions and of new machines already installed."

Another and more famous case is that involving the Paper Bag patent, 150 Fed. 741, in which the complainant owned two patents covering machines for making paper bags, one of which patents was deliberately suppressed, and on this unused patent suit for infringement was brought. The suit was successful, although in both the Court of Appeals and the Supreme Court of the United States there were dissenting opinions, contending that the complainant, having purchased and suppressed the patent to prevent competition, was not entitled to the aid of a court of equity to enjoin and infringe it.

Other cases may be cited to show the harmful practice of buying up and suppressing patents, the effect of which is to shut out competition and to build up a monopoly of monopolies, equivalent to a patent on the industry, and such a combination is not a monopoly in the beneficial use of a specific invention (148 Fed. 25) but is a monopoly created by commercial cunning in the use of great wealth, and it is to cure this evil and prevent the continuation of such a practice that compulsory working is provided.

Another practice that has grown up is for a vendor of a patented device to place a notice on the product, requiring the purchaser to obtain his unpatented supplies, to be used with the patented product, *exclusively* from the owner of the patent under penalty of his being dealt with as an infringer if he fails to do so, and also, patented articles are sold with notices stipulating a fixed retail price below which the purchaser is forbidden to sell the article. This practice was first recognized in the case of Heaton Peninsular Button Fastener Co. *vs.* Eureka Specialty Company, 77 Fed. 288. The complainant owned a patent for a machine for fastening buttons to shoes by means of metallic staples, and placed a notice on the machines which it sold, to the effect that the purchaser was licensed to use the device only with staples purchased from the owner of the patent on the machine. The staples were not patented. The defendant sold staples to the purchaser who used the same on the patented machine, and the Court held that the act of selling the staples was one of contributory infringement, and enjoined a further sale of the *unpatented* staples.

The most recent upholding of this doctrine was in the case of Henry *vs.* Dick Co., which the Supreme Court decided March 11, 1912. In this later case, the Dick Company made and sold a patented mimeograph with a notice that it was to be used only with ink, paper and other supplies made by the Dick Company. The decision of the Court was that the sale of ink by Henry, who knew of the restriction, to the owner of the mimeograph for use therewith was contributory infringement.

The restriction as to resale price was however invalidated by the Supreme Court in the more recent case of Bauer & Co. *vs.* O'Donnell, decided May 26, 1913. According to the facts in this case, the complainant prepared and sold a compound made according to a patented formula with a notice stating that the contents of the bottle was patented, and that it was sold under license whereby the purchaser must retail it at not less than one dollar, and that anyone selling it for a less price or using it when so sold would be prosecuted for infringement. A druggist in Washington sold a quantity of the patented goods at a cut price and was sued for infringement, and the Supreme Court, by a five to four decision, declared that there had been no infringement of the patent, and while the court endeavored to distinguish this case in principle from the earlier case of Henry *vs.* Dick, involving the mimeograph they have failed to convince many persons that any distinction really exists that should cause the application of different principles to the two cases. I will not endeavor to reconcile these cases, and do not care to enter into any discussion as to whether the Supreme Court was right or wrong in the decision in either case, but am citing them to draw attention to the changed order of things that business conditions have brought about, whereby the highest court in our land has been influenced to decide by a most narrow margin in favor of one doctrine that has prevailed practically since the establishment of our patent system, and to throw down utterly another doctrine closely analogous. Something must be wrong with our laws that needs remedying, so that the public will at least be in better position to judge of the probable result in any case, and so that the people may not be forced to suffer individually or collectively under an illegal use of patent monopoly at the hands of any combination, built up directly or indirectly, for the purpose of restraining trade and competition.

I have here a statement of the working laws in the important civilized countries which may be of interest, but I will not burden you with reading this entirely. The laws in Germany and Great Britain are practically the same and require working only in the event that the patented article or process is manufactured or carried on exclusively or mainly outside the country. Only three applications for revocation of a patent on the ground of non-working were filed in Great Britain in 1912, and only one patent was revoked during the same year, and this was by consent of the patentee. A second application was withdrawn, while in the third case the patent was revoked in 1913.

During 1913, according to the official notice, eight applications for revocation were filed, of which seven were withdrawn, and only one patent was revoked, and this by consent of the patentee. Considering that more than a hundred thousand patents were in force in England on 1913, the figures above indicate that manufacturers are not in any way prejudiced by the working act.

One of the chief objections to a compulsory working law is that inventions are not suppressed, and that the supposed evil is fanciful and has no reality, but if there are no instances of suppressed inventions, and the proposed law is directed to an imaginary evil, it is strange that opposition should be made to it when it should affect no one according to this argument.

Let me read you some extracts from what Mr. Walter Reid, Chairman of the Institute of Inventors of Great Britain, had to say before the Imperial Industries Club on April 1, 1914.[1]

"We for a very long time had no compulsory working; we had allowed foreign inventors here to acquire monopolies in certain branches of industry and they had made use of those monopolies in a way which those who were acquainted with the details of the subject could no longer permit Great Britain to labor under the disadvantage of. On the occasion when we had the last deputation to Mr. Lloyd George a number of cases and details were given of industries that had suffered in Great Britain because foreigners had been granted monopolies here and had not worked the patents in this country, but, having the monopoly, they could demand from our own people prices which they at home could not obtain. A very familiar case was that of the alizarine industry, where our manufacturers here who had to use such dyes were paying about half a crown, and the practical real value of the material was about seven pence. Of course, our manufacturers were suffering there under a great disability as regards foreign competition because they required that dye, it was a dye which was necessary and the wool dyers in Bradford and elsewhere had those excessive prices to pay whereas their German competitors had not.

Now, I think, if we consider that, it is a clear case where the British industry is handicapped and unfairly handicapped; and I would ask you to bear in mind that the first and original idea of a patent was a monopoly for the introduction of an industry into this country, and it was only at a later stage that the inventor was given a monopoly for the produce of his brains.

[1] See THIS JOURNAL, 7 (1915), pp. 307–308.

Nobody will deny that an inventor ought to have something for inventing a thing; otherwise we should have no inventors in this country; they would go elsewhere. But I do think, myself, and, so far as I have been able to learn, the opinions of inventors generally are, that it is an unfair thing to British inventors that a foreign inventor should come here and acquire a monopoly and not do what the British inventor in most cases has to do from the very nature of the subject, namely, work the invention. I think that we, as an Imperial Industries Club, ought to see to it that the British inventor is not, at any rate, worse off than the foreign inventors. He cannot in many cases acquire foreign patents abroad in the same way that a foreigner can acquire a patent here because there is compulsory working.

"Now, as a consequence of that Act during the time when, if I may use the word, it was active, several firms abroad came and established factories in this country and a number of factories have undoubtedly been established under the pressure of the Act as we interpreted it. It is not enough to say that one firm or another has put up a factory in England, and they are not doing much, that they have done it just simply as a blind, and so on; that is not so much the question; those who are behind the scenes know very well that a number of patents have been introduced into this country under royalty to British firms that would not otherwise have been introduced. When an industry is introduced into this country, whatever it may be, there is employment for British capital, there is employment for British workmen and the industry becomes established in this country and after the lapse of the patent the industry becomes an English one."

The same reasons apply in the United States that apply in England in favor of compulsory working. The evil of illegal monopolizing of patents exists beyond a doubt. Only several days ago a decision was handed down in the United States District Court for Eastern Pennsylvania by Judge Dickinson against the Motion Picture Patents Company, the General Film Company and many other concerns and individuals manufacturing moving picture films and accessories or controlling the rights of their manufacture, and by this decision the so-called moving picture trust has been dissolved. The Court discusses the rights of the holders of patents in the following language:

"It is the right of a patentee through having the exclusive sale of the patented article to control and in that sense to monopolize the trade in it. It is wrong by an illegal restraint of trade to monopolize it or any part of it."

"We feel constrained on the authority of this case alone, to find that the agreements and acts of the defendants in the present case went far beyond what was necessary to protect the use of the patents on the monopoly which went with them and that the end and result which would be expected to be and was accomplished, was the restraint of trade condemned by law."

Let me call your attention to the fact that the entire world-wide industry of moving pictures and film manufacture has been dominated by probably less than ten men, and were it not for the obstruction which the United States has placed in their way under the Sherman Law, it is not improbable that in a little while the public would be compelled to pay one and two dollars for moving picture exhibitions that now cost five and ten cents. There should be some other way to prevent this practice than the slow and difficult procedure, responsibility for carrying on which rests with the United States Department of Justice, and a compulsory working law would in a large measure prevent the evil, as it would compel a controlling company either to operate under all of its patents or else lay the patents open to public competitive operation and under the present existing conditions it is submitted that the United States people as an entirety would derive benefits from a compulsory working system that would more than counterbalance any bad effects that might be found to accrue therefrom.

WILDER BUILDING, ROCHESTER, NEW YORK

## DISCUSSION

By B. C. HESSE

Whether the language of the Bill in respect of "definite process" excludes generic processes and in respect to "obtain it from a manufacturing plant" is or is not mandatory, is open to question. Under the stress of litigation, on the Bill as it now stands, it might very well be that the quoted language would be stretched to the limit to curb generic process claims on the one hand and to enforce sale of goods made by patented processes in the U. S., on the other hand. Practice under the Rules of the U. S. Patent Office would favor limiting "definite process" to "specific process," thus excluding "generic processes." Under these conditions the only safe course for the chemists of this country to pursue is to assume the, to them reasonable, adverse extreme of the purport of the Bill and its language and the conditions that wou'd likely thereunder arise.

In view of the doubtful and limited protection afforded by U. S. chemical process-patents and in view of the way in which Germany, England and France have each stretched chemical process-patents into product-patents there is no doubt that the chemists of this country would be greatly hampered and harrassed by elimination of product-patents, as such. If a product-patent does not contain tests for the certain identification of its product and for its differentiation from all other like substances, then that is due to improper and defective patent-drafting and is not a defect in the patent-law, as such.

As to specific instances of harm done by compulsory working: while the summing up by Lord Moulton:

"No, the applications to revoke patents are not for the purpose of increasing manufacture in England; they are for the purpose of increasing importation into England,"[1] is a general statement, yet it is so clear and authoritative in its statement of final result and outcome as to satisfy any reasonable demand for specific effect. In an endeavor to get specific and precise instances I addressed letters in May of this year to two of the supporters of the Compulsory Working Act under discussion at the Symposium of the Imperial Industries Club[2] requesting them to send me specific instances of benefits and directed their specific attention to their own generalized statements of benefits; to these no reply has been received; I also sent at the same time a like letter to one of these opponents of Compulsory Working and asked him for specific instances of harm—no additional information was received. In addition to Lord Moulton's statement, just referred to, are the statements of Gevers in my paper of this evening and those of A. J. Walter,[3] H. A. Colefax[4] and of J. Hunter Gray;[5] as against these set the statements of Walter F. Reid,[6] of Alexander Siemens[7] and of Ivan Levinstein[8] for specific benefits and compare them with the statement of actual results achieved.[9] The balance is not in favor of the supporters of Compulsory Working. In reading the quotation from Mr. Reid as given by Mr. Stonebraker, above, it must be remembered that commercial forms of process of making alizarine were patented separately in England by Perkin, of England, B. P. 1948 of June 26, 1869 and by Caro, of Germany, B. P. 1936 of June 25, 1869; that the British Alizarin Company was originally based upon the above Perkin Patent.

[1] THIS JOURNAL, 7 (1915), 314, 2d. col. last half and top of p. 315.
[2] *Ibid.*, 7 (1915), 307–317.
[3] *Ibid.*, 7 (1915), 311–312.
[4] *Ibid.*, 7 (1915), 313.
[5] *Ibid.*, 7 (1915), 316.
[6] *Ibid.*, 7 (1915), 307–309.
[7] *Ibid.*, 7 (1915), 310.
[8] *Ibid.*, 7 (1915), 305.
[9] *Ibid.*, 7 (1915), 306–307.

Compulsory working will *not* force manufacture of coal-tar dyes in the U. S.; France, Russia and England have all and long ago found that out.

A law like the Paige Bill will in no wise influence the U. S. coal-tar dye market. On the other hand it would discourage any American inventors from attempting to break into the business because the American is not yet industrially equipped to compete with foreigners and when he does become so equipped he will recognize in legislation like that of the Paige Bill, an enemy and not a friend.

Whether compulsory working would overcome the improper acquisition of patents and concentration of their ownership is something into which I have not looked with any detail; however, the habitual concentration of chemical patents (other than coal-tar dyes) in a few hands in Great Britain and in France and its comparatively rare occurrence in Germany does not, at first sight, seem to augur well for the success of compulsory working in that direction; having failed in so many different directions and in all directions for which glowing success was confidently predicted,[1] there does not seem to be any real ground to hope that compulsory working would effectively help the Sherman Law or the Clayton Law.

## APPLIED CHEMISTRY[2]

By L. H. Baekeland

It is only three years ago that a Brooklyn alderman, who, in the absence of the Mayor of New York, had to welcome the visitors to the International Congress of Chemistry, addressed them as if they were druggists or pharmacists.

After all, he made not much greater a mistake than many so-called educated men who obtained a B.A. and yet are ignorant enough of elementary scientific knowledge to imagine that the main occupation of a chemist is to analyze substances and detect falsifications.

Even in England, a pharmacist is currently designated as "chemist," while a real chemist is called an "analytical chemist."

But the European war has done much to correct some of these mistaken notions of the public at large. Our daily press has to a certain extent acquainted this country with the fact that in our national make-up, there are such things as chemical problems. I doubt, however, whether the unthinking masses have begun to realize that aside of the so-called chemical industry, practically every other industry, in fact, every enterprise, has chemical questions to contend with, and that chemical industry itself is intimately interwoven with the great network of every modern industrial or agricultural condition; that the economic welfare of our country, and the health of its citizens is largely dependent on the way we utilize our chemical knowledge.

### CHEMICAL WARS

The present war has been aptly called a "chemical war," because efficient work of every department of the fighting armies, from the Red Cross service to the manufacture of guns and explosives, involves incessantly chemical knowledge and—still more chemical knowledge.

But do not imagine that this is the first chemical war. The art of killing and robbing each other became "chemical" the day gunpowder was invented; at that time, however, the existing knowledge of chemistry was just of pinhead size. Napoleon knew very well how to use adroitly exact knowledge and chemistry for furthering his insatiable ambition to dominate the world; so he surrounded himself with the most able chemical advisers and scientists, and, for awhile at least, he placed himself at a decided advantage over his many enemies; incidentally, he thus helped to lay the foundation for some very important branches of chemical industry.

"Les chiens ont appris quelquechose," exclaimed the Corsican conqueror when he realized that his enemies began to adopt the same means which had given him temporary mastership over them; but those whom he called so contemptuously "the dogs" finally beat him at his own game.

Ever since then, science, technology and chemistry in particular, have played a rôle of increasing importance in the armament of nations. This accounts perhaps for the strange fact that the really great military inventions have practically all emanated from civilians and from non-military nations like our own. If the men of the military class, essentially conservative in all countries, had been left to their own devices, they would probably still be fighting with bows and arrows—or perhaps, with the traditional sling. Nor should the pacifist blame the chemist if the latter's most beautiful conquests in science, if his proudest discoveries, have been turned into means of relentless destruction and human slaughter. Do not reproach chemistry with the fact that nitrocellulose, of which the first application was to heal wounds and to advance the art of photography, was stolen away from these ultra-pacific purposes for making smokeless powder and for loading torpedoes. Do not curse the chemist when phenol, which revolutionized surgery, turned from a blessing to humanity into a fearful explosive, after it had been discovered that nitration changes it into picric acid.

As well might you curse written speech or language or the art of printing—by which the most noble thoughts of the human race have been expressed, disseminated and preserved—if it has been used also to distribute the vilest lies and the most damnable errors.

Knowledge is like a knife: in the hands of a well-balanced adult, it is an instrument for good of inestimable value; but in the hands of a child, an idiot, a criminal, a drunkard, or an insane man, it may cause havoc, misery, suffering and crime.

Science and religion have this in common, that their noble aims, their power for good, have often, with wrong men, deteriorated into a boomerang to the human race. Our very successes will threaten to devour us as long as all of us have not yet become imbued with the truth that greater knowledge, like greater possession of wealth or power, demands a greater feeling of responsibility, greater virtues, higher aims, better men.

Let us hope, in the meantime, that war carried to its modern logical gruesomeness, shorn of all its false glamor, deceptive picturesqueness, and rhetorical bombast, exposed in all the nakedness of its nasty horrors, may hurry along the day when we shall be compelled to accept means for avoiding its repetition.

Will you take it amiss if I made a digression from my subject as an answer to some repeated attacks which have been made of late by men who blame our increasing scientific knowledge in general and our chemical science in particular, for the excesses of the present European war?

### THE PEACEFUL WORK OF AMERICAN CHEMISTS

But let us turn our attention to more peaceful chemical pursuits and more particularly to the chemists of this country.

Their work is difficult to understand and still more difficult to be appreciated by the uneducated or uninitiated; nor do chemists court the plaudits of an ignorant public that cannot understand them; they feel fully compensated by the results of their work if it only meets with the approval of a few of their fellow-chemists, irrespective whether it brings them financial results or not; in fact, most chemists are so much in love with their work, that very often they neglect the financial side to their own immediate detriment.

Unlike the physician, lawyer, clergyman, actor, writer, artist, or business man, the chemist does not depend on the public at large; he is either engaged in some private enterprise or he acts in a consulting capacity for a few people, if he is not engaged

[1] This Journal, **7** (1915), 301, top of 2nd col.

[2] Presented at the 51st Meeting of the American Chemical Society, Seattle, August 31 to September 3, 1915.

as professor or teacher in some educational institution. Popularity in the usual sense has little or no value for the chemist.

No wonder then that the chemists of this country, numerous and active as they are, have hardly been noticed among the daily noise of newspaper sensation and shrieking publicity—no more than a skillful watchmaker would be noticed among the hammering of a busy steam-boiler manufacturing plant.

And yet, right here in the United States, the chemical profession has taken such a root, such a development during the later years, that we have here assembled at this very meeting, the representatives of our national American Chemical Society, which counts over 7000 members, by far the largest membership of any chemical society in the world, with all due respect to England, France and Germany—a society which finds it possible to spend yearly over $100,000 on its three chemical publications, copies of which are to be found all over the world in every well-equipped scientific library. Nor is the study of chemistry in this country a matter of recent occurrence. Our European friends are astonished when we tell them that as far back as 1792, there existed already the Chemical Society of Philadelphia, which was probably the first chemical society ever organized in the world; even to-day, some of the papers read at the meetings of that early scientific body furnish very interesting reading. Some of our American universities equipped chemical research laboratories for students, at a time when exceedingly few of the best-known European universities possessed any such facilities.

Nor should we overlook the fact that notwithstanding the essentially pragmatic tendencies of our country, the United States has given to the world a Willard Gibbs, who outtheorized existing chemical theories and whose mathematical deductions are still, after his death, furnishing food for profound thought to the most renowned physical chemists of Europe, to whom they have opened entirely new fields in the study of chemical dynamics.

### THE ANILINE-DYE SITUATION

I mention this more particularly because some of our aniline dye consumers have taken the chemists of the United States bitterly to task and have made decidedly unfavorable comments on their abilities, because since the European war, dyes could no longer be imported from Europe. But Dr. B. C. Hesse, an American-born chemist, a graduate of the University of Michigan, has already ably answered this indictment of the American chemists. In a paper full of information on this subject, which he presented at our last General Meeting,[1] but which, unfortunately, has received little or no attention from our daily press, he has clearly demonstrated that the aniline dye consumers of the United States can have all the chemists and all the dyes they want; provided they are willing to make the necessary investments of capital and to submit to the risk of uncertain profits by starting their own dye-manufacturing establishments here in the United States instead of, as in the past, favoring imported dyes, either through personal choice, or by fostering legislation which forbids the home manufacturers to utilize such methods as selling agreements, "Kartels," or other consolidation of interests, "dumping,"—so as to kill new competitors in the field, while making up the temporary loss by increasing the price of other products,—and in general, any of the many other trade arrangements and trading tricks freely and openly utilized by European manufacturers so as to stifle possible competition of our home aniline dye producers.

The outcry which has been raised as to our shortage of artificial dyes is out of all proportion if we take into consideration that the annual importation of dyes and synthetic products from Germany amounts only to about $9,000,000. As our former President, Mr. A. D. Little, pointed out[2] this represents about the same sum of money as the amount of candy sold annually by the Woolworth Ten-Cent Stores.

### LOCAL OPPORTUNITIES OF AMERICAN CHEMICAL INDUSTRIES

The development of any chemical industry is a matter of local opportunities; for instance, the manufacture of cellulose, as well as the industry of wood distilling, have taken a greater development in the wood-covered sections of the United States than in Germany or any other country in the world.

The magnitude and earning capacity of the largest German chemical enterprises, however imposing they may be, look less astonishing if you take into consideration that some of these companies have been in existence for more than half a century. Much younger American chemical enterprises, which make American specialties—for instance, the Eastman Kodak Company, which sends its films and photographic papers throughout the whole world—have annual earnings decidedly greater than the most successful German chemical works of much older existence. Nor is the value of the output of our largest purely chemical companies much less important than that of the German concerns.

### SULFURIC ACID

This country is now the greatest producer of sulfuric acid with an annual production of about 3,000,000 tons. Yet it is not so long ago that the first maker of sulfuric acid could not even find a purchaser for a trifling small production of a few tons per week. It needed the opportunity of a home market; by and by this was created by the refining of petroleum after the discovery of our oil fields, the discovery of natural phosphates and the resultant industry of superphosphates, the use of dynamite for blasting, the development of the glucose industry, and electrolytic copper refining. These and many other new industries all required large amounts of sulfuric acid, and gave this country an opportunity of developing sulfuric acid manufacturing to its present importance. In fact, the same reasoning holds good for all of our industries. I doubt very much whether the talented foreigners, who have now beome proficient in chemical manufacturing, would have tied their initiative and enterprise by specializing in coal-tar dyes manufacturing, if they had had the limitless opportunities of an immense undeveloped country like ours, to which to give outlet to their spirit of pioneership in mining, transportation, agriculture, and similar subjects, all beckoning for more urgent attention, and offering at the same time, more immediate rewards.

### AMERICAN ELECTROCHEMICAL INDUSTRIES

In the meantime some of our other chemical industries, better suited to our local conditions, have taken such an enormous development here as to make the United States an undisputed leader in at least some of them. Such products as the various acids and salts, aluminum, artificial abrasives, soda and caustic alkalies, bleaching powder, chlorine products, electrolytic copper, are decidedly more important in value and in economic importance than the few million imported coal-tar dyes.

Mr. F. A. Lidbury[1] pointed out rightly that if there had been a shortage in some of the products of our electrochemical industries in which the United States has been a pioneer, the consequences to our national economics would have been so serious that the present complaint of our aniline dye users would have sounded like a timid whisper, compared to the bellowing lamentations of so many more important industries which would have become absolutely paralyzed. The fact is that few men realize how many industries are directly dependent on the work of American chemists. If the aniline dye industry has been somewhat neglected in this country, there are many other good reasons for it; not only was the possibility of reasonable profits too scant to offer special inducement to clever-headed business

[1] THIS JOURNAL, **7** (1915), 293

[2] *Ibid.*, **7** (1915), 237.

[1] F. A. Lidbury, *Metallurgical and Chemical Engineering*, **13** (1915), 277.

men to risk their capital in this branch of manufacturing when they had so much better choice in other channels of enterprise, but the first raw material, suitable coal tar, was not abundantly available here as it is in Europe, for the simple reason that this country long ago discarded the older and more expensive methods of gas manufacturing generally used in Europe, and which give coal tar as a by-product. The less expensive and simpler water-gas process, adopted in the United States, gives no suitable gas tar; it is only of late, by the introduction of the by-product coke ovens that we can look forward to an almost unlimited supply of coal tar.

In the meantime, the German manufacturers had every opportunity in specializing in these coal-tar industries and could afford to concentrate their efforts so as to supply not only their home consumption and that of the United States, but that of the whole world; in about the same way as the United States sends to the remotest corners of the globe its sewing machines, its typewriters and its Ford cars.

Judging from the past history of the chemical industry in America, I have little doubt that the day it will be found profitable to manufacture all kinds of synthetic dyes here in the United States, instead of a few as is the case now, there will be little further delay in supplying the demand by a hustling and bustling home production.

In fact, it is quite possible that under present abnormal conditions, this branch of manufacturing may be stimulated to the point as to result in overproduction after the war is over.

### CHEMICAL RESEARCH IN UNITED STATES

If hitherto our chemists have been deficient in this special line, we can, with some satisfaction, point to better efforts in other chemical industries. For instance, it is not sufficiently known how many research chemists in our different American manufacturing establishments are busily occupied in studying and improving manufacturing processes, nor what large sums of money are devoted every year to industrial chemical research. If we hear it constantly repeated that some of the largest German chemical companies have hundreds of chemists and engineers, it is less known that right here in the United States, the number of chemists employed in some of our better organized chemical enterprises is scarcely less; but nobody finds it necessary to boast about it. In fact, the most striking symptom is that so many engineering enterprises, for instance, some of our large electrical companies—although their field of action seems rather remote of chemical subjects—have now elaborate chemical research organizations, of which the record is well known by their excellent results.

Conditions were quite different some fifteen or twenty years ago; but this country has grown, and as the requirements and opportunities grew up at the same time new chemical problems arose thereby.

### THE ANALYTIC AND CONSTRUCTIVE TURN OF MIND

The urgent nature as well as the magnitude of some of these new chemical problems, is shaking our chemists awake,—is making new men of them.

Professor Whitaker is probably right when he says that the chemists are thirty years behind the engineers as far as method and attitude of mind is concerned, but this same criticism holds good for chemists all over the world. The fact is that the engineer was called first, and he was born centuries before the chemist, but the latter is now making up for lost time.

New conditions, new problems, are compelling the chemist to learn to tackle a proposition in a true engineering spirit and—to hitch some business sense to it. He is learning to forget thinking or acting on the test-tube plan; he is thrown more and more in contact with business men; he begins to realize that too one-sided theoretical considerations are sometimes more dangerous than complete ignorance and that a sense of proportion and relative values is the first requirement for good practical effort.

Here, indeed, is one of the weakest spots of the chemist. Aside from the fact that the chemical profession seems one of those vocations which have fascinated a large number of intellectual freaks, it has generally attracted men of an analytical, rather than a constructive turn of mind. Successful engineering is essentially constructive. The most urgent work for the chemist of to-day must be constructive—he must learn how to cement together the vast amount of data which already lie at his disposal, even if he, himself, has to provide this very cement by further research.

### THE CHEMIST IN OTHER INDUSTRIES

The chemist of to-day is no longer confined to purely chemical enterprises; even the most stubbornly conservative manufacturers have learned, through competition, that every industry, however mechanical be its nature, has its chemical problems. Things have changed rapidly since the day Andrew Carnegie listened with a sly twinkle in his eyes to the fun his competitors were poking at him when he first engaged a spectacled professor to investigate the chemical problems in his iron works. Conditions have now become reversed; to-day, a steel or iron works without a competent chemist justly provokes contempt and distrust.

Nor is the time so far distant when even our biggest railroads had not begun to realize how they missed the constant services of a staff of chemists, so as to advise them in the endless chemical problems which present themselves in the operation of a well-organized railroad.

Some time ago, I visited the plant of the National Cash Register Company, in Dayton, Ohio; one of its most interesting departments was its well-equipped chemical laboratory, where no end of chemical questions relating to the manufacture of purely mechanical devices have to be studied and solved.

No up-to-date motor-car works is complete without its chemical department and the same remark holds good for all well-organized engineering concerns.

In this country, the importance of chemistry has been first appreciated in its relations to agriculture. So obvious was this, that we set an example to all other nations of the world by the number of our federal and our state chemical agricultural laboratories. This, more than anything else, was the entering wedge of applied chemistry in this country, which extended later on in the Government Service, Geological Survey, Bureau of Standards and the Bureau of Mines. Nor did the useful effect stop there. Many of our federal chemists, our state chemists, have left public service to accept better-paying positions in private industries; but the men trained in public service implanted their high aims and scientific ways in some of our commercial enterprises which needed it badly. I know of some cases where this beneficial influence changed radically the whole spirit of the commercial organization, from its manufacturing to its selling department, and introduced instead of reckless, sordid commercialism, a spirit of fairness and efficiency which soon proved the more profitable policy.

### ETHICS OF THE CHEMIST

In this and similar directions the chemist can exercise a valuable moral influence on the community. If you think it over, you will find that the quest of efficiency lies quite close to the path of honesty, justice, and equity.

Here also the chemist has much to learn. In some instances, I have been astounded at the almost childlike attitude of mind of some of our chemists who are too ready to sell their services to anybody who has a temporary use for them, irrespective of the underlying motives or purposes.

Some lawyers tell me that they never have the slightest difficulty in hiring chemical experts to defend contradictory

opinions. It is quite amazing how some chemists in their eagerness of pleasing their employers will overlook their own ignorance of the most elementary principles of patent law, as well as their superficial acquaintance with the many details of intricate technical questions while not hesitating to furnish cocksure opinions which encourage infringers or industrial pirates to trespass on the rights of intellectual property of others. Much ruinous patent litigation would be avoided in this country, and invention would be better encouraged if we had more men of the type of a well-known British electrical expert, who never hesitates in Court to tell the simple and direct truth, regardless whether it kills or saves the case of his client; his statements are so highly valued and respected that the judges accept them without suspicion, and the same expert is frequently retained by the two opposing parties, whom he serves impartially, and who gladly pay him higher fees than to a mere litigation-acrobat-expert, or a chemical "ambulance-chaser."

EMPLOYERS AND EMPLOYEES

The ethics of our profession have been dealt with by the American Institute of Chemical Engineers, and have been embodied in its recently adopted Code of Ethics, which may furnish a good guide for younger or less-experienced chemists. And this leads me to state that many more manufacturers or business men would be induced to utilize the services of chemists, if they could feel confident that in so doing they are not putting themselves at the immediate mercy of a stranger, by confiding to him facts or processes which it has cost them many sacrifices of time and money to accumulate, and the undivided knowledge of which constitutes sometimes one of their most valuable assets. On the other hand, a chemist can hardly be of any service unless his client or employer is just as frank with him as he would be with his lawyer or physician. However, this mooted point is easily overcome by referring to the Code of Ethics to which I have just alluded, or, better, by making a preliminary agreement between the chemist and his client or employer, safeguarding the interests of both parties. But in such a case, the compensation to the chemist should be made commensurate to the occasion.

This same principle holds good in the employment of chemists in manufacturing plants, where the chemist is either engaged in research or in a manufacturing capacity. An employer should not expect an intelligent chemist to render him important services without proper compensation, and in as far as the practical value of the work of a chemist can seldom be determined in advance, it will pay the employer to offer special inducements or rewards for initiative; he can well afford to give his chemist some share of the increased profits he has received through his work; to do otherwise would be narrow-minded, short-sighted, and detrimental to the direct interests of the employer. The work of a research chemist cannot be performed nor measured like that of a bookkeeper or a laborer; the results of his work are uncertain; delays and obstacles beset him at every turn; sometimes luck plays an important rôle; but good-will, enthusiasm, and persistent endeavor are indispensable factors and these may be encouraged or killed by the attitude of the employer. An employer who is unfair, or who cannot arouse the respect or the enthusiasm of his chemists, cannot get the best there is in them. He must make them feel that if their work turns out well for him, they will get some decent share of compensation. Therefore, a reasonable salary ought to be supplemented by the possibility of a bonus or some share in the profits based on the earnings brought about directly by the work of the chemist.

On the other hand, the chemist must not overlook the financial sacrifices and business risks assumed by his employer. He should specially bear in mind that knowledge or experience gathered at great cost by his employer, or through expensive factory equipment, or other facilities, have in most cases enabled him to take up his own work at an advanced stage. It would be rather unfair, unless otherwise stated, that a chemist should be allowed during or after his period of employment, to divulge or take advantage of all knowledge or information gathered around the plant in which he is engaged; or patent for his exclusive benefit, any inventions he may make on those particular subjects for which he is engaged, as long as the stimulating ideas themselves have been gathered by the very means put at his disposal by his employer. All these questions should be provided for and embodied in an equitable contract which will necessarily vary with special circumstances. But here again, niggardliness, or too great cunningness of the employer, will hardly pay. Unless his chemist be a fool—and a fool of a chemist is not worth anything—he will lose the good will and confidence of the very man whose work is primarily dependent on these factors.

Faithful and generous observance of these conditions have brought about the most excellent results in many instances. I know that the contract system, with a salary supplemented by a bonus, or participation in profits in special departments, has been used with great advantage to all concerned, by some of the most successful chemical companies in Continental Europe, and in some of the more progressive American enterprises.

It has been objected that a contract of the kind merely binds the employer who has tangible assets, while in most cases it would be difficult to enforce it against faithless employees. But even then, a clear and well-defined contract will prevent many misunderstandings which will crop up in the course of time. It has been my experience that direct dishonesty and faithlessness are merely exceptions among chemists, whatever their other shortcomings may be.

THE CHEMIST AS A RESTLESS PROSPECTOR

We know where the work of the chemist begins. We can never tell where it ends, and through what unexpected ramifications it may lead. It is just this fact which adds some zest to the life of the struggling, hard-working chemist, and brings to his work frequently as much excitement as the best of sports; his hopes and disappointments can be compared to those of the restless prospector.

Pasteur, while he was professor at the University of Lille, was consulted by a local alcohol distiller about some irregularities in the fermentation processes. Little did the great French chemist dream, when he tried to solve this purely industrial problem, that by doing so he was going to establish such an amount of new and unsuspected scientific facts, destined to upset all formerly accepted notions, not merely on fermentation, but on life, disease, contagion and epidemics; that he was about to revolutionize surgery, sanitation and medicine, and create several new departments of medical science; that he was going to save millions of lives, reduce sorrow and misery. So little were the men of that period prepared for all these stupendous revelations that this great benefactor of the human race had to suffer most from the gibes and violent attacks of some of the best-known men of that very medical profession into which he was going to infuse new life by placing it on a true scientific basis. The history of the stubborn polemics and angry discussions at the French Academy show that, at that time at least, the imagination even of men of science could not expand to the point of perceiving that medicine and surgery were to be remodeled by the hands of a mere chemist.

YONKERS, NEW YORK

## THE INDUSTRIAL RESOURCES AND OPPORTUNITIES OF THE NORTHWEST[1]

By H. K. Benson

The industrial aspect of the Northwest has been towards the East. From thence flowed the great streams of capital which

[1] Presented at the 51st Meeting of the American Chemical Society, Seattle, August 31 to September 3, 1915.

have furrowed the continental barriers and spread a network of transportation to every storehouse of natural treasures; or locked in mountain fastnesses have generated the power with which the wheels of industry may be driven. The time is coming and is now here when we may well turn from the broader phases of external development to a more minute and critical inspection of the resources about us on every hand and utilize them in the greater intensification of industry and commerce.

The Pacific Northwest constitutes an industrial unit which comprises the states of Oregon, Idaho, and Washington, the Province of British Columbia in Canada, and the territory of Alaska. Although composed of different political parts, whereby the natural course of industry may be hindered or benefited, yet the ultimate outlet for commodities is largely confined to the cities touching the waters of the Pacific Ocean. Material development of any portion of this area is felt throughout all of it. While it would be of great interest to comprehensively discuss the potentialities of the Pacific Northwest as a whole, the lack of published data would make it necessary to collect and compile at first hand much of this information. Time does not permit of such an extended investigation at present, and it is proposed therefore to present in some detail the resources of the State of Washington as a typical example of what may be found in varying degrees throughout the entire Northwest.

The total area of the Pacific Northwest includes nearly a million and a quarter square miles, distributed as follows:

| Oregon | Washington | Idaho | British Columbia | Alaska |
|---|---|---|---|---|
| 96,607 | 69,180 | 83,888 | 395,500 | 586,400 sq. mi. |

Harney County, alone, in Oregon, contains as much tillable land as the State of Maryland, while the area of Alaska is greater than that of Norway, Sweden, Finland, England, Scotland and Ireland taken together. While a large portion of Alaska is mountainous, less than 1 per cent of its area consists of permanent snow fields and its agricultural valleys contain as much tillable land as is cultivated in the States of New York, Pennsylvania, and Ohio.

### LUMBER AND WOOD PRODUCTS

We call Washington the "Evergreen" State, because its hills and mountains are enveloped with forests of fir, cedar, spruce and hemlock. With the pines of Oregon and Idaho, these forest species represent the greatest resource of the Pacific Northwest. In the states of Oregon, Washington and Idaho there are still uncut more than 50,000,000 acres of merchantable timber, from which it is estimated that over 850,000,000,000 feet, board measure, of lumber may be cut. This is more than one-third of the standing timber of the United States. The annual cut of lumber in the two states of Oregon and Washington is slightly in excess of 5,000,000,000 feet in lumber and 8,500,000,000 shingles. Over 2,000 wood manufacturing establishments, employing about 65,000 men, are required in the production of the lumber and timber products of Oregon and Washington annually. The value of the timber products annually manufactured exceeds $80,000,000, of which 80 per cent is paid out for wages, taxes, rent and other production costs. When there is added to these forest areas, the 180,000,000 acres of forest lands in British Columbia with its annual cut of $1^1/_3$ billion feet and an estimated stand of merchantable timber amounting to 130,000,000,000 feet and the more or less indefinite content of 20,000,000 acres of merchantable timber in Alaska, it becomes apparent that the timber products of the Northwest will continue for many years as an asset of great importance.

### FERTILIZERS

FISHERIES PRODUCTS—The fertilizer resources of the Pacific Northwest are almost of equal importance with its forest products. From the waters of Puget Sound and the North Pacific the annual harvest of fisheries products exceeds $53,000,000. In 1913 the fisheries products of British Columbia were almost one-half of the total production of the Dominion, amounting to $14,500,000 and twice the value of those of Nova Scotia. The salmon industry of Alaska now extends from Ketichan in Southeastern Alaska for a distance of 2000 miles to beyond the Bay of Bristol in Bering Sea. In 1913 the 79 salmon canneries of Alaska represented an invested capital of $31,341,670.00 and the annual catch of halibut, codfish, herring and whales required an additional investment of over $6,000,000.

From the annual packing of 8,000,000 cases of salmon on the Pacific Coast results an annual production of 140,210 tons of cannery waste, which might be augmented considerably by the non-edible fish which are rejected and never reach the cannery. This waste contains in the fresh condition 10 per cent oil, 3.5 per cent bone phosphate, 1.5 per cent phosphoric acid, and 3 per cent nitrogen. Of the total waste in 1913, only 16,300 tons were utilized on the Pacific Coast of the United States. From this waste were obtained 1630 tons of dry scrap and 293,000 gallons of oil. More complete utilization would increase the possible output of fertilizer and oil by tenfold.

POTASH—Floating upon these same waters are the great beds of the giant kelps or sea weeds. These have been mapped by the United States Bureau of Soils, and according to this survey, they yield annually over 20,000,000 tons of kelp equivalent to 750,000 tons of potassium chloride. The total imports of potash salts of all kinds in normal times is equivalent to about 400,000 tons annually. From the kelps of the North Pacific waters may be extracted not only the potash salts for domestic consumption, but a surplus as well, which eventually may enable this country to export potash salts to other countries.

ROCK PHOSPHATE—Until the discovery of the rock phosphate deposits of the Northwest the only commercial quantities that were known to exist in the United States were found in Florida and Tennessee. The phosphate deposits of Idaho are thirty times greater than the other known deposits of the United States. In the areas thus far surveyed by the United States Geological Survey it is estimated that over 2,500,000,000 tons of phosphate rock with 35 to 37 per cent phosphoric acid ($P_2O_5$) may be found.

In the ultimate utilization of cannery waste and of non-edible fish, of the potash in kelps, and of phosphate rock, the Pacific Northwest offers a most promising field for the upbuilding of a great fertilizer industry.

### POWER

COAL AND OIL—In the past, the industrial welfare of a community was dependent upon its nearness to a coal deposit but in the Northwest coal has competitors in the great quantities of oil from California and the electrical power of the mountain streams of the Northwest. The annual production of coal in the State of Washington is nearly 4,000,000 tons, while that of British Columbia is 2,500,000 tons. The total supply of coal in the Pacific Coast states is estimated by Campbell and Parker at 22,000,000,000 tons of which 20,000,000,000 tons are located in the State of Washington. The coal fields of Alaska cover 12,667 square miles. The estimate of the Geological Survey places the minimum coal resources of Alaska at 150,000,000,000 tons, which are far in excess of the original coal supply of Pennsylvania. Unlike the latter, however, much of this coal consists of lignites, the utilization of which calls for new methods and processes. Even in the State of Washington and adjacent to the coal fields themselves fuel oil is transported from California displacing annually a quantity of coal greater than that consumed.

WATER POWER—The water power resources of the Pacific Northwest constitute an important factor in power productions. The estimated developed water power of the Pacific Northwest, exclusive of Alaska, exceeds 650,000 H. P. The estimated undeveloped power of the Columbia River Basin is approximately 20,000,000 H. P., or one-third of all the undeveloped water power

in the United States, and equivalent to all the water power found in the twenty-six states east of the Mississippi River. Within economical transmission of our larger cities on tide water may be generated at least one-fifth of the available water power of the United States, exclusive of Alaska. The water power resources of the latter are said to exceed those of the Pacific Coast states.

### MINERALS

METALS—Much has been written of the mineral industry of Alaska and the Northwest, and it would become tedious to particularize concerning its extent and importance. The annual production of gold and silver in normal times is approximately $35,000,000. For the year 1913, the production of copper was valued at $11,300,000, of lead at $15,600,000, and of zinc at $2,500,000. The development of deposits of minor minerals has not been extensive, due to their remoteness from suitable smelting facilities. On the Seward Peninsula is a tin-bearing district of 450 square miles. Alaska has produced since 1902 over 560 tons of tin. Antimony ores are found in Alaska and Washington, molybdenum in British Columbia and Washington, tungsten in Alaska and Washington, while platinum is found in the sluice boxes of many of the placer camps of Alaska. Arsenic ores abound in the Monte Cristo district of Washington, and are smelted with the recovery of white arsenic at the Tacoma smelter.

GRAPHITE, GYPSUM AND BARYTES exist in commercial quantities in Alaska. In Washington and adjoining portions of British Columbia occur the only large deposits of LIMESTONE located on deep water along the entire Pacific Coast of the United States and Canada. Extensive deposits occur in the northern tier of countries from Puget Sound to the Idaho boundary. These deposits constitute the sources for six Portland cement, one hydrated lime, and numerous lime-kiln plants now located within the State of Washington.

CLAY—Clay deposits suitable for use in common brick manufacture are widely distributed throughout the Pacific Northwest, as are also those adapted to the manufacture of drain tile. In numerous places are also found deposits of clays which can be used for the manufacture of paving brick, sewer tile, terra cotta, and firebrick. Both Washington and British Columbia are producers of refractory brick of a high grade. Washington now ranks fifteenth in the production of clay products in the United States, forty-five firms being engaged in the industry, and producing wares valued at over $2,000,000 annually.

MISCELLANEOUS—Deposits of diatomaceous earth of superior quality have been investigated in five locations within the State of Washington. Apparently enormous quantities of this material exist in this state. Deposits of magnesium carbonate, and other magnesium salts have been reported but are not utilized. Among other raw materials available in the Pacific Northwest are iron ores suitable for mineral paints and perhaps for pig iron; talc for use as a filler in paper manufacture; silica for glass and sand-lime brick; and large deposits of stone for structural purposes. Among the latter especial mention should be made of the Alaskan marble and of the granites and sandstones of Washington. At least three extensive deposits of tufa rocks occur in Oregon and Washington.

### MANUFACTURING INDUSTRIES

The opportunities of the Pacific Northwest are to be found in the utilization and distribution of the resources heretofore cited. Less than 100,000 persons are now engaged in manufacturing industries, which produce products valued at $400,000,000 in the States of Oregon and Washington. An inspection of the foodstuffs of the city of Seattle reveals what is typical of the entire Northwest. In this city of 300,000 population, during the past year 7,207 cars of vegetables and fruit were shipped into the city. This is equivalent to a carload for every seven families. Of three million packages making up the total receipt, a million and a quarter came from outside the State of Washington.

### AGRICULTURE NEGLECTED

Agriculture is a dormant, undeveloped industry. Less than 10 per cent of the agricultural land of Washington has been improved and is utilized for agriculture. More than 2,500,000 acres of logged-off land of agricultural character remain uncleared and idle. This is due chiefly to the high cost of clearing the land by the methods which are commonly in use. The farms which have been developed from the wilderness of débris left by the logger represent a monument of industry to those who have reclaimed them and made them factors of production. In Eastern Washington the problem has been different. Instead of the jungle the desert must be overcome. Irrigation has transformed large areas into orchards and meadows of great beauty and wonderful productiveness. But even there, out of 2,000,000 acres of irrigable land, not more than 25 per cent has thus far been reclaimed. In British Columbia the estimated acreage of tillable land is 253,000,000 acres, of which not more than 12 per cent is occupied, and only about one-fifth of that is under cultivation. The great need of the Pacific Northwest is settlement by colonists. Transportation is available, water and power are abundant, natural resources of unknown extent and character await development: in brief—the harvest is great, but the laborers are few.

### CONSERVATION NEEDED

In the industries already established greater intensification and closer utilization are urgent. Fully as much timber as is manufactured into lumber is either wasted by burning or used in an uneconomic manner. As will be shown in papers presented before the Convention, the fir slabs of the sawmills contain nearly as much tannin as the chestnut wood which is the basis of the tannin extract industry of the United States. But no extract plant exists in the Northwest, and even tanneries have had hard struggles for existence in spite of the fact that great quantities of hides are readily available. Men have looked at our great forests and have seen nothing but lumber in them, and, following the line of least resistance, they have cut down these forests and manufactured a single product.

In the fisheries industry the results have been largely similar. Mr. John N. Cobb, editor of the "Pacific Fisherman" calls attention to the neglected fishery resources of the Pacific Coast in an admirable paper presented before the first annual meeting of the Pacific Fisheries Society. In the 120,000 tons of salmon offal annually wasted are millions of pounds of salmon eggs. Siberia in 1913 prepared 500,000 pounds of salmon eggs as caviar, while 24,000 pounds were prepared upon the Pacific coast of America in the same time. In Japan whale meat is of considerable economic importance as a food product. The whaling stations of the Pacific Coast ship certain portions to Japan, but by far the largest portion is either made into fertilizer or else wasted. Methods of processing whale meat so that it could be marketed as a food product should be worked out by the technical men of the fisheries industry, whereby millions of pounds of meat might be added to our national supply annually.

These are random instances of the wasteful methods whereby our natural resources are being developed. A more complete study of existing conditions would simply tend to multiply their number. The Pacific Northwest needs to apply the methods of self-examination which have been so successfully applied to the industries and resources of the more congested sections of this and other countries. It needs a closer alignment with the technical thought and progress of the day. In a word, it needs not capital, but captains of industry. With more care

for the utility of natural resources and with the coöperation of the technical skill of the day, opportunities will spring from hidden places, and industries will multiply, and the Pacific Northwest will take its place in the moving streams of commerce and trade.

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## CHEMICAL PATENTS—III AND IV

### III—CONTRACTUAL RIGHTS RELATING TO LETTERS PATENT

By SEABURY C MASTICK[1]

#### 1—ASSIGNMENTS

An assignment of a patent or application for patent is an instrument in writing which, in the eyes of the law, purports to convey the entire title to that patent or application, or to convey an undivided share in that entire title.

The patent or application assigned ought to be described in the assignment by its number and date, or serial number and date of filing, as the case may be, and by the name of the patentee or applicant and the title of the invention. In the case of assignment before or cotemporaneous with the application, it should specify the name of the inventor and the title of the invention in manner sufficient to identify it, giving also the date of execution of the application papers, if possible. Where the assignment is made before the payment of the final fee, if so requested in the assignment, the patent will issue to the assignee.

The assignment, whether of a patent or of an application, should be acknowledged before a Notary Public, although this is not requisite for validity, and unless the assignment of an issued patent is recorded in the Patent Office within three months of its date it is void as against any subsequent purchaser or mortgagee for a valuable consideration without notice.

An assignment of an application is not required to be recorded, although as a matter of practice it should be. Such assignment, even though unrecorded, is valid against all subsequent assignments, even though the latter assignees have no notice of the prior unrecorded assignment. Even though the patent issue to the inventor or to the assignee of an assignment subsequent to the prior unrecorded assignment, the assignee of the latter has both equitable and legal title to the patent and may lawfully bring suit for infringement thereof.

Rights of action for past infringement of a patent are not conveyed by the mere assignment of that patent but should be specifically mentioned in the assignment. No action can be brought for acts of infringement occurring before the issue of the patent, so such need not be mentioned in an assignment of an application.

Interests in patents may be vested not only in assignees but in grantees of exclusive sectional rights, in mortgagees, and in licensees.

(1) An assignee is a transferee of the whole interest of the original patent or of an undivided part of such whole interest, extending to every portion of the United States. The assignee of an undivided interest, no matter how small, has the same right to make, use or sell the patented invention, or to license others to do so, as have the owners of the remainder of the interest, even though the latter interest is much greater than the former, subject only to an accounting of profits to the other owners of the patent in the proportion of the respective interests.

(2) A grantee acquires by the grant, which must be in writing, the exclusive right, under the patent, to make, use and sell and to grant to others the right to make, use and sell, the thing patented within and throughout some specified part of the United States.

(3) A licensee takes an interest less than or different from either of the others. It may be exclusive and for the whole country, or exclusive for a part of the country, or limited to the making, or using, or selling or in any other way. A license may be oral or written and need not be recorded in order to be valid against subsequent purchasers of the patent or subsequent licensees. In the case of a license the title to the patent remains in the patentee or assignee and all suits for infringement must be brought in the latter's name.

A license not expressly limited in duration continues until the patent expires or the license is surrendered or forfeited in accordance with its own terms.

No license is assignable by its licensee to another unless it contains words which show that it was intended to be assignable.

#### 2—LICENSES, EXPRESS AND IMPLIED

Express licenses are those given directly either orally or in writing. Implied licenses may arise from the conduct of patentees or assignees, or from the recovery by them of profits or damages for certain classes of infringements.

Implied licenses arising from the conduct of owners of patent rights are generally found to arise by virtue of acquiescence in acts which constitute a license or by action of estoppel. For example:

Where the patentee knows of the use and does not object, especially if he receives a portion of the profits for such use.

Where the owner of a patent explains the invention to another who is ignorant of the patent and advises the latter to make, use or sell the patented invention with intent to cause him to infringe unwittingly, an implied license would result by estoppel to the person thus misled.

Where a patentee sees an infringing article sold without authority from him, but makes no objection, an implied license by estoppel results to the purchaser.

A recovery of damages by way of royalty as against an infringing manufacturer operates an implied license to the purchaser from that manufacturer. But a recovery of profits only from an infringer for use of a patented device gives no license to the subsequent purchaser as each infringer by way of use stands alone to account to the owner of the patent for his profits in its use.

#### 3—EMPLOYER AND EMPLOYEE

Where a man is employed for the purpose of making inventions, all such inventions are the property of the employer, who can compel assignment of them to him, the inventor having no property right in them whatsoever.

Where a man is employed generally by another to work in the business of the latter, and not specifically as an inventor, and, during the period of such employment, conceives an invention, applicable to the employer's business, and uses the property and time of the employer to reduce the invention to practice, an implied license or "shop right" results to the employer. This is especially the case if the employee sees the employer make, use or sell the thing invented, without making objection.

If the invention was made and the drawings prepared outside the hours and shops of the employer, but the invention was reduced to practice and made in the employer's shop at the employer's time and expense, an implied license results to the employer.

Where a person has discovered a new and useful principle in a machine, manufacture or composition of matter, he may employ other persons to assist in carrying out that principle, and if they, in the course of experiments arising from that employment, make discoveries ancillary to the plain and preconceived design of the employer, such suggested improvements are in general to be regarded as the property of the party who discovered the original principle, and they may even be embodied in his (the employer's) patent as part of his invention.

[1] Special lecturer on Chemical Patents, Department of Chemical Engineering, Columbia University, 1915.

But persons employed, as much as employers, are entitled to their own independent inventions, and if the suggestions communicated constitute the whole substance of the improvement then the patent should be applied for and would be the property of the employee subject to the qualifications as to actual employment as an inventor and implied license as above pointed out.

If you are an employer the safe way is to have a definite contract in writing with the employee, specifying that all inventions made while in said employ are to be assigned to the employer, together with any future improvements on the several specific inventions.

If you are an employee the safe way is either to have a definite agreement in writing with your employer or not to do any inventing or reducing to practice of such invention on the premises or on the time or at the expense of or with the tools of the employer.

### IV—ACTIONS FOR INFRINGEMENT

#### 1—THE CASE IN THE LOWER COURT

The District Courts of the United States in the several States and the Supreme Court of the District of Columbia have original and exclusive jurisdiction of all suits, either at law or in equity, arising under the patent laws of the United States. The action must be brought in the district in which the defendant is an inhabitant, or in any district in which the defendant, whether a person, partnership or corporation, shall have committed acts of infringement and have a regular and established place of business.

Actions brought to enforce or set aside contracts relating to patents, such as license contracts, contracts to assign patents or applications, or for specific performance of such, are not actions arising under the patent laws of the United States and are not within the jurisdiction of the United States Courts unless diversity of citizenship and the amount involved give such jurisdiction. Such actions are properly within the jurisdiction of the several State Courts.

In any suit or action brought for the infringement of any patent there shall be no recovery of profits or damages for any infringement committed more than six years before the filing of the bill of complaint or the issuing of the writ in such suit or action.

In any suit for infringement brought by a party failing to mark the patented article with the word "patented," together with the day and year the patent is granted; or when, from the character of the article, this cannot be done, by fixing to it, or to the package wherein one or more of them is enclosed, a label containing the like notice, no damages shall be recovered by the plaintiff, except on proof that the defendant was duly notified of the infringement, and continued, after such notice, to make, use, or vend the article so patented.

The decisions of the District Courts of the United States may be appealed to the proper one of the United States Circuit Courts of Appeal for the several Circuits (nine in number) and the judgments or decrees of the Circuit Courts of Appeals are final in all cases arising under the patent laws, excepting that said Court may certify to the Supreme Court of the United States any questions or propositions of law concerning which it desires the instruction of that Court for its proper decision; and excepting also that it shall be competent for the Supreme Court to require, by *certiorari* or otherwise, any such case to be certified to the Supreme Court for its review and determination.

As a matter of practice the decision of the Circuit Court of Appeals is generally final and very few cases go up to the Supreme Court.

Actions at law for infringement of patents may be before a jury or, if both sides waive a jury, before a judge without a jury, or before a referee appointed by the Court with consent of both parties. The only relief in actions at law is to give damages for past infringements of patents. Actions at law are infrequent excepting where the action is brought for damages for the infringement of an expired patent.

Actions in equity for infringements of patents are before a judge without a jury and must be so brought where an injunction to restrain future infringements is desired. The Court sitting in equity has jurisdiction to direct an accounting for profits and damages which the complainant has sustained on account of the defendant's infringement. Almost all actions for infringement are brought on the equity side of the Court as an injunction is almost universally the chief remedy desired.

It is unnecessary to go into the details of a trial in these lectures further than to state that the pleadings comprise a complaint and an answer; that the complaint must set up the patent, that the complainant has title thereto, that it is valid and that it has been infringed by the defendant; that the answer must set up the defense, controverting the allegations of the complaint, and specifically setting forth the prior uses or prior patents relied upon for invalidating the patent or restricting it so that infringement cannot be held.

The testimony, where possible, should be given in open Court but when the witness lives at a greater distance than one hundred miles from the place of trial or the Court, upon application of either party (in cases permitted by the statute), for good and exceptional cause for departing from the general rule, gives permission, the testimony may be taken by deposition before an Examiner or other qualified officer.

The question of the validity of the patent sued upon is determined in accordance with the rules heretofore given in the two preceding lectures. At the outset of the trial the patent is presumed to be *prima facie* valid and the complainant is not required (and generally not even permitted) to introduce any evidence as to validity. He must, however, prove infringement. This is done by offering in evidence a sample of the infringing device or by introducing testimony clearly describing the alleged infringement if, from the nature of the case, such as in certain process or certain complicated or cumbersome devices, it is not possible to produce bodily the matter constituting the infringement. Expert evidence may be introduced to explain the operation of relevant arts, processes, machines, manufactures or compositions of matter, and of the meaning of terms of art or science and of diagrams or formulae, but the witnesses are not permitted to give their opinion as to the meaning of any patent claim or specification. This latter is solely for the Court to consider.

A patent for a process is infringed by one who, without authority, uses substantially the process of the claim, whether or not he uses substantially the apparatus or materials which the patent describes, or uses equivalents therefor. The definition of an equivalent has been given in one of the preceding lectures as "a thing which works in substantially the same way to accomplish the same result or perform the same function as the thing for which it is substituted." No process patent claim is infringed if one of the steps of the process is omitted by the alleged infringer unless some equivalent step is substituted for the one omitted.

A patent for a composition of matter or a machine is infringed by one who, without authority, makes, uses or sells the thing covered by any claim of the patent. It is not an infringement of a patent, whether in a process patent or in one for a composition of matter or a machine, to use, or to make, use or sell, a thing described in the specification but not claimed in the claims, as the measure of the patent protection is defined only by what it claims. Of course the rule of equivalents also applies in composition of matter and machine cases.

Whoever infringes any one claim of a patent infringes the

patent, whether or not it contains other claims which are not infringed.

Addition to a patented machine or article of manufacture does not void infringement. Addition to a process or to the ingredient of a composition of matter does not avoid infringement, unless a substantially different process or composition results.

Omission of a claimed part of a machine or of a claimed ingredient of a composition of matter, no equivalent being substituted, negatives infringement of said claim, as a combination is an entirety and if one of its elements is omitted, the claimed thing disappears. Every part of a combination claimed is material, and evidence to the contrary is inadmissible.

Changes of proportions of the ingredients of a composition of matter, unless the claim gives specific proportions, will not avoid infringement.

It is not necessary that the infringer should have known of the patent at the time he infringed it or should have known that what he did was an infringement even if he did know of the patent. In either case an action for injunction will lie although profits and damages could not be recovered unless the patented article was marked "patented" or the infringer had received actual notice. If the patented article had never been manufactured and the patent was a mere "paper" patent, or in the case of a process where marking "patented" is impossible, profits and damages could probably be recovered in the absence of marking "patented" or of actual notice, although, in this case, actual notice is usually required.

As is stated above, it is unnecessary to go into details in these lectures. The subject of infringement is a large one and it has been the intention to point out only certain of the more prominent features. For greater detail it will be necessary to consult the text-books on Patent Law.

### THE HALL PATENT LITIGATION

In order to illustrate the practice in connection with patents, both with relation to the trial of a case and the way in which the Courts handle the matter, I have chosen the litigation concerning the Hall Patent (No. 400,766, April 2, 1889) for the electrolytic production of aluminum. We have already traced the history of this patent through the Patent Office. Now let us trace its history through the Courts.

We shall see the practical application of many of the rules heretofore stated and shall learn something of the trials and tribulations of the patent litigant.

About the first of July, 1886, Hall was introduced to the Cowles brothers who had already organized the Cowles Electric Smelting & Aluminum Co. and later entered into an optional agreement with them to sell them his patent. The option ran for a little less than a year. During the period of the option, which expired sometime in July, 1888, he was given facilities to experiment and develop his process at the Cowles plant at Lockport, New York. His proposed process was one wherein the crucibles were heated externally and copper anodes were used. Hall was unable to satisfy the Cowles Company that his process was a success as they believed that internally heated crucibles with carbon rods for anodes were necessary. Internal heating, however, was alleged to be within the scope of certain prior Cowles patents and applications and Hall would not, at that time, deviate from his original idea.

Early in July, 1888, one of the employees of the Cowles Company resigned and went to Pittsburgh, where he began the organization of what became The Pittsburgh Reduction Company. At the close of July, after the option had expired, Hall went to Pittsburgh also, joined forces with the organizers of the new company and in November, 1888, began work at the factory at New Kensington, near Pittsburgh, producing some 50 pounds of metal a day which sold at $2 per pound. For the first six months they operated according to Hall's original ideas. At the close of this period they lined their crucible with a heavy coat of carbon and adopted internal heating with carbon anodes. This proved successful and their progress was rapid.

It is to be noted that the final amendment to the Hall application, wherein a new specification was filed (corresponding to that of the issued patent) and the claims for copper anodes were dropped and those involving carbonaceous anodes substituted, was filed on September 4, 1888, after he had left the Cowles Company and while he was beginning work at Pittsburgh.

Immediately following Hall's departure from Lockport, the Cowles Company began working on cryolite and alumina, keeping the bath fused by the current. For a period there was an attempt made to merge the two companies and when this failed a suit was brought in 1891 by the Cowles Company against the Pittsburgh Reduction Company for infringement of certain Cowles patents and a counter-suit was brought against the Cowles Company by the Pittsburgh Reduction Company for infringement of the Hall patent. Before the taking of testimony had started in the suit brought by the Cowles Company, the Bradley patent (No. 464,933 dated Dec. 8, 1891, but applied for February 23, 1883) had issued. We shall discuss this patent later. We might note here, however, that it covered one of the chief points at issue between the two companies but did not enter into the controversy until later and after the Cowles Company had acquired it.

The case brought by the Pittsburgh Reduction Co. against the Cowles Electric Smelting & Aluminum Co. was brought to final hearing and on January 20, 1893 (55 Federal Reporter 301) an interlocutory decree in favor of Hall was rendered upon an opinion written by Judge Taft, then U. S. Circuit Judge. The case then went before a Master who eventually assessed an amount of $292,000 against the Cowles Company, damages and profits, in favor of the Hall Company. In view of future developments, to be hereinafter considered, this sum was never paid. The litigation involving the Bradley patent was pending so that no effort was made to push the case before the Master and it dragged along until 1903. A rehearing in the Hall case was then ordered but was never had. After the Cowles Company obtained title to the Bradley patent, as we shall see, it brought suit against the Hall Company on the Bradley Patent, which suit was lost in the lower Court but reversed and decided in favor of the Cowles Company on appeal. We shall take up these various phases of the litigation in order, referring first to the decision in The Pittsburgh Reduction Co. *vs.* Cowles Electric Smelting & Aluminum Co. In this case the Court said in part as follows:

"TAFT, CIRCUIT JUDGE—This is a suit *in equity* by the Pittsburgh Reduction Company against the Cowles Electric Smelting & Aluminum Company, to restrain the infringement of a patent process for reducing aluminum by electrolysis (letters patent No. 400,766) owned by the complainant under an assignment from the original patentee, Charles M. Hall. The patent was applied for July 9, 1886, and was granted April 2, 1889. The defenses to the suit are: *First*, that the patent is invalid for want of novelty; and, *second*, that the defendant does not infringe. * * * *

"The two claims of the patent in suit which are here involved are as follows:

"'1—As an improvement in the art of manufacturing aluminum, the herein described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum, and a metal more electro-positive than aluminum, and then passing an electric current through the fused mass, substantially as set forth.

"'2—As an improvement in the art of manufacturing aluminum, the herein described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum and sodium, and then passing an electric current, by means of a carbonaceous anode, through the fused mass, substantially as set forth.'

"The defendant is said to infringe both these claims. The

validity of the first, so far as it covers defendant's process, and of the second, is attacked by the defendant.

"We shall first consider the validity of the claims, and in that connection must refer to the history of the art. It is said on behalf of the defendant that as far back as 1859, De Ville, a famous French chemist, published to the world the process which Hall has included in his patent. De Ville gave a great deal of time to aluminum and its production from its compounds. He was the discoverer of the purely chemical process by which, without the aid of electricity, pure aluminum has been manufactured since his day down to the present time. He also gave some attention to the manufacture of aluminum by the process of electrolysis. In the publication by De Ville on aluminum, its properties, its manufacture, and its uses, in the year 1859, we find this statement:

"'*Aluminum by the Current.*—The same bath of the double chloride of aluminum and sodium can be used for coating with aluminum, especially copper, on which Captain Caron and myself have worked. In order to succeed well, one must employ a bath of the double chloride, which has been carefully purified from all metallic substances by the action of the current itself. When the aluminum which deposits at the negative pole appears pure, one attaches to this pole the piece of copper to be aluminized, and to the negative pole a bar of aluminum.

"'(NOTE—A compact mixture of carbon and alumina, which is transferred into chloride of aluminum gradually and in measure as the deposit of aluminum takes place, keeps the composition of the bath constant for an indefinite period of time.)

"'(The temperature must be kept somewhat below the melting point of aluminum. The deposit takes place with great facility. It is very adhering; but it is difficult to prevent the metal from getting impregnated with double chloride, which attacks it the moment one washes the piece, while, with some precaution, one succeeds. The washing of the piece must be done with much water, and for a long time. Cryolite, in the same way, can be used in this operation, but it must be made more fusible by mixing it with a little double chloride of sodium and aluminum, and with potassium chloride.'

"The process here described is not for producing pure aluminum, but for plating aluminum on copper. It will be seen that the bath which is first and chiefly recommended by De Ville is not a fluoride of aluminum and sodium, but a double chloride of aluminum and sodium, *i. e.*, a double compound of chlorine with each of these metals. Alumina will not dissolve in a double chloride of aluminum and sodium, heated to a fused state. * * *

"Finally, it will be observed that De Ville suggests that instead of the double chlorides of aluminum and sodium, cryolite may be used, but that it must be made more fusible by mixing it with a little double chloride of sodium and aluminum and with potassium chloride; and it is the proposition of De Ville to use cryolite in this way as the main part of the bath, and an anode of carbon and alumina in accordance with the foot-note, which the defendant's counsel and experts contend is substantially the same process as that on which Hall claims a patent.

"We are clear in our opinion that this is not an anticipation of Hall's patent. The primary and most important step of Hall's patent is the dissolving of the alumina in the fused bath of the double fluoride of aluminum and sodium. This happens before any electrolysis occurs at all. When the electric current is applied, it disrupts the alumina, sending the aluminum to the cathode and the oxygen to the anode, where it unites with the carbon anode, and becomes carbonic oxide gas. The bath material in which the alumina was dissolved—that is, the double fluoride of aluminum and sodium—is not affected by the electric current, and the process is made continuous by the simple addition of alumina to the bath. In the De Ville process, however, alumina is not dissolved in the bath. The fused mass subjected to the current is composed of a double fluoride of aluminum and sodium with no alumina in it. No effect comes from the presence of the alumina in the anode until after the electric current is passed through, and the fluoride of aluminum has been disrupted, and fluorine gas has been produced at the anode; then the gas unites with the aluminum of the alumina, and restores the bath, in a manner, to its former state, to be again disrupted by the application of the current. In the one case there is a simple solution of the alumina in a bath and its disruption by the current, the bath remaining constant; while in the De Ville process the bath itself is disrupted, and restored again by the union of one of the disrupted elements with an element of the alumina in the compact anode. In the Hall process there is simply solution of the alumina and electrolysis; in the De Ville process there was electrolysis, followed by what is called an 'electrochemical solution of the alumina.'

"Defendant's counsel and experts, in their effort to make the two processes the same, rely upon the supposition that when the compact anode of carbon and alumina was inserted by De Ville into the bath of cryolite some of the alumina was necessarily dissolved in the cryolite, and so the current electrolyzed that alumina as in the Hall process. In the first place, the experiments made on behalf of complainant demonstrate that a compact mixture of carbon and alumina (which can be made only by the use of some binding material) may be kept in a bath of cryolite for many hours without dissolving the alumina at all. Some counter-experiments by defendant are by no means so satisfactory, because the results may be attributed to the presence of other causes than the solution of the compact anode.

"But suppose it to be a fact that in De Ville's process alumina was dissolved in the bath from the anode, and that thereupon it was electrolyzed as in the Hall process, it was a mere accident, of which De Ville made no note, and which, therefore, we may reasonably infer, he did not observe. Accidents of this character cannot be relied on as anticipations of a patented process (Tilghman *v.* Proctor, 102 U. S. 707,711) when the operator does not recognize the means by which the accidental result is accomplished, and does not thereafter consciously and purposely adopt such means as a process for reaching the result. De Ville did not intend that the alumina should be dissolved in the bath. If he did, why did he unite it with carbon by means of pressure and a binding material? If he had intended to dissolve the alumina, he could not have done anything which would have so interfered with his purpose. Just as Prof. Langley says, such a course would have been as reasonable as it would be for a man, wishing to dissolve a lump of sugar in his coffee, to varnish it or grease it. De Ville did not intend to dissolve the alumina in the bath: *First*, because as we shall see hereafter, he had no knowledge that it would dissolve therein; and, *second*, because, until the fluoride of aluminum had been decomposed in the bath by the current, he did not need anything with which to restore that fluoride to the bath. He felt that it was necessary to have the alumina in a solid form in close connection with the carbon, because, without the strong attraction that the carbon would have for the oxygen of the alumina, the fluorine gas could not get at the aluminum of the oxide.

"De Ville was seeking to electrolyze the fluoride of aluminum, while Hall was seeking to electrolyze alumina. It was a condition precedent to Hall's success that his alumina should be in a liquid state. As we have seen, it was essential to De Ville's process that his alumina should be where it was, *i. e.*, mixed in solid form with the carbon. * * * * * * *

"We have read with care every part of this voluminous record of over 1,500 pages, and, while we are not chemists, we have obtained a sufficient understanding of the principles applied in the Hall and De Ville processes to be entirely confident that they are wholly different, and that no skilled chemist and electrician could have developed the Hall process from the De Ville process without a real discovery.

"The Bell patent of 1861, the Johnson provisional specifications of 1879, the Johnson specification of 1883 and the Graetzel patent of 1884, which are all recorded in the English patent office, and are produced here by the defendant and relied on as anticipations of

Hall's patent, are mere reproductions of the De Ville bath-regenerating process, with various attempts to avoid the difficulties which the process presents in its practical operation. The Graetzel patent—the latest of them—was a failure. This is admitted by the patentee himself, who was a witness in the case. The Johnson specifications were never even proceeded with to the procuring of a patent, and the Bell patent has never been used at all to make aluminum commercially. It is said that one reason why these electrolytic processes, including De Ville's, were not brought into actual use, was that, until within a very few years, there were no dynamos capable of furnishing sufficient electric volume and force to make them practicable for commercial purposes. That the improvements in the machines for producing electricity have greatly facilitated the use of electrolysis as an agent in commercial processes is not to be denied, but the failure of the De Ville process for making aluminum by electrolysis finds a far better reason in the inherent difficulties of the process itself than in the mere expense of electricity. If the De Ville process is operative with the present modes of producing electricity, why does not the defendant adopt it? It is free to any one. The various futile attempts to relieve the De Ville process of its defects are strong proof that it was and is a failure without regard to the development in the making of electricity.

"There are other patents introduced to show anticipation than those which involve the De Ville process, but of these there is only one which, it is seriously contended, discloses the Hall process. This is a French patent of Fuerst, dated August 8, 1884. In this patent the patentee says:

" 'The process of which I claim the industrial property consists in making the electrolysis of alkaline aluminates, or alkaline earthy aluminates, in the condition of solution or of fusion. For this I take an alkaline aluminate, or earthy alkaline aluminate; that is to say, one of the aluminates of potassium, of sodium, or of barium, etc. Into this body, in solution or fusion, according to the circumstances, I introduce the two poles of an electric current of suitable tension. There is nothing further to do than to receive the aluminum upon the cathodes employed (negative poles), where I collect it in order to melt or utilize it alone or in different alloys for all the industrial uses to which it can lend itself. As to the anodes (positive poles), these anodes can be, according to my desire, soluble or insoluble, and I reserve to myself the industrial property of each of these two cases. While I employ anodes which are insoluble, or are considered such industrially, I reserve to myself to maintain a constant composition in these electrolytic baths by adding to them, as is needed, oxide of aluminum.

" 'The electrolytic decomposition produced by the electric current in an alkaline aluminate, or in an alkaline earthy aluminate, can also be produced equally well whether this salt be in a state of purity or whether several aluminates be mixed together, or whether they be mixed with other salts or foreign materials giving rise to double salts or any secondary combinations whatever, provided, let it be understood, that these salts of foreign materials, whatever they may be, will not produce decomposition of the aluminates employed. It is thus that I reserve to myself to introduce into these baths salts of ammonia, alkaline sulfites, alkaline phosphates, alkaline cyanides, alkaline chlorides, etc., the presence of which seems to have the power of improving the practice of this electrolysis.'

"Later on, Fuerst deposited an addition to his patent, in which he says:

" 'In this certificate of addition I claim as my industrial property my process for the industrial production of aluminum by electrolysis of alkaline aluminates or alkaline earthy aluminates in solution or igneous fusion. And by 'alkaline aluminates,' I mean every compound into which alumina and alkaline base enter, even if there should enter into that compound one or more of the following bodies, which I shall call 'useful' or 'indifferent' auxiliary bodies: Hydrocyanic acid, cyanides, cyanates, phosphoric acid (pyro and meta), boric acid, silicic acid, hydrofluoric acid—in the state of acids or salts. For me there is aluminate of alkali as soon as there is in a body alumina and an alkaline base, even in the presence of the auxiliary bodies above mentioned, whatever otherwise be the hypothesis that might be established respecting the numerous molecular groupings which might exist or be supposed to exist.'

"An alkaline aluminate is either an aluminate of potassa or an aluminate of soda. Aluminate of soda is a compound of alumina and soda, *i. e.*, of the oxides of aluminum and sodium. It is a triple compound of oxygen, aluminum and sodium. An alkaline earthy aluminate is an aluminate of baryta, strontia, lime, or magnesia; *i. e.*, a compound of alumina with baryta or strontia or the other substances. The three elements of such a compound are oxygen, aluminum, and barytum, or strontium, or the other substances. The theory of the patent—and it is only a theory, as we shall see—is that if these triple compounds of oxygen, aluminum, and some other metal can be reduced only to a liquid form either by aqueous solution or igneous fusion, the current will decompose the compound by depositing the aluminum at the cathode, and will leave the compound of oxygen and the other metal in the bath. By adding alumina to the bath he proposed to restore the aluminate in the bath. Now, the electrolysis of an aqueous solution of the aluminates to produce aluminum is impossible. This is not denied. One-half of Fuerst's patent is demonstrably inoperative. Secondly, so far as the patent calls for the igneous solution of the aluminate of soda, it is also inoperative, because that compound is infusible; and even if it were fusible, the current would precipitate the sodium, and not the aluminum. This is conceded by defendant's experts. Such facts are strong evidence that Fuerst wrote out a theory for the production of aluminum by the current without knowing by experiment whether it would work or not. All the experts in the case agree that he was a very poor chemist. In order, however, to catch future inventors in the toils of his dragnet, he mentions a great many chemical compounds which could be added to his bath of aluminates, and not interfere with its working, and might even aid the electrolysis. It is perfectly obvious that he never tried any of them, and it has not been shown at the bar that one of the innumerable baths proposed by him would, when electrolyzed, produce aluminum. It does appear, however, that if hydrofluoric acid, which is one of the indifferent auxiliary bodies mentioned by Fuerst, be mixed with aluminate of soda so that the mixture shall contain eight times as much acid as aluminate, the acid will entirely decompose and destroy the aluminate, and, after evaporation and fusion, we shall have a bath, not of the aluminate at all, but of the fluorides of aluminum and sodium. If, then, alumina be added, and the current applied, we shall have the Hall process exactly. An experiment of this kind was tried on behalf of defendant, and an account of it is produced in evidence as demonstrating the identity of the Fuerst and Hall processes. It is perfectly evident that no one without a knowledge of the Hall process, and without the deliberate intention of producing Hall's bath, would ever have derived from the Fuerst patent any information leading to such a treatment of the aluminate of soda with the hydrofluoric acid. In the first place, according to Fuerst's specifications, the acid is to be only indifferent or auxiliary. Who would think, therefore, of using eight times as much acid as aluminate in preparing an aluminate bath? Again, one imperative injunction which Fuerst imposes in his specifications was flatly disobeyed in defendant's experiment. He says he has no objection to the introduction of foreign materials as indifferent or auxiliary bodies, 'provided, let it be understood that these salts or foreign materials, whatever they may be, will not produce decomposition of the aluminates employed.' The addition of hydrofluoric acid in excess to aluminate of soda completely decomposes and destroys the aluminate, so that the bath which results after evaporation and fusion has nothing like an aluminate in it, but is a bath of fluorides. In view of the necessity for this flagrant violation of Fuerst's injunction in order to produce the Hall bath, it is absurd to say that the bath can be found described within the four corners of the Fuerst patent. Fuerst does suggest that his bath can be kept constant by adding alumina, but, as his bath is not Hall's bath, he does not thereby come any nearer the Hall patent.

"The other patents pleaded as anticipations of Hall's are even

less like it than those already considered, and they were not pressed in argument.

"It is objected to the validity of the Hall process that it is not operative. The argument is that it has no utility, as described in the patent, for three reasons: '*First*, because the fusion of the bath is maintained by external heat, and except with internal heat, produced by the current, the process is worthless and inoperative; *second*, because it contemplates continual interruptions in the process to remove the aluminum already deposited from the cathode, which would make the process too cumbersome and expensive for commercial use; and, *third*, because it does not provide for sprinkling powdered alumina over the top of the bath, to be gradually stirred down into it, without which the depositing of aluminum cannot go on without interruption.'

"There is nothing in any of these claims. The patent disclosed a process and suggested an apparatus by which the process could be operated. * * *

"Now, it may be that the changes in the mode of using the Hall process, indicated in the objections of defendant stated above, from that recommended by Hall in his patent, are great improvements, but that does not in the slightest degree affect the validity of the patent if it appear that at the time when the application was made a new and useful result could be accomplished with the process by the mode which Hall suggested. * * * *

"Hall's process is a new discovery. It is a decided step forward in the art of making aluminum. Since it has been put into practical use the price of aluminum has been reduced from $6 or $8 a pound to 65 cents. This is a revolution in the art, and has had the effect of extending the uses of aluminum in many directions, not possible when its price was high. An effort has been made to show that this reduction in the price is due to the improvements in the application of electricity to the manufacture of aluminum. That the new inventions in the line of producing electric currents of great volume and intensity have contributed to render the Hall process an economical one is true, but without the Hall process the manufacture of pure aluminum must have continued to be a purely chemical one. The Cowles brothers made aluminum alloys by the use of electrical furnaces which they have brought to a high state of perfection, doubtless, and that had an effect to reduce the price of aluminum alloys, and perhaps indirectly affected the price of pure aluminum. The fact was that the price of pure aluminum was so high that its uses were few, and the market for it was small. When Hall's process, however, came into the field of commercial manufacture, pure aluminum was largely substituted for aluminum alloys, and, if alloys are now desired for particular purposes, they are generally made from pure aluminum. Hall was a pioneer, and is entitled to the advantages which that fact gives him in the patent law.

"One other thing must be alluded to before we close the long discussion of the validity of Hall's patent and that is the French patent of Héroult. Héroult has a patent granted to him by the French Government, dated April 23, 1886. The process he described is substantially one of those described by Hall. He uses a fused bath of cryolite in which alumina is dissolved, and from which, by the electric current, aluminum is deposited at the cathode. His anode is of carbon. Héroult made application for a patent to the United States patent office May 22, 1886. Hall did not make his application until July 9, 1886. An interference was declared in the patent office between Hall and Héroult. Hall adduced evidence to show the Commissioner of Patents that he made his invention and put it into operation February 23, 1886. The same evidence has been introduced here. It establishes beyond all reasonable doubt by written evidence that Hall did put his process into successful operation on February 23, 1886. The patent office decided the interference proceeding in Hall's favor, and it was clearly right. There was no evidence, there or here, to show that Héroult discovered the process before Hall, and the fact that Héroult's French patent antedates Hall's application does not affect Hall's right to a patent, because by Section 4887, Rev. St., an inventor's right to a patent in this country is not debarred by reason of the fact that the invention has previously been patented in some other country, provided that it has not been more than two years in use in the United States. The counsel for defendant do not dispute the correctness of this conclusion, but they rely on the Héroult interference proceedings to attack the validity of that part of the second claim in the Hall patent where he specifies as part of his process the use of a carbonaceous anode. It is conceded by them that Hall had used a carbon anode in his process before filing his application, but the contention is that because in his application he alluded to it as having some disadvantages, and did not include it in his first series of claims, which he afterwards amended, and did not finally include it in his claims until Héroult's patent suggested its value to him, and more than two years after his application, he thereby abandoned the use of a carbon anode to the public. No authority is cited to sustain this argument. * * * *

"And now we come to the question of infringement. The evidence leaves no doubt that the defendant company began their manufacture of pure aluminum in January, 1891, with the aid of one Hobbs, who had been the foreman of the complainant company, and engaged for it in superintending the manufacture of aluminum by the Hall process. By that time the complainant company had adopted several improvements in the apparatus described in the patent for working the process. The defendant copied these improvements, as well as the process, and has sought to escape responsibility by maintaining that without these improvements the process was inoperative, and the patent which did not contain them was invalid. Much the same course is taken as to the defense of infringement. The improvements are said to make the present process a different one from that described in the patent, and, therefore, the defendant does not infringe. It is needless to say that a court is not inclined to favor such defenses. There is evidence tending to show that the defendant used Hall's preferred bath, but with the admissions in this case it is unnecessary to consider the issue made on that point. It is admitted that the defendant is using a process in which alumina is dissolved in a fused bath of the double fluoride of aluminum and sodium and in which an electric current is passed through the bath containing the alumina thus dissolved, whereby aluminum is deposited at a carbon cathode and oxygen is released at a carbon anode. It is said, however, that they are not infringing the Hall patent, because the Hall patent does not cover the particular double fluoride of aluminum and sodium which they are using, which is cryolite; and because the Hall process contemplated and called for a fusion of the double fluoride by external means of heating, whereas the defendants are using, to fuse the bath, the heat generated by the resistance of the bath to the electric current. The whole defense of infringement is based on a narrow and wholly impossible construction of the Hall patent. * * * *

"Coming now to consider the claim that the patent does not cover fused cryolite as a bath, it should first be noted that cryolite is a double fluoride of aluminum and sodium, a metal more electropositive than aluminum. It is, therefore, exactly within the words of both claims here in suit. But the contention is that the patentee has disclaimed any right to the exclusive use of cryolite. It is not denied that the patentee had used cryolite as a bath before he made his application, but it is said that he described its use in his first application, and stated, in substance, that it was not so good as a different proportion of the fluorides, and then subsequently omitted reference to it as a bath altogether in his final specifications. * * * *

"The patentee states first the proportion of the aluminum fluoride and sodium fluoride which he prefers for his bath. They are 84 parts of sodium fluoride and 169 parts of aluminum fluoride. Then he proceeds to tell a convenient way for reaching those proportions. Cryolite, as we have said, is an article of commerce. He suggests that the best bath can be made by taking cryolite and adding to it 338/421 of its weight in aluminum fluoride. After this, for the very object of including cryolite, which, as we know, he had used for the purpose, and all other double fluorides of sodium and aluminum which would work, he says that the proportions may be varied. What proportions does he mean? Why, the proportions of the two fluorides, of course. The labored construction that the proportions to be varied are those of the cryolite and the aluminum fluoride is wholly untenable. How may they be varied? Within certain limits. What does that mean? The patentee goes on to state when he says 'that any proportions which may be found suitable may be employed.' Cryolite is now found suitable, and the patentee had found it suitable when he made his application. Could anything be more unlikely than that Hall or his patent solicitor, after they had been successful in an interference controversy with Héroult, whose only bath was one of cryolite, would have framed his specifications with the intention of not including a cryolite bath in the monopoly he was seeking? We think the patent very aptly drawn to cover the use of every double fluoride of aluminum and sodium which can be made to produce aluminum when used as a bath in the Hall process. The proportions are immaterial so long as it is a double fluoride of these metals.

"Next is the defense based on the use of external heat in Hall's apparatus as described in his patent, and defendant's use of internal heat. Hall's claims do not say what heat shall be used to fuse the bath. The process is described as beginning with a fused bath. The argument is that because Hall in his specification describes an apparatus for the fusion of the bath by external heat, therefore he limits himself to a process in which external heat is used, and confers upon the world at large the right to use his process if only some other mode of applying the heat is employed; and this in the face of the words of the patent: 'Nor does this apparatus described herein with more or less particularity form any part of the invention herein.' We do not see how the patentee could have used stronger words to avoid the difficulty in which defendant wishes to involve him. Then, too, we have the refined point that the language of the claim itself excludes the possibility of electric heating because it speaks of dissolving alumina in a fused bath of the double fluorides, 'and then passing an electric current by means of a carbonaceous anode, through the fused mass.' This language is as applicable to electric heating as to any other. The word 'then' is used to indicate that the electrolysis is to follow the solution of the alumina in the fused bath. Now, whether the current or a furnace fire fuses the bath, the current which is passed through the fused mass to perform electrolysis is passed through after the fusion. * * *

"Finally, it is said the defendant does not infringe, because the claim calls for a carbonaceous anode and the defendant uses a carbon anode. 'Carbonaceous' means 'pertaining to carbon,' or 'made of carbon.' It includes anodes made partly of carbon and partly of some other substance, but it certainly covers an anode made all of carbon.

"A decree will be entered for the complainant, finding that complainant's patent is valid, and that the defendant infringes both the first and second claims thereof, and perpetually enjoining the defendant from further infringement, with the usual reference to a master to determine the damages."

Following this decision the defendant took an appeal to the United States Circuit Court of Appeals, but when the appeal was called by that Court in June, 1893, it was dismissed on motion of the appellant. The master then proceeded with the hearing of evidence on the question of damages. Pending this hearing and on June 21, 1894, a motion was made by the defendant to reopen the case, for leave to introduce new evidence, and for a rehearing.

The principal ground for asking the rehearing was that the Court made an error in holding that the De Ville process for making aluminum by electrolysis was not an anticipation of the complainant's process, which error it was purposed to show more fully by subsequent experiments made by the defendant and now offered in evidence.

In the opinion denying the rehearing (64 Federal Reporter 125), the Court said in part:

"'The evidence which the defendant now seeks to bring to the court's attention consists of certain patents issued to the Cowles Brothers and to Bradley for the reduction of refractory metallic ores by electric currents of great intensity, of quotations from books on chemistry to show that cryolite was known to the art for many years before Hall's alleged discovery as a suitable flux for the reduction of alumina, and of subsequent experiments with the De Ville electrolytic process. Cowles' patents describe an electric furnace into which he introduces the aluminum compound mixed with small granular particles of carbon. An intense electric current is passed through the furnace, and is carried by the granulated carbon. A degree of heat is thereby produced which is intended to smelt the aluminum compound, and to permit an alloy with some other metal, as copper. The Bradley invention contemplates the introduction of the refractory ore into a furnace in which are a movable carbon anode and a cathode. These are placed so near together at the beginning of the operation that, when the current is applied, an electric arc is formed between them. The arc generates enough heat to melt the ore near the anode and cathode, and this melted portion of the ore thereafter carries the current, and gradually effects the melting of the entire mass of ore in the furnace. As soon as any part of the ore is melted, electrolysis is intended to take place. The gist of the invention is the use of the electric current, first to fuse the refractory ore and subsequently to electrolyze it, and disrupt it into its constituent parts. * * * * *'

"The Cowles patents, here relied on, were in evidence at the original hearing. The Bradley patents were not introduced in evidence, though well known to defendant and its counsel. The present claim of the defendants is that, as cryolite was a well known flux for alumina, it was mere mechanical skill, and involved no discovery or invention, to use alumina in the Cowles and Bradley furnace (which were patented some years before the patent in suit), with cryolite as a flux; that the use of cryolite as a flux for alumina in the Cowles or Bradley furnaces must result in the electrolysis of the alumina, and the deposit of the aluminum at the cathode and would be the patent process claimed by complainant. * * * *

"The evidence which has been introduced by the defendant consists of the deposition of another expert and further quotations from De Ville's works and from subsequent chemists. Everything which has been shown is carried back to the process for making aluminum by chemical reactions discovered by De Ville, and which was the only practical process until Hall's process by electrolysis was discovered to the world. The evidence is simply cumulative, and does not at all change the conclusion of the Court with reference to its effect. Neither the Bradley nor the Cowles patents contain the slightest suggestion that cryolite should be used as a flux for the refractory alumina, and no evidence is sought to be introduced that any one ever actually used cryolite in furnaces for that purpose. The question presented by the defendant, therefore, is exactly the same as that which the Court originally passed upon, and which was fully argued to the Court. * * * * * It should be remarked, moreover, that the Hall process would still be a patentable process, and the only one known for practically making aluminum by electrolysis, even if it had been well known that alumina would freely dissolve in fused cryolite; for it was conclusively shown by the evidence that never before Hall did it, had alumina been disrupted by electrolysis

into its constituent parts. It therefore follows, even if the conclusion already reached is not well founded as to the effect of the evidence touching the solubility of alumina in fused cryolite, that Hall's patent would still be a valid one. * * * *"

After this rehearing was denied the inquisition of damages before the master was continued and about 10 years later, at the beginning of 1903, a second petition for rehearing was made, based on the question whether the commercial success, which had so greatly influenced the Court before, resulted from the practice described in the Hall patent or from some important modification of, or addition to, such process, and whether or not internal heating sufficient to fuse is necessarily incident to the use of the electric current in electrolysis.

The Court granted the rehearing on condition that defendant pay all the costs of the accounting before the master. This rehearing was never actually had. Other matters intervened and subordinated the interest in this case to one in which the former defendant was the complainant and the former complainant was the defendant.

This latter case and one of the conditions precedent to it will be considered next.

*(Part IV to be concluded in December issue)*

2 Rector Street, New York

## THE STATUS OF THE CHEMICAL INDUSTRIES IN THE UNITED STATES AT THE END OF 1915[1]

By I. F. Stone

Mr. Chairman and Gentlemen:

When your Chairman asked me to address you on the status of the chemical industries in the United States at the end of 1915, I considered the subject with much trepidation, and felt that if I tried to speak on this topic I would be falling into a teeming cauldron of trouble, as with conditions so abnormal as they are to-day, any one trying to describe these conditions as they are and as they may be for the next year or more, is very likely to prove a false prophet. But notwithstanding these conditions, I will do the best I can, and hope anything I may have to say will be of interest to you.

Right after the beginning of the war there was an immediate demand from all sides for products which had formerly been supplied from Europe, which were apt to be scarce as a result of the war. Buyers attempted to secure as large supplies as possible in order to carry them through during this war. As a result the prices of European products immediately commenced to advance and finally reached the most fabulous figures. Those of us connected with the lines of business dealing in these products then thought that no more abnormal and exciting condition could be possible. But strangely enough, now, a year after the war, conditions are more exciting than ever, in that most of the European products which were then procurable in some quantity, have practically disappeared, while the demand for them still continues to a great extent, but is impossible to meet.

The products manufactured in America, not dependent entirely on Europe, did not follow immediately the advance of the European products, but gradually, as the manufacturers commenced to see how things were developing and what their cost of raw material would likely be in the near future, they advanced their prices until they are now many times the normal in a good many instances.

American manufacturers also began to consider the question of manufacturing larger quantities of what they were already making, and also taking up new products which formerly could be obtained only from Europe, and I am glad to say that a great deal of progress has been made along these lines. I can say definitely that the chemical industries in the United States at this time are developing rapidly, and are in a stronger and better condition at this time, the end of 1915, than ever in the past. Many of the products which are now being manufactured will, in my opinion, continue to be manufactured after normal conditions are again in vogue, and we need no longer be dependent on Europe for such products. I will be more specific as I go along, but simply want to mention the fact at this time that the condition and progress of the chemical industries have developed and are now in a stronger position than ever before.

At the time of the war, or just before the war, the two most important chemical products furnished by Europe to the United States, in this case by Germany, were potash and coal-tar products. We were entirely dependent on Germany for muriate and sulfate of potash, which as you know are used very largely for fertilizers, and in a smaller way for the manufacture of potash products such as bichromate of potash, yellow prussiate of potash, caustic potash, etc., the manufacture of which was dependent on Germany for their supply of raw material. Unfortunately, since the war and the embargo on the shipment of potash to the United States, none now being received, no substitute has been found, and in spite of the reports from the Department of Commerce that large quantities could be secured from a seaweed called kelp, which is in beds or meadows along the Pacific Coast, belonging to this Government, nothing so far has been practically done to recover it. There are reputed deposits of potash in Utah and California, but again nothing practical has ever been done with them, so that at the present time consumers of potash or potash products are entirely dependent on what is left of the German shipments before and right after the war; when these stocks are exhausted, no one knows what can be done.

### PRODUCTS FORMERLY OBTAINED FROM EUROPE

Benzol.—On the other hand, as to coal-tar products, it was immediately discovered by investigation in this country, that we had large quantities available if they only could be recovered and developed. In other words, the production of benzol, which is the principal base for the manufacture of most coal-tar products and chemicals, could be immediately increased, and this was and is being done. Some of the large steel works, who formerly did not recover their benzol, are now producing it, and the production, which was about 3,000,000 gallons before the war, is now increased to about 15,000,000 gallons. While, unfortunately, its demand for war purposes in the manufacture of explosives, etc., is so great that even the present supply is not sufficient, and prices are almost too high for manufacturers to use it for the manufacture of ordinary products not connected with war products, yet the fact remains that this product has increased in production over five times, and that this production is here to stay; at normal prices it will be largely used for the manufacture of other products, which will develop with it. There is one use for benzol, for instance, which is practical and sure, and that is its use for motive purposes in automobiles in place of gasoline. It is being largely used in Europe for this purpose, and the only reason it has not been used here has been the limited production and the higher price, it normally being about double the cost of gasoline. With the present immense production, however, the cost has been reduced until now I believe that it can be manufactured and sold at a profit at the proportionate price of gasoline, and that this will be done as soon as the present war is over. When I say proportionate price I mean that careful experiments for automobile purposes show that benzol has a motive power about 25 per cent better than gasoline; it consequently would have 25 per cent advantage at the same price, so that even with benzol 25 per cent more in cost it would still be money value, but I also really believe that it could be actually produced now and sold at the same price as gasoline if it were necessary to do so. Therefore, the importance of this matter is obvious. Not only is the above true, but it is a fact that the use of gasoline

[1] Address before the New York Section of the American Chemical Society, Chemists' Club, October 8, 1915.

for automobile purposes is so large (100,000,000 gallons) that it is very difficult for the oil companies to produce enough to meet the demand; consequently the entrance of the new product for the same purpose will be very important, and a great relief.

ANILINE PRODUCTS—Another large increase in production through the present conditions, is the manufacture of aniline colors and other coal-tar products in this country, which will be much to the relief of consumers who at the present time are unable to get anything like the supply of colors which they need in the conduct of their business. The five factories already established in this country before the war, are all extending their production to their utmost capacity in keeping with safety for their investment, and I believe that in 1916 the production of aniline colors in this country will be at least three to four times the production before the war. This production could again be largely increased if the manufacturers were sure of some protection from the Government in the way of higher tariff, or Government manufacture of intermediate materials, which would enable them to get the same at the same price as paid by European manufacturers; then again putting into effect some anti-dumping clause, which is now promised by the Government, to prevent the dumping into this country of colors at lower prices than they are sold elsewhere, for the purpose of preventing their development and manufacture here. Whatever the Government may finally decide to do towards the protection of this industry, there remains the fact that a great impetus in the development is already under way, with the hope of Government protection, so that the Europeans will find them strongly entrenched in any event after the close of the war. I am speaking now of the factories already in operation, but in addition to these there are many new factories projected, and some in operation. I have a list of 23 new factories, the last of them with a proposed capital of $15,000,000, and while a good many of these may not materialize, something will surely come of some of them. Up to now none have actually manufactured any aniline colors, but some are operating with a production of some intermediate products like aniline oil, beta naphthol, paranitranilin, etc. Speaking of aniline oil, with the one factory established before the war and the increase in its works since the war, and the number of new factories making or about to make aniline oil, it looks as if the production of this product would be 4,000 to 10,000 tons as against the normal consumption of about 4000 tons; in other words, the proposed manufacture seems larger than the consumption, but as the consumption is also increased, possibly the whole amount projected can be used. At any rate, there will be enough manufactured in this country to take care of the whole consumption, so that Europe need not be depended upon.

CARBOLIC ACID—Another article which has increased largely in production is carbolic acid, the consumption of which in the United States is about eight to ten million pounds yearly. It is true, however, that this has not been available for ordinary use, as most of the new factories have used their product for the manufacture of picric acid, which is sold for war purposes, with the exception perhaps of the works of Thos. A. Edison, who, in an interview, said that his production was about 12,000 lbs. daily, which is used for his records. The point about this article is that practically none of it was manufactured here prior to the war, but it is now produced in large quantities, and after the demand for picric acid is over, for war purposes, then the production can be used for other commercial purposes to the advantage of the country, and so relieve them of depending on Europe for their supply.

NAPHTHALINE—Another article which has increased largely in production here is naphthaline, which is also a coal-tar product. Before the war the production in this country was about 2,500,000 pounds, while now it has increased to something like 7,000,000, perhaps more, the normal consumption being about 9,000,000; the difference between what was produced in America and the total was obtained from England and Germany, which countries hereafter should be practically unable to ship over here, by reason of the new large production here.

BARIUM PRODUCTS—This is about all I will say in connection with aniline or coal-tar products, but as it is obvious that there is a great development taking place in this industry, it is certainly a very satisfactory condition at this time. Leaving the aniline industry, and going to other products not connected with aniline, but the development of which has gone on very quickly since the war, I shall refer first to barytes and barium products. Before the war there had been a yearly average importation to this country of crude barytes of about 40,000 tons coming from Germany, practically all of which was used in the manufacture of lithophone, which was about the only product of barytes made largely in this country prior to the war. There are now six manufacturers who are turning out large quantities, and the business on this product will remain with the American factories. I wish to say, however, that since the beginning of the war no barytes has been coming in from Germany but it has been supplied from mines and deposits in the States of Tennessee, Kentucky, Virginia and Missouri, and possibly some others, so that now the thing to do is to continue to use this American product and keep away from the European barytes. Formerly there was a duty of $1.50 per ton on foreign barytes, but this was reduced in the last tariff to 15 per cent which was only about half the former duty. The German barytes was formerly delivered at a cost of about $5.00 per ton at such ports as Philadelphia and New York, the duty of 15 per cent per ton included, while the American barytes under normal conditions could not compete and can sell now only because no German goods can be secured. The German barytes tests higher in barium sulfate content, averaging about 96 per cent and is almost free from objectionable impurities, so that the consumer obtains a better yield at a lower cost than by the use of the available American barytes, which analyzes only from about 83 to 95 per cent barium sulfate, averaging, say, 92 per cent and much of it is contaminated with iron. The point is then that a duty should be placed on foreign barytes high enough to offset the difference in quality and price, and insure the continued use of American barytes by American manufacturers. In other words, the duty should be advanced, instead of standing at the present rate of 15 per cent per ton. In addition to using the American barytes for the manufacture of lithophone, since the war four or five responsible factories have started up to manufacture other barium products such as chloride of barium, carbonate of barium, hydrate of barium, nitrate of barium, and binoxide of barium, which means an increased use of the crude barytes, giving still further production to American producers, possibly double the quantity formerly used. It is important that American producers should continue to furnish the crude barytes to these factories in spite of the German competition, which is bound to come again after the war, and, as far as I know, an additional duty is the only way it can be done. With the manufacture in this country of the products just mentioned, *viz.*, chloride, carbonate, hydrate, nitrate and binoxide of barium, most of which were never made in this country before successfully, we have a practically new industry created, which will make us independent of Europe in the future, some of these factories being already in operation successfully, and the full production of all of them will undoubtedly be on the market before very long. This makes the barytes and barytes products in this country practically a new industry and one which could be held in the future, and is of great importance.

CARBON TETRACHLORIDE—Another product, the manufacture of which has increased largely in this country since the war, is carbon tetrachloride, which was formerly made exclusively

in Germany, but later taken up by American manufacturers, who at the time the war began were probably producing half the consumption here. Since the war they have increased their plants very largely so that they are now supplying all of the American trade, and while still somewhat short of the requirements, new factories are being constructed so that in the end the whole consumption of the country will be manufactured here. This article is perhaps not so well known, but is one of considerable importance, and the consumption is continually increasing in view of the many purposes for which it can be used.

INCREASED PRODUCTIONS IN ESTABLISHED INDUSTRIES

I have given, up to now, the situation on those articles for which we formerly depended largely on Europe, but the manufacture of which has increased largely in this country, which gives a distinct advantage, and increase in our chemical industry. I will, therefore, now refer to a number of products which have always been produced largely in this country, and are not so susceptible to European competition, simply to advise you the condition of the manufacture of these articles and the present and future conditions regarding them.

ACIDS—First in importance, I presume, is the manufacture of such acids as sulfuric, nitric and muriatic, which are the basic materials for practically all of the great chemical industries of the country, and on which there has never been any foreign competition because largely of the heavy expense of transportation, the fact being that American manufacturers were able to make at such prices as rendered importation unprofitable. Up to within a few months ago they were able to supply the demand of the country as usual, but as the war ran on, and the demand for ammunition and explosive purposes became larger and larger, the demand for acids increased to such an extent that at this time the manufacturers are absolutely unable to supply it; as a consequence American consumers find themselves unable to get enough to conduct their business, or, when they do get enough for their present business, they are unable to obtain any additional quantities for an increased business, so that the general situation on acids is very serious at this time. Many increases are planned and under construction, but it will be a number of months before they can be completed, and not much relief is expected for some time to come.

ALKALIS—Perhaps the next important manufactures in volume and value, are caustic soda, soda ash, and bleaching powder, all of which are now manufactured largely in this country, the quantity I am told being from 1,250,000 to 1,400,000 tons of the three products together. For a short time after the war, the manufacturers were able to continue their supply in their ordinary way, but the stopping of shipments from European countries to other countries by reason of the war, led to a demand for American manufactures to supply this shortage, *i. e.*, countries who had formerly bought from England and Germany and who could not get any from Germany at all and not enough from England, turned to America for their supply; this created a large export business which brought the manufacturers to their full production and has kept them very busy up to this time. By reason of this unusual export demand, and the consequent shortening of stock, the condition of these products means great prosperity to the American manufacturers.

CHLORATES, PRUSSIATES, BICHROMATES—Other products manufactured largely in this country are such products as yellow prussiate of soda and potash, chlorate of soda and potash, bichromate of soda and potash, the manufacturers of which hold the whole American trade, as there are practically no importations from Europe. The manufacture of yellow prussiate of potash, however, is somewhat limited, owing to the inability of manufacturers to get muriate of potash from Germany, so most of them are working almost exclusively on soda, and the paint manufacturers, who are large users, are now trying to make their Prussian blues from soda instead of potash, and if successful, as some of them seem to be, the soda will probably be used exclusively for a long time to come, and there will be no need to depend on European sources for potash.

The manufacture of chlorate and bichromate of soda continue without hindrance, and in increasing quantities, but chlorate and bichromate of potash are apt to be somewhat limited, owing again to their inability to get proper quantities of the muriate potash, these manufactures depending, as far as I can find out, on muriate of potash which was brought in from Germany before or just after the war; while they are fortunate in having enough to go on with their manufacturing, it must be evident that sooner or later their potash products must stop, and soda products substituted wherever possible.

CAUSTIC POTASH—The condition of caustic potash, another potash product, is also interesting; its manufacture was commenced in this country some years ago and up to the time of the war was constantly gaining in importance and production. Unfortunately, however, the manufacturers were dependent entirely on Germany for their muriate of potash; when shipments of this were stopped the factory was compelled to slow up and is now in a position where they can only make that quantity of caustic potash for which they can secure the raw material. Should the muriate of potash be found or produced in America, then this caustic potash could be made largely, but while depending on Germany, muriate of potash must necessarily continue to be limited.

OXALIC ACID—Another important article, the manufacture of which has developed in this country, is oxalic acid. The factory was established some years ago, but up to the time of the war had trouble competing with the European product on account of the reduction of duty in the last tariff, and was not able to develop the production as they wished; but since the war practically stopped the importation of foreign acid, they have taken care of practically the whole American consumption, and will continue to do so to the limit of their ability. They are not yet able to produce the full quantity, so there is a considerable shortage in supplies. Consequently the price is very high, but eventually there is no reason why this product should not be manufactured to the full extent of the American consumption, and the business held here.

There are many other chemical products which are manufactured in this country, but not of enough importance to enumerate separately, so all I can say in finishing is that the status of the chemical industries in the United States at this time is very satisfactory, practically every manufacturer being engaged to the limit of his capacity, and from every indication this prosperity will continue for the following year, for the reason that most of them have made contracts covering their production for this period.

You will notice that in speaking of these various products manufactured in America, I have made frequent reference to tariff, and the necessity of advancing the duty if articles manufactured are to be developed successfully. While I have no intention of making this an address on tariff, at this time, it is so obvious that the tariff should be reformed upward to retain the present manufactures successfully, that I cannot help mentioning it.

100 WILLIAM STREET, NEW YORK

## THE BARIUM INDUSTRY IN THE UNITED STATES SINCE THE EUROPEAN WAR[1]

By MAXIMILIAN TOCH

Within the last eighteen years there have been three attempts to establish a barium industry in the United States prior to August 1, 1914, and all three of them were unfortunate failures.

[1] Address before the New York Section of the American Chemical Society, Chemists' Club, October 8, 1915.

I have investigated the cause of these failures and I find that two of them failed through financial and chemical mismanagement, and one of them was utterly destroyed on account of its inability to compete against foreign competition.

I have been identified with the manufacture of barium products for nineteen years, and while the venture of my firm has been successful it was never very large and was confined to one particular barium salt, which sold entirely on account of its quality rather than its price.

A well known and successful chemical corporation manufactured barium chloride and barium sulfate in New York City a little over fifteen years and made very, very good products. As soon as they turned out reasonable quantities some foreign chemical manufacturers undersold them to such an extent that they found they were unable to continue, and as soon as they were promptly and properly put out of business the foreigners raised their price and have kept the trade ever since, for they taught the American manufacturer the unfortunate lesson that if he were to establish an industry he could not continue it successfully, for the well-known methods of "dumping" large quantities on this market, in addition to the meagre tariff, would soon teach them that they had better not try to make American goods again.

I believe I was the first one who pointed out to the Department of Commerce the shortcoming of our own laws. If a manufacturer in this country attempts to put a competitor out of business by what is known as unfair methods, all one has to do is to file a complaint with the Federal Trade Commission, and the matter is considered at once by its examiners and attorneys; but it is quite obvious that any law made in this country has no sanction against a foreign corporation outside of the jurisdiction of the United States any more than a firm in the United States can be held responsible for its actions according to the law of England, France or Germany.

Two weeks after the great war in Europe was under full swing, my firm recognized that a very interesting portion of its business would be obliterated if we could not obtain barium compounds, and, to be exact, on the 14th of August I started negotiations for a plant at Sweetwater, Tennessee, for the purchase of a large tract of land containing the mineral barite, and in October, just a year ago, the first carload of barium salts was shipped from Sweetwater, Tennessee, to our Long Island City works. From that day to this the plant has been working night and day, additional mines have been purchased, additional installation has been erected, and the corporation is destined to continue to grow, provided our own parsimonious and short-sighted Government will not aid in its final destruction.

There has been a great deal of talk about the dye industry in the United States, and any number of capitalists would invest the necessary funds to-morrow to establish a permanent aniline industry in the United States if they had some kind of assurance that the laws which prohibit unfair competition among ourselves could, in some manner, be made active as against those outside of the United States. There has been a tremendous amount of talk with reference to enacting an "anti-dumping" law. For months this has gone on and up to now it is simply nothing but talk. A great deal of publicity has been given by public officials about the new and wonderful methods and short cuts that have been discovered for the manufacture of aniline dyes out of soft coal to such an extent that it has made the finest and best method for stock jobbing that has ever existed, but there is not a color maker in the United States who can buy for immediate delivery the necessary aniline colors for the manufacture of the lake colors in any reasonable quantity in spite of all this caloric atmospheric discussion.

The barium industry in the United States is not an industry that can be started over night, and among the failures that I referred to one of them was due to the fact that theory took the place of practice. The starting point of the barium industry in the United States is the admixture of barium sulfate and coal, both of which are finely divided, and heated, when the coal converts the entire oxygen into carbon dioxide and leaves barium sulfide behind. The best that any man can do in practice is to get 70 to 75 per cent reaction. In our works we have had runs where we have gone as high as 85, but I think this is purely accidental; yet theoretically the reaction ought to be complete, and the difference between theoretical chemistry and chemical engineering shows that the chemical engineer must devise apparatus which will fit his raw material. Not all barite is suitable for reduction. I have seen disastrous results where calcium fluoride was contained in the barite, and where certain forms of iron would actually produce a paralysis in the reaction, and if up to now I have had a slight measure of success in the manufacture of these compounds it is because I had a knowledge of the manufacture of these compounds prior to the European war. Chemical engineering is 49 per cent chemistry and 51 per cent business acumen. I place the business end ahead of the chemical end for the obvious reason that ability to finance, ability to sell at a profit, and ability to organize are ahead of the chemical reactions involved. You can buy chemical talent, but you cannot buy business efficiency. You can buy barytes of any kind, but you cannot buy in the open market the skill necessary to design this apparatus so that the results will be uniform. I have seen a chemical industry fail because no commercial method of water purification necessary for the reaction was at hand, and if the subject had been carefully studied in advance a fortune could have been saved.

There are many arguments in favor of protection of the chemical industries in the United States, and what I say about the barium industry might refer practically to any other chemical industry, for we have economic differences between Europe and America which cannot be neutralized excepting by a system of protection in addition to an "anti-dumping" law. The freight rate from Tennessee to the coast on our raw material is about $4.50 per ton; that is to say, barite cannot be shipped for less than that except by rail and water, which is a purely theoretical rate, for under existing circumstances a fifty ton car of barium ore cannot be transferred to a steamer unless the material is packed in sacks or barrels. The same material pays $1.80 freight from Bremen to New York, and I have it on very good authority that the rate from the mines of Germany to New York is $2.00 per ton, because the German Government has always fostered its commerce by making special freight rates to export shippers. The railroads in this country, which are, of course, all privately owned, show that they cannot carry trade for less than a fixed sum, owing to their overhead charges; but their overhead charges, which start with the interest on their watered stock, are so great that the shipper must suffer. An 800 mile haul from Tennessee to New York pays $5.00 per ton, and a 1200 mile haul from Missouri to New York pays $4.00 per ton, and the one railroad can afford to do it and the other railroad cannot afford to do it. If the unsuspecting public is forced to support an overburdened railway the Government should, at least, equalize this matter by giving us a protection in the form of tariff.

It is very amusing to read in the papers almost daily about wonderful new methods and new corporations who are about to manufacture all the dyestuffs in the United States and that the shortage of dyes and chemicals necessary for dyeing is about to disappear. It seems to be a pity that any Government employee will lend himself to the exploitation of what looks like stock jobbing schemes without due investigation, for I have not been able to buy any American dyes and no one else that I know of has been able to buy any American dyes such as are generally used for the manufacture of lake colors. On the same sheet of the daily press in which these forthcoming industries are heralded

you could invariably find a news item stating that the dye works are practically shut down for want of even simple dyes.

It is at once amusing and pitiable to note the superficiality with which these investigations have been conducted. Three weeks ago in the *New York Times* there appeared a statement that a corporation was formed and very shortly there would be no dearth of the barium chemicals necessary for the manufacture of mordants and paper glazing material, and that a great deal of credit should be given to this concern as being the first concern to manufacture the barium chemicals in the United States, and this just exactly one year after the industry with which I am connected has been steadily turning out hundreds of carloads. It may be true that I have not trumpeted from the housetops that the concern which we started was supplying material with great regularity and of chemical uniformity, and our own Government did not know it. On the other hand, last Spring a friend of mine sent me a clipping from the German commercial reports giving a full description of the materials that we are making, and an item concerning myself, for the investigator had stated that many German chemists would recognize my name as having been president of a section of the Eighth International Congress of Applied Chemistry. This was last Spring, and now our own wide-awake Government is noting the fact that soon there will be a barium industry started in the United States.

One of the very serious drawbacks concerning the new barium industry in the United States is the inability to obtain raw materials and equipment. There isn't a steel factory in the United States that is not working overtime at high prices on appliances which are designed to kill people, and as long as this condition obtains we peaceful manufacturers who want new rotaries and new apparatus will simply have to abide our time and pay exorbitant prices until we can obtain parts of new equipment. To give you a striking example, we needed in one of our works a set of bevel gears made of a special metal, and after waiting twelve weeks, because there was no shop in the country which would pay any attention to us, we finally had to devise gears ourselves as a makeshift. Nor does this apply to machinery alone, for no one could take any contract on any of the barium salts like the chloride, nitrate or sulfate and hope to deliver any part, because it is absolutely out of the question to obtain acids. The people with whom we have dealt for our acids for years are simply either refusing to give us any materials or supplying us with ridiculously small lots at enormous prices, for there are other channels which buy larger quantities and pay more than the peaceful manufacturer can afford.

I mentioned before that industrial chemistry was 51 per cent business and 49 per cent chemistry, and these figures will serve for an example. I was often asked why we located at Sweetwater, Tennessee, and while I did not have very much time to look around I found that that was the logical and strategic location for coal, labor, water and ore, for all of these materials combined are perhaps more reasonable at that locality than anywhere else I know of. In the lantern slides, which I will show you later, you will see a graphic description of the method by which the ore is mined, and in order to make a success of this enterprise the works should be located within such a radius of the mine that the ore can be delivered at a reasonable rate.

The great and only question with reference to the barium industry is, shall this industry live after the European war is over, and I could not answer that categorically without some explanation. It depends entirely upon our own Government. If, on account of the economic conditions which I have described, foreigners are prevented from underselling us, we shall be able to live. Our own manufacturers should get together and understand that the underlying principle of successful business is to have a profitable business, for no argument is necessary on this point other than to prove that when you have a growing and going manufacturing concern, in order to have peace and success you must be able to pay your men a living wage, and you must be able to pay them regularly, for the shut-down of any works in any community, particularly in a small one, produces disastrous results. Innocent women and children are made to suffer through it, so that in the greed of obtaining business manufacturers must understand that cut-throat methods lead to bad results for all parties concerned. I hope that when this war is over the barium industry will be firmly established and protected, as the economic conditions in this country would demand.

What a remarkable difference there is between the enterprise in Japan as compared to the United States. Japan has suffered from a lack of chemicals and dyestuffs just as much as we have, and both Houses of the Japanese Government have voted to subsidize all corporations and firms who are about to engage in the manufacture of chemicals and dyestuffs that were not formerly made in Japan to the extent of $3,500,000, the other half to be subscribed by the manufacturers themselves. It is understood that the subsidy granted is for ten years in order that the new manufacturing concerns may pay a dividend of at least 8 per cent. In addition to this it is understood that the Japanese Government has protected these manufacturers in the form of a high tariff. And that is the country to whom we have been sending missionaries in order to convert them from their archaic beliefs and notions. The old order of things could be reversed and Japan could now send missionaries to this country. It seems to me that it is a great pity that nothing has been done up to now to protect the American manufacturer, for a subsidy from the Government is out of all reason, even though this is at present the richest Government in the world and Japan rated as one of the poorest. As I said before, we can hope to succeed only if our Government will help us from being destroyed by outside influences.

320 Fifth Ave., New York

## NOTES ON THE EUCALYPTUS OIL INDUSTRY OF CALIFORNIA

By P. W. Tompkins

Received April 26, 1915

*Eucalyptus globulus* oil produced in California has been characterized, since the Pure Food and Drug Act, by its nonconformity to the U. S. P. solubility standard in three volumes of 70 per cent alcohol by volume, a guarantee now required by wholesale druggists. While this difficulty can be readily overcome by appropriate fractionating, it is at the expense of a certain portion of the oil and a cost not favorably comparable with Australian conditions of production, with which we must compete.

A feature developed during an investigation of the industry begun in 1912 satisfactorily explains the wide variation occasionally encountered in California oils. A considerable proportion of the trees cut are topped or stumped and the subsequent growth develops a very prolific and dense foilage. Since this new wood is sometimes recut, its influence on the oil derived exclusively from mature trees was determined.

Two sections were found where the new foilage (all globulus) was fairly accurately established as being five years old and was from topped trees while the other was a lot of one year sucker shoots from tree stumps. Each batch of 400 pounds (with a minimum of terminal twigs) was separately distilled and is compared with an oil from trees about 30 years old, with salient characteristics briefly determined as follows:

OILS FROM *Eucalyptus globulus*, ALL FROM SAN FRANCISCO CO

| | 1 year | 5 years | 30 years |
|---|---|---|---|
| Yield, per cent | 0.09 | 0.21 | 0.84 |
| Sp. gr. —25° | 0.890 | 0.906 | 0.908 |
| Sol. 70 per cent alcohol by wt. | 15 vols. | 3.25 vols. | 1.5 vols. |
| Sol. 70 per cent alcohol by vol. | Insoluble | 45 vols. | 15 vols. |

Obviously the young growth furnishes much less oil in proportion to its age, and its inferior quality would have an un-

desirable influence on any run. Aside from a very marked difference due to locality, observed in oil from mature trees, this young growth would apparently account for the abnormal character of California oils noted from time to time. What age the new growth must attain before its oil fully matures, would be an interesting subject for those having the opportunity to investigate.

However, the greatest difficulty the California industry has to contend with, aside from the decreased oil recovered, in order to bring its product up to present U. S. P. solubility, lies in the fact (practically speaking) that *Eucalyptus globulus* is the only species available, in quantities for oil production at the present time, whereas in Australia more productive species requiring no treatment are almost exclusively worked for export. This subject is best illuminated by quoting some correspondence with Richard T. Baker[1] in part as follows:

"There is, however, an erroneous opinion commercially as to the percentage content of cineol in the oil of *E. globulus* and we have species growing naturally in Australia, the oils of which are much richer in cineol than that species, and also yield a much greater quantity of oil. These oils are now largely exported from Australia, particularly that of *E. polybractea* and are without doubt often sold as the oil of *E. globulus* as indicated by the records of their sale. In fact, there is at the present time very little oil of *E. globulus* distilled in Australia, as it cannot compete against the more prolific oil-yielding species which are richer in cineol.

"It is not usual to fractionate the oil of *Eucalyptus globulus* and the other rich eucalyptol oils so as to remove terpenes and thus endeavor to increase the eucalyptol content, as this is unnecessary with these species. Rectification by steam distillation is all that is necessary. There are species, however, the oil of which can be much improved by fractional distillation and the oil of the New South Wales form of *Eucalyptus amygdalina* can be, and is so increased in eucalyptol, by separating the large fraction boiling at about the temperature of eucalyptol; the other portions of the oil are then used for industrial purposes other than pharmaceutical. As a rule fractional distillation, on a large scale, is not practiced to any great extent in Australia in preparing eucalyptus oils for market."

In addition to this unequal basis of competition they now employ, in Australia, digesters of much greater capacity than are used here, some of these taking over 3 to 4 tons of green leaves to the charge. A most interesting feature was developed in the fact that the raw globulus oil from Australia does not conform to U. S. P. solubility, unless fractionally distilled like our own, though with less loss. Notwithstanding the popular idea that the raw Australian globulus oil is soluble in 3 volumes of 70 per cent alcohol by volume, it is in reality not so.

Through the kind assistance of Mr. Baker this valuable comparison was made possible and in submitting the first sample (broken in transit) Mr. Baker stated in part:

"After considerable difficulty I have at last been able to obtain a sample of the oil of *Eucalyptus globulus* which has been forwarded, etc." "The oil was without doubt distilled from *Eucalyptus globulus* and is typical of the oil of this species as grown in Tasmania."

The second sample also from the Island of Tasmania was received with the comment:

"I have after considerable trouble secured another sample of *Eucalyptus globulus* oil," etc.

Compared with the average raw California globulus oils from San Francisco County, and normal extremes observed from properly distilled leaves (mature) of several localities, the Australian sample gave the following, compared with Baker and Smith's observations of the New South Wales growth:

| Various Samples of Oils | California mature growth: Extremes observed | | Average S. F. Co. | Australia: Tasmania Our sample | Australia: N. S. W. Baker & Smith |
|---|---|---|---|---|---|
| Sp. gr. —25° | 0.901 to 0.909 | | 0.906 | 0.913 | 0.915 |
| Rotation $\alpha_D$ | −11 to −7.0 | | −8.0 | −3.9 | +9.2 |
| Sol. 70% alc. by wt. | 1.7 to 1.4 vols. | | 1.5 | 1.2 | 1.8 |
| Sol. 70% alc. by vol | 35 to 13 vols. | | 15 | 8 | 2 |
| Per cent cineol (U. S. P. Method | 47 to 54 | | 52 | 54 | About 80 |
| Phellandrene test | Negative | | Neg. | Neg | Neg. |

[1] Curator of the technical museum of Sydney. Baker and Smith: "A Research on the Eucalyptus with Particular Reference to Their Essential Oils" published by the Government of Australia in 1902.

(a) Burke and Scalione, THIS JOURNAL, **7** 1915, 206 found $[\alpha]_D^{20} = +14.4$ from trees at Berkeley, Cal.

Inasmuch as most oils from Australia are soluble in 1.8 to 2.2 volumes of 70 per cent alcohol by volume, it would lead to the conclusion, particularly in view of Mr. Baker's statement and our examination of the Tasmania globulus oil, that this species is not represented in the products received here. Merely in support of its scant production, is the fact that of some ten commercial varieties of eucalyptus oil representing the Australian exhibit at the P. P. I. E., *Eucalyptus globulus* is the species conspicuously absent.

It could hardly be considered guess work to assume that the raw globulus oil of Australia is in reality as variable in 70 per cent alcohol by volume as our own, when we compare the constants of the Tasmania sample and those found by Baker and Smith, with over twice the specific rotation and 0.3 cc. less soluble in 70 per cent alcohol by weight, a very great factor of influence on the solubility in 70 per cent alcohol by volume.

Probably the greatest relief home industry could receive, would be by appropriate modifications of U. S. P. requirements in the coming edition, which would permit within reasonably practical limits the use of our globulus oil. The limitations should be sufficiently broad to include normal variations, particularly the solubility in 70 per cent alcohol by "volume." Among the proposed requirements are: specific gravity at 25° —0.905 to 0.925 (same as at present); soluble in 4 volumes of 70 per cent alcohol (undoubtedly meaning 70 per cent by volume); and containing not less than 70 per cent cineol by the resorcin method.

However, if 70 per cent cineol is to constitute the minimum limit, then a gravity as low as 0.905 is unnecessary. The proposed solubility in 4 volumes of 70 per cent alcohol by volume with oils containing a minimum of 70 per cent cineol when the present U. S. P. calls for solubility in 3 volumes with not less than 50 per cent cineol, reverses the needs, since the solubility increases as the cineol increases. That is, if by increasing the solubility to 4 volumes, a more liberal scope is intended, the 70 per cent cineol makes this increase unnecessary and would be a solubility more in keeping with present U. S. P. requirements for 50 per cent cineol. If, on the other hand, a gravity of 0.905 (about that of California's) is meant to include the conditions of a broader range of oils, then the solubility in either 3 or 4 volumes of 70 per cent alcohol by volume is entirely inadequate; nor could a natural oil of this gravity contain as much as 70 per cent cineol.

## SUMMARY

I—Appropriate fractional distillation will render California eucalyptus oil up to present U. S. P. requirements, but at the expense of about 15 per cent of the original volume as determined by the present official method. The quality is further improved by the use of caustic soda.

II—Neither Australian nor California globulus oils in the raw state or redistilled in a current of steam are soluble in 3 or 4 volumes 70 per cent alcohol by volume, without fractionating, though this variety is not the competitive species we have to deal with in the Australian trade.

III—If the phosphoric acid method is retained as official in the coming U. S. P. the minimum per cent of cineol should remain as at present, 50 per cent. If the resorcin method is

adopted the minimum per cent of cineol could be placed at 60 per cent without materially interfering with the California industry, but the proposed 70 per cent would entail a loss of at least 30 per cent of the original volume to bring it up to this figure if determined by the phosphoric acid method, and about 15 per cent loss if the cineol is determined by the resorcin method.

IV—The solubility in 70 per cent alcohol by volume should be increased to at least 18 instead of 4 volumes, if the average raw California oils redistilled in a current of steam without fractionating (Australian practice) are to be included on an equal basis with the foreign importations.

V—The by-product oil of refining as well as the crude (if sufficiently reasonable and in quantities) might be utilized for the separation of metallic sulfides by the flotation process, as extensively applied in Australia and to some degree here with the foreign oil.

LABORATORIES CURTIS AND TOMPKINS
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# CURRENT INDUSTRIAL NEWS

## MARKET CONDITIONS

Active inquiry, alarming advances and continued scarcity have been noted for many chemicals and raw materials during the past month. A combination of peculiar circumstances that is unprecedented has resulted in a very sensitive market. Conditions prevailing are such that quotations seldom hold for more than a day. Manufacturers having a surplus of some articles are selling at a handsome profit and small fortunes have been realized by speculators. Manufacturers in many lines have been compelled to alter their formulae to allow for the use of substitutes where the necessary materials are abnormally high or impossible to obtain.

These unusual conditions are justly attributed to the European war but there are some features only remotely connected with the hostilities of nine nations and some causes entirely independent of the European situation. The cessation of all shipments from Germany is probably the largest single factor although home requirements and embargoes have prevented England, France, Russia and Italy from permitting or making normal exportations of many commodities. The war has resulted in a scarcity of freight room on ocean vessels, higher rates for freight and insurance, and a general uncertainty.

Contracts for the manufacture of explosives for the entente Allies are responsible for the scarcity and high prices noted for carbolic, picric and nitric acid, nitrate of soda, glycerine, ether, benzol, toluol, aniline oil and many other coal-tar derivatives.

Nitrate of soda in normal times enters commerce principally for fertilizer. During the early months of the war, large stocks were held at most receiving and shipping points; with a large portion of foreign markets closed, operations in Chile were brought almost to a standstill and prices were very low. As the war continued the demand for nitrate increased and operations at producing points were increased to normal with quotations slowly advancing. About a month ago unusually large purchases in Chile were credited to explosive interests and great strength developed. Then came the last big slides in the Panama Canal and the subsequent announcement that Canal traffic would be suspended indefinitely. This resulted in the market reaching $3.00, the highest point in several years. Cargoes will now come "round the Horn" and increased freights and the growing scarcity will probably result in further advances.

Glycerine was not attracting any particular attention in the markets a month ago and C. P. was available at 26 cents and "dynamite" at 25 cents. To-day it is difficult for any buyer to secure supplies, except subject to delays, although the current quotation is 60 cents per pound for both C. P. and dynamite grades. One consumer was in the market a few days ago for 1,500,000 pounds. The high prices and active demand have resulted in an increased production and this is proving the most profitable business to most of the soapmakers. Vegetable oils are being purchased in large quantities for this purpose and linseed oil appears to be the only one not profitable.

Inability to secure supplies of potash salts has resulted in abnormal prices for many chemical compounds and the elimination of some from the market. Dealers and brokers have verily scoured every corner of the globe in search of old stocks of German potash, so that now little muriate or sulfate is to be had except from third hands who naturally look for a substantial profit. Muriate of potash, however, is available in a limited way at $245 to $250 per ton.

Scarcity of the various forms of potash has found the soda compounds being substituted to such a degree that sharp advances are common. Yellow prussiate of potash is to-day selling at 87 cents per pound as compared with $11\frac{1}{2}$ cents before the beginning of the war. Red prussiate of potash commands $2.60 to $2.75 per pound as compared with 21 cents in July, 1914. These advances result in such an increased use of soda compounds that prussiate of soda is to-day selling at 44 to 45 cents per pound, as compared with $8\frac{1}{2}$ to $8\frac{3}{4}$ cents during July, 1914. Bichromate of potash is held at 21 cents per pound as compared with a normal price of 7 cents or less. Bichromate of soda is selling at 15 to 16 cents and quoted at 14 to $14\frac{1}{2}$ for winter deliveries as compared with $4\frac{3}{4}$ cents before the war. Chlorate of potash is to-day bringing 37 to 38 cents per pound as against the old price of $7\frac{1}{4}$ to $7\frac{1}{2}$ cents. Chlorate of soda sells to-day at 22 to 23 cents per pound on spot with contracts for future deliveries commanding 14 to 16 cents f. o. b. works, as compared with $7\frac{1}{4}$ to 8 cents a little more than a year ago.

In July, 1914, aniline oil was selling at $10\frac{3}{4}$ to 11 cents per pound while to-day one can sell at 95 cents to $1.50 per pound, according to urgency of the consumer's requirements. Aniline salts at present command $1.35 to $1.50 per pound whereas 9 cents was the average price fifteen months ago. Benzol is now selling at 80 to 90 cents; not long ago many orders were filled at $1.25 to $1.40; just a little over a year ago, plentiful supplies could be had at 22 cents.

The foregoing are only a few instances of the upward trend; further reference to a price current of July, 1914, shows the price of oxalic acid at $7\frac{1}{4}$ to $7\frac{1}{2}$ cents; this week sales were recorded at 45 and 46 cents and quotations are as high as 50 cents. We have depended on Germany and other foreign sources to supply us with oxalic.

Lead products were very high for a time but present levels are close to normal. Zinc products are high and scarce but not as high as a few months ago. Quicksilver sells to-day at $93 to $95 per flask as against a normal figure of $75.

One of the principal reasons for the extreme high prices is that manufacturers have contracted for their entire output and consumers not fortunate in holding a contract for regular deliveries are at the mercy of second hands who are reaping profits while they may. How long present conditions will prevail is a question that interests many. The duration of European hostilities is the most important factor although this may be overcome, to a degree, by more generous supplies of needed raw materials. Further advances are predicted and are to be expected for many articles. A sudden cessation of the war would result in declines but well-posted factors claim that it would be many months before the old levels were restored.

But few commodities have remained practically unchanged

during the fifteen months of the war or have found lower levels. These include most of the vegetable oils, naval stores and a small list of articles that are of domestic origin.

Unusual opportunities have been opened for American chemists and manufacturers and it is pleasing to note that most of them are being grasped and developed.

## THE VALIDITY OF EMPLOYMENT CONTRACTS

In a Court of Appeals of England, an interesting decision has been rendered, affecting the relation of employer to employee. An account of this appears in the *India Rubber Journal*, for April 24, 1915, as follows:

A draughtsman in a certain plant reached the position of chief draughtsman, and eventually became head of the sales department in the company. On attaining this position he signed an agreement, that if he left the company's employ he would not for seven years thereafter enter the employ of any other concern in the same business. This agreement he did not observe, but shortly after leaving the first firm he was engaged by a second,—a competitor. Action was taken by the first company to compel its former employee to observe his agreement. The trial Justice rendered a decision in favor of the employee, on the ground that such an agreement was against public policy and could not be enforced. The case was appealed, and the Court of Appeals upheld the original decision on the same ground stating: "On the one hand it was in the public interest that a covenant should be observed and enforced but it was also in the public interest that a man should be free to use his skill and experience to the best advantage."

This decision is of considerable interest to Industrial Chemists in the United States as numerous attempts have been made by employers limiting or seeking to limit the usefulness of former employees. It would seem that the German industrials had found a better way out of the difficulty by keeping a former employee on half salary for five years in case he promises not to enter the employ of a competitor within that time.

## DEVELOPMENT OF SOUTH AUSTRALIAN COPPER AND OIL RESOURCES

A recent bulletin of the South Australian Official Intelligence Bureau at Adelaide states that with the object of making a systematic attempt to provide a means whereby the relatively low-grade copper deposits of South Australia may be turned to profitable commercial account, the Government, with the assistance of the University of Adelaide, has secured the services of a metallurgist for a period of two years, to experiment in hydrometallurgical methods.

The direct aim of this experimental work will be the drawing up of working schemes, wherever practicable, for the treatment of ores that have been tested.

A small experimental plant will be erected in South Australia for the carrying out of a series of tests on the copper ores of the State. Should this experimental work be successful, it is hoped that some of the copper mines of the State which are now lying idle or being worked on a restricted scale, will become important contributors to the annual output of copper.

With reference to the offer made by the Government of South Australia of a bonus of £5000 to the person or body corporate first obtaining from a well or bore, situated in the State, 100,000 gallons of crude petroleum containing not less than 90 per cent of products obtainable by distillation, the South Australian Department of Mines reports the results of investigations into the supposed oil-bearing areas of South Australia. It is stated that the prospects of obtaining a supply of petroleum from the districts investigated are very slight indeed. The far South-east carries a faint possibility which is based on surmise and no evidence. In the interior of the continent the Coomanna Bore gave some signs which have resulted in nothing tangible when tested by further boring. Shales which may produce oils on distillation are also known to occur in these far removed areas, but difficulties connected with climate, water, and communication will probably cause a long period to elapse before the actual value of these interior deposits can be adequately tested and made known, and will largely discount their economic value for many years.

With regard to lignite beds which underlie areas nearer the coast, the analysis of average samples shows them to be of such poor quality that all attempts to utilize them at present would result in financial loss.

The report concludes with the suggestion that the offer of the bonus should be extended so as to include oil obtained by distillation from shales or lignites.—D. G. ANDERSON.

## GLAUBER'S SALT FROM THE CASPIAN SEA

The Russian *Agricultural and Land Gazette* calls attention to the immense riches in Glauber's salt, soda, etc., to be found in the Karabagasky Gulf, of the Caspian Sea. This gulf had been particularly investigated already in 1897, when it was shown that there are beds of Glauber's salt, unequaled in purity by that ordinarily prepared in the chemical factories. It is estimated that the deposits there contain 181,000,000 pounds of the salt. The production of this article, as well as others which do not lie deep in the gulf, might be undertaken with simple excavating machinery. Naturally, stress is laid on the value of exploiting these deposits at the present moment, as their exploitation would free Russia of dependence on foreigners in respect to Glauber's salt, and might bring about a complete revolution in the soda business.—A.

## BRITISH BOARD OF TRADE

During the month of August the British Board of Trade have received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles:

Acetanilide
Borax
Caliper gauges
Combs, vulcanite
Cobalt oxide
Cobalt chloride
Cocaine
Codeine
Glass chimneys
Glass ampoules
Graphite
Iceland spar
Irish moss
Leather, imitation
Lithophone
Magnesium ribbon
Milk, powdered
Mica
Manure, artificial
Manganese dioxide
Naphthaline
Papier mâché
Phenazone
Phenyl salicylate
Rubber sponges
Silica
Stearine pitch
Steel wool
Tungsten powder
Wood wool
Acetyl-salicylic acid
Asbestos and asbestos goods
Boxes with aluminum lids
Compressed air brushes for applying color
Copper tubes, elliptical section
Felt tape for insulated wire covering
Glass capsules for holding soup
Glass tubes for pills
Hexamethylenetetramine
Horn and tortoise shell waste
Incandescent mantles
MACHINERY FOR MAKING
  Metal clips
  Press buttons
  Safety pins
  Tin cans
  Stamping ivory nut buttons
  Grinding barytes
  Wire-stitching
Paper for wrapping crystallized fruit
Phosphor bronze, hard spring quality
Pumice, rough lumps
Quebracho extract
Resin, powdered
Spirit level bubbles as used in clinometers
Steel cylinders for compressed gas
Steel rings, polished, 1 in. diameter
Steel wire for bookbinding
Tinfoil for packing
Ultramarine-blue powder

Firms who may be in a position to supply any of the above articles are asked to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.—A.

## POTASH DEPOSITS IN SPAIN

Extensive deposits of sulfate and carbonate of potassium are reported to have been discovered at Cordova. A Belgian company paid £20,000 for an option on the bulk of the deposits

and has now taken over all the land on which it had an option. Sinking operations to determine the extent and commercial value of the deposits are still being carried on, however, and the deposits are, so far, not being worked as a commercial success, being hardly out of the experimental stage.—A.

## CHINA CLAY

The export of China clay from Cornwall has been prohibited except to British possessions or protectorates, but supplies will be allowed under licenses granted by the War Office Department. It is feared, however, that licenses will not be granted very easily and difficulty may arise in Cornwall from which about 60 per cent of the clay exported goes to the United States. Representations are being made to the British Government that the export trade in China clay with the United States should be continued as what is sent there is so used that there is little chance of it finding its way into the hands of the enemy. —A. McMillan.

## PRODUCTION OF ZINC

According to the *Chemical News*, the Swansea Vale Spelter and Zinc Smelting Works, Wales, which were built and until recently controlled by Germans, have now been taken over and will henceforth be under the control of an entirely English group, with the consent and approval of the British Government. The works, which have been erected upon the most modern principles, are likely to be enlarged on an extensive scale and the development of the zinc ore deposits of Great Britain is likely to be encouraged. The head of the group is Mr. R. Tilden Smith, who is associated with many important enterprises of the kind, including the zinc mines of Burma from which he intends to obtain supplies of metal. The plant is exactly similar to those which have been erected in Germany, Belgium and France, and was part of the organization which enabled the owners to dominate the zinc market of Europe.—M.

## CONCRETE PLUGS IN MINES

Concrete plugs have been used by the Warwickshire Coal Company at their colliery at Keresley, near Coventry, England, in order to stop the inrush of water and as a result of the treatment in one shaft practically no water is being met with instead of 2,600 gal. per minute before applying this treatment. A concrete plug 20 feet thick was placed at the bottom of each shaft which cut off completely the water and allowed boring (twelve holes in each shaft) for the injection of cement from the bottom of the shafts.—M.

## TUNGSTEN MARKET IN GREAT BRITAIN

According to the *Engineer* the British-made tungsten powder market is being well supplied from various sources. The element tungsten is recovered from Wolfram ore, well nigh inexhaustible supplies of which are available within the British Empire. In order that these ore reserves may be better handled, the Government has assumed control of them and now it is understood that it has decided to control the tungsten supplies. One of the first evidences of this is seen in the regulation of values. After the outbreak of war the price quoted was about four times the price of pre-war days. It appears that under the Government scheme the market is fixed at $1.24 per lb. for tungsten powder and 4 cents less for ferro-tungsten. In some quarters, exception is taken to this arrangement, but if the scheme gets into working order, high-speed steel makers should benefit considerably.—M.

## THE NEED FOR PETROL SUBSTITUTES

Professor Vivian B. Lewes, lecturing recently at the Royal Society of Arts, London, stated that the need of petrol substitutes lay principally in the fact that in the next, say 50 years, the natural supplies would be diminished to such an extent that the depth from which the oil would have to be obtained would render them practically commercially unavailable. The world's total output of crude oil, which in 1914 amounted to 97 million tons, had, he said, increased at an annual rate of only 6 per cent for the past three years and the amount of petrol obtainable from the crude oil could be put at only 10 per cent. America itself used no less than 1,200,000,000 out of the world's 1,700,000,000 gallons and England in 1914 imported 120,000,000 gallons, making a total of 1,320,000,000 gallons, leaving only 380,000,000 gallons for the remainder of the world.—M.

## HARDENED FILTER PAPER

Writing in the *Pharmaceutical Journal* on a process for toughening ordinary filter paper, Mr. W. R. Rankin states that a substitute for the smooth, hardened filter paper of German make may be prepared by dipping the best English filter paper very quickly in nitric acid (sp. gr. 1.4), draining and washing in running water until most of the acid is removed. The remainder is neutralized by immersion in 0.5 per cent ammonia solution. The paper is afterwards washed thoroughly, pressed and dried at 100° C. When dry, the paper is subjected to the same treatment. Excessive temperatures should be avoided in drying, as the cellulose is nitrated to some extent. A shrinkage of about 10 per cent should be allowed for. An inferior substitute may be got in a single operation by dipping filter paper in a mixture of 65 parts sulfuric acid (sp. gr. 1.84) and 35 parts nitric acid (sp. gr. 1.42).—M.

## BORNEOL FROM WASTE SULFITE LIQUOR

In a note on the distillation of waste sulfite liquor given in *Papierfabrikant*, the isolation of inactive borneol is described. When methyl alcohol is distilled from waste sulfite liquor, a heavy oil is recovered towards the end of the distillation. This oil contains furfural and, when cooled, deposits small crystals. These are washed and crystallized from petroleum ether. They form large, flaky, translucent crystals which have a camphor-like odor. The results of elementary analysis, the melting point, boiling point and the fact that it forms bornyl chloride on treatment with phosphorus pentachloride, confirm the substance as being inactive borneol.—M.

## THE WORLD'S COAL SUPPLY

A matter of great interest, though not an acute problem at present, is the probable nature and extent of the coal fields yet in reserve and of known locality. According to the 12th International Congress of Geology held at Toronto, close on to 72 billion tons are still available.

| | Anthracite (in million tons) | Common coal (in million tons) | Lignite (in million tons) | Totals |
|---|---|---|---|---|
| America | 22,542 | 2,271,080 | 2,811,906 | 5,105,528 |
| Asia | 407,637 | 760,098 | 111,851 | 1,279,586 |
| Europe | 54,346 | 693,162 | 36,682 | 784,190 |
| Australia | 659 | 133,481 | 36,270 | 170,410 |
| Africa | 11,662 | 45,123 | 1,054 | 57,839 |
| Total | 496,846 | 3,902,944 | 2,997,763 | 7,397,553 |

Naturally it is impossible to claim great accuracy for the above estimates and for years to come we may reasonably expect the discovery of further deposits that will compensate for current consumption.—M.

# NOTES AND CORRESPONDENCE

## NOTE ON "CHEMISTS' PROTECTIVE ASSOCIATION"

*Editor of the Journal of Industrial and Engineering Chemistry:*

The recent proposal [THIS JOURNAL, **7** (1915), 798] to form a "Chemists' Protective Association" seems to call for discussion.

In the first place, as a loyal and interested member of the American Chemical Society, the present writer feels that this Society *is* intensely practical in that membership in it tends to increase the efficiency of its members as chemists.

Any organization which has this effect is bound to react favorably upon those responsive to such influences, and this reaction will ultimately find expression in a fatter pay envelope, if we wish to look at that aspect of increased efficiency, apart from all other considerations.

In the second place, any attempt to define a "chemist" as a person having "spent four or more years at an accredited technical school or University in the didactic and laboratory study of all the regular branches of chemistry, and who has received formal statements represented by a degree or degrees that the prescribed courses of study have been satisfactorily completed," will justly be doomed to sure and certain failure. There are many men who have had all the advantages of technical training but who are lacking in the essentials of interest, clear-headedness and broad-mindedness. Such men, it is needless to say, will never be successful chemists. On the other hand, many so-called "quasi chemists" and "laboratory boys," in the proper surroundings, may develop into very competent and efficient workers. Men of this type, with a little encouragement, succeed in spite of a lack of technical training.

In the third place, the proposed salary scale based on a classification of chemists as "Assistant Chemists" and "Chief Chemists" is artificial, academic, and impractical. Most chemical work in a technical laboratory naturally falls into one of the following classes: (*a*) analytical and control; (*b*) factory development; (*c*) fundamental research. A given piece of work may overlap the boundaries of two or even all three of the above divisions. It also happens that the aptitude of different men for different classes of work is different so that some men make good research men, but would be dismal failures in developing processes on a commercial scale, or in analytical work. The training a man has had, of course, plays a large part in making him fit or unfit to do a given class of work, but the native ability of the man himself, his enthusiasm, his "chemical instinct" and "optimistic activity," or lack of these qualities, must surely be considered in placing men in laboratories and in their subsequent advancement.

Looking at this same subject from another point of view, it so happens that, in different laboratories, the relative importance of the above classes of chemical work may differ. Thus, one company may require but little research work and a great deal of analytical and control work; or a great deal of factory development work may be necessary to put into practical operation the results of some fundamental research. Now, this question of the class of work required in any one instance, the native ability of a man and his attitude toward his work are all inseparably connected with his advancement. Of these, his ability to take on added responsibility; to grow and become more efficient; the proper receptive attitude which enables him to apperceive new ideas and meet new conditions, are of the greatest importance, in determining his salary. If he is capable of doing low-grade routine work, and nothing else, it is but right that he should receive a low salary; for, the lower the grade of work required, the easier it is to train an ordinary boy to do the work. In all laboratories that the writer knows of, there is considerable routine work which is easily mastered by any boy of average intelligence and no trained man should be foolish enough to waste his time doing such work; if such a chemist should be found he could rest assured that the business man would pay him no more than he would pay the laboratory boy, because he would be worth no more.

On the other hand, some of the so-called "laboratory boys" or "quasi chemists" happen to be above the ordinary in intelligence and men of this sort will rise and justly so.

It seems to the present writer that these questions of the definition of "chemist," the classification of chemists, and the salaries they are to receive, should be, and are generally in actual experience, answered on the basis of the efficiency of the individual worker: $1200.00 per year is too much to pay to an inefficient chemist who lacks interest and enthusiasm in his work and whose growth is at a standstill; $5000.00 per year is too low a limit to place for an active, energetic and growing head of a laboratory. In fact, why place any limits in either direction?

In conclusion, the writer feels that any proposal to form a "Chemists' Protective Association" should be most emphatically opposed by all chemical workers and chemically trained men who have the real interests of the chemical profession at heart.

CLEVELAND, OHIO — WILLIAM C. MOORE

## ON GERMICIDAL EFFICIENCY OF DENTAL CEMENTS

*Editor of the Journal of Industrial and Engineering Chemistry:*

A letter written by W. V-B. Ames, representing the W. V-B. Ames Company, referring to my paper on "The Germicidal Efficiency of Dental Cements" (THIS JOURNAL, **7**, 195), appeared in THIS JOURNAL, **7**, 723.

In the first paragraph Ames misquotes from my article as shown by comparing the following excerpts:

From Ames' letter—THIS JOURNAL, August, 1915:

In THIS JOURNAL, March, 1915, appeared an article by Paul Poetschke, entitled "The Germicidal Efficiency of Dental Cements." The concluding paragraph promised reports on the comparative strength and other properties. These reports would be, as Mr. Poetschke states, "of more immediate interest to the dental profession," and it will be by clinical experience in the hands of the dentist that the subject will receive its final analysis and probably be reported mainly in the dental literature.

From "The Germicidal Efficiency of Dental Cements" by Paul Poetschke, THIS JOURNAL, March, 1915.

FROM INTRODUCTION

"It is possible to measure the germicidal efficiency of material of this character in precisely the same way as it is possible to measure the germicidal efficiency of disinfectants. It is therefore obvious, especially in view of the varied composition of these cements, that a thorough investigation of this subject is of immediate interest to the dental profession, as well as to chemists and bacteriologists who may be called upon to report on the germicidal power of dental cements. The object of this paper is to show the comparative germicidal power of these cements, and also some of the compounds used in their production."

FROM CONCLUSIONS:

"The germicidal efficiency of a dental cement is merely one of the properties which are of importance. Many other physical properties such as resistance to saliva, hardness, crushing strength, constancy of volume, etc., are also of importance. The relation of the germicidal efficiency to these other properties is being investigated in this laboratory, and the results will be published in future papers."

The exact quotations from Ames' letter and my article are given because of the evident intention of Ames to minimize the importance of this investigation to the dental profession. As far as the clinical significance of these bacteriological tests is concerned, one can hardly fail to appreciate that a copper

cement is used primarily on account of its germicidal properties. Therefore, such tests must be relied upon to secure first-hand evidence in this direction. In surgical practice the carbolic coefficient of a disinfectant is accepted as a reliable criterion of its efficiency, and likewise the germicidal efficiency of a copper cement can be accepted as a reliable indication of its clinical efficiency.

In connection with this letter Ames reproduces an illustration which he says is "the one illustration criticized by Mr. Poetschke, the criticism being mostly that only comparative inhibition has been shown and that there had been no bacterial count." Here again, Ames attempts to minimize the criticism which I made of his paper. This illustration was the only one which appeared in Ames' paper, and therefore the only one which was open for consideration. However, reference to my article will show that every statement made by Ames, bearing directly on the subject of germicidal properties, was fully quoted and criticized in my paper.

A copper cement exerts its germicidal effect in two distinct stages, that is, both in "plastic" and "set" condition. It thus exerts an initial sterilizing influence when inserted and a permanent germicidal influence after it is set. The initial sterilizing influence is not of much importance because the local application of a liquid disinfectant would accomplish the same purpose. The permanent germicidal action of the cement in the set condition is the main desideratum. Ames apparently fails to appreciate these facts in referring to "a cavity from which all infected material had not been removed, there being, for this reason, a need of a sterilizing filling."

Ames further states in his letter: "It is well known by the dental profession that a real copper oxid cement will furnish the means of sterilizing of such an infected area, and yet furnish a mass, after proper setting, which is so highly insoluble that it would show potency only in the hardened state equal to the best of the so-called copper cements tested by Mr. Poetschke, including that made by the L. D. Caulk Co., the employers of Mr. Poetschke." In this statement Ames intends to create the impression that the dental profession accepts and knows these statements to be facts, when as a matter of fact, the dental profession does not know or accept these statements. Nowhere in the dental literature does any authoritative statement or proof appear which substantiates this assertion. Ames insinuates that the black copper cement of his manufacture, which is referred to in the illustration, is not more highly germicidal in the hardened state, because of its "highly insoluble" character. My experimental data, which I shall shortly publish, shows that this black copper cement, made by Ames and referred to as so "highly insoluble," suffers the greatest relative loss in strength in saliva of twelve copper cements which are on the market to-day with but one exception, and that is also a black copper cement. Ames has attempted to claim the authority of the dental profession for a statement which has absolutely no basis in fact.

The ambiguous statements made by Ames regarding the "cement-making property of the cuprous and cupric oxids" have absolutely no relation to the subject under discussion, because a copper cement need not contain cuprous or cupric oxides in order to possess the requisite germicidal power, strength, resistance to saliva, or any of the properties demanded of a copper cement. It is immaterial whether a copper cement contains cuprous or cupric oxide, but it must contain some compound of copper which in itself has sufficient germicidal power to secure the required germicidal efficiency in the finished cement. Of course, it is understood that any copper cement must have, in addition to germicidal power, secured by the addition of a potent compound of copper, all of the other physical and chemical properties demanded of a product of this character. My investigations, which will be published shortly, show that cuprous and cupric oxides need not be depended upon for any cement-making property which they may possess, and their elimination from copper cements, as Ames infers, is greatly desired by the dental profession, because of the limitation imposed on copper cements containing cuprous and cupric oxides on account of their color.

Ames refers to a "difference in germicidal efficiency between a real copper oxid cement and an oxyphosphate of zinc cement, more or less modified by a copper compound, each in the freshly mixed state" as being "so great that results may be shown which appeal to the naked eye instead of needing microscopical count." I have referred at length, in my paper, to the fallacy of testing a dental cement for its germicidal efficiency in the "freshly mixed state," and I wish to emphasize the statement contained in my original article, namely, that the tests employed by Ames failed to give any information concerning the germicidal efficiency of a dental cement. I fail to understand Ames' reference to "microscopical count" except to assume that Ames does not know that the colonies of bacteria are not counted by the aid of the microscope, but by the naked eye.

In the last paragraph of his letter Ames describes his illustration in part by stating, "No. 2, a zinc oxid cement carrying a small percentage of oxid of mercury (yellow)," whereas his original paper read, "No. 2, oxyphosphate of zinc containing a small percentage of mercurous iodid." This certainly cannot be a typographical error and it is needless for me to call attention to the radically different character of these two compounds of mercury. This does not inspire confidence in the illustration. Ames states that this illustration shows "inhibition of bacterial growth" and that the "inoculation was overwhelming," yet reference to the illustration fails to show a single colony of bacteria, notwithstanding the fact that it is supposed to depict an inoculated Petri dish. The illustration is plainly not a photograph and naturally cannot be accepted as showing "inhibition of bacterial growth." Even if it did show what is intended, the test is of no value as regard establishing germicidal efficiency of the material.

In conclusion, I wish to point out that Ames does not present a single criticism of my article but merely repeats and adds to the statements contained in his article which I fully criticized as being of pseudo-scientific character. In this letter additional erroneous statements and conclusions are presented by Ames which have no basis in fact and are unsupported by any evidence whatever. The illustration presented is not worthy of consideration, because it does not show "inhibition of bacterial growth," and further, the description does not agree with Ames' original article.

PAUL POETSCHKE, *Director*

DEPARTMENT OF CHEMISTRY, THE L. D. CAULK CO.
MILFORD, DELAWARE, AUGUST 26, 1915

## THE "PURE FOOD LAW"

*Editor of the Journal of Industrial and Engineering Chemistry:*

For the past nine years it has been of profound interest to follow the prosecutions under the "Pure Food Laws." Being of an analytical mind I carefully went into the fundamental conceptions of the law, its rigid legal and logical interpretation, its effect upon commerce, international and interstate, and finally I examined the details of the administration of this, and attempted to ascertain, as nearly as possible, whether justice or injustice had been inflicted on those who had come into contact with the law as defendants in criminal prosecutions brought by the government.

My conclusions, after the nine years of investigation, are that in many cases the defendants pleaded guilty to the charges brought against them, although they were neither *legally* nor *morally* guilty, merely to escape the annoyance of a trial, always distasteful to busy and enterprising men of affairs.

To confirm my conclusions, I shall give a strict legal interpretation of the law in such particulars as are of essential importance for the views advanced above.

Section 3 of the law *does not* confer legislative power on the three secretaries—

Purely executive powers are conferred, and therefore the rules and regulations of the Bureau of Chemistry are of a similar nature, as rules and regulations enacted by the district attorney of New York County for the purpose of administering the *executive* functions of his office.

The legal reasoning is clear, for Congress cannot delegate *its legislative* powers to any other body. Notwithstanding the efforts of certain editorial writers on various trade journals, no decision of the Supreme Court exists which contradicts this statement: Congress cannot delegate its legislative powers.

The second point I wish to make is the definition of the word, Drug.

Many definitions for various purposes may be found but for the enforcement of the "Pure Food Law" only the definition given by that law may be used. It has surprised me how rarely, if at all, courts have attempted to dwell on this point. Section 6 of the law reads: That the term Drug "as used in this Act shall include all medicines and preparations recognized in the United States Pharmacopeia or National Formulary for internal and external use, and any substance or mixture of substances intended to be used for the cure, mitigation, or prevention of disease of either man or other animal."

Let us examine this definition. The phrase, "all medicines and preparations *recognized* by the United States Pharmacopeia or National Formulary for internal or external use" requires that the prosecution must prove

1—That it is medicine or preparation.

2—That said medicine or preparation is *recognized* by the United States Pharmacopeia.

3—That it is so recognized for internal or external use.

What a medicine or preparation is the law does not say, and that question is, therefore, a question of fact for the jury and not a question of legal definition.

But whatever a medicine or preparation is, it must be such as is *recognized* by the United States Pharmacopeia or National Formulary.

Now examining the history of pharmacopeia for the last two centuries throughout all parts of the world, it must be agreed upon that no pharmacopeia recognizes any commodity that does not comply with its tests or definitions.

Therefore, an article of commerce that does not comply with such tests or definitions cannot be defined as a drug under that part of the laws, phraseology as stated above.

Furthermore, such medicines and preparations must be recognized for internal or external use. There are many substances in the U. S. P. *not* recognized for internal or external use. Clearly, then, if an article of commerce does not come under the phrase, of the laws' definition, as stated above, we may proceed and examine the definition as it continues: "And any substance or mixture of substances intended to be used for the cure, mitigation or prevention of disease of either man or animal."

We note the words "intended to be used," and also the words, "for the cure, mitigation or prevention of disease."

A mere intent to be proven by the circumstances of each particular case is all that is necessary, but it must be a direct intent; of indirect intent the law takes no notice.

Furthermore, it must be for the *cure, mitigation* or *prevention* of *disease*. Therefore, articles of commerce used or intended to be used for manufacturing, even though the products resulting from such manufacture are substances intended to be used as a cure, mitigation or prevention of disease, do not come under the law. I call particular attention to this fact, because the administration and enforcement of the law has not always been conforming to this legal conclusion, especially in cases of importations of articles of commerce into United States.

Finally, Section 11 of the law deserves some notice. The notice has gone abroad as evidenced by numerous communications on the subject, that executive officers have absolute legislative and executive powers to exclude goods offered to be imported into this country, that there is no legal remedy for any wrongful acts on the part of such executive officers.

Let me say that the writ of injunction still exists, and that it is applicable where "there is no adequate remedy at law," a statement that should be considered where an executive officer is about to usurp legislative functions.

1221 LINCOLN PLACE, BROOKLYN, N. Y. LOUIS HOGREFE
September 3, 1915

## PAPER REAGENT

Some time ago the writer noticed the following article in a drug journal, the name of which he does not at present recall: "Detection of Wood Pulp in Paper:

"The *Repertoire de Pharmacie* republishes from the *Bulletin de la Société de Chemie Belge* a reagent for the detection of wood pulp in paper. It consists of paranitroaniline, 20 cgm., dissolved in 80 cm. distilled water and sulfuric acid, sp. gr. 1.767: 20 milligrams. This has the advantage over the alcoholic solution of phloroglucin and hydrochloric acid in that it may be kept for years. It is also preferable to anilin sulfate, which, although it is stable, gives with wood pulp a yellow color, which is not easily distinguished by artificial light. The paranitroaniline colors wood pulp orange to brick-red, and it can be seen under any mode of illumination. The reagent has the further advantage of yielding a color to unbleached cellulose."

The writer made up this reagent and tested different papers and pulps with the following results:

1—Mechanical wood-pulp ⟶ dull orange to orange.
2—Unbleached sulfite pulp ⟶ very similar to above.
3—Bleached sulfite pulp ⟶ yellow

The writer found that the distinction between the mechanical wood pulp and the unbleached sulfite pulp was not very marked and proved rather troublesome when testing unknown pulps.

The writer has discovered, however, a method whereby the detection is made plainer. He used the above reagent in conjunction with ammonium molybdate solution and obtained the following results:

1—Mechanical wood-pulp ⟶ bright reddish orange.
2—Unbleached sulfite pulp ⟶ dull orange, faint; or faint brown.
3—Bleached sulfite pulp ⟶ colorless.

By experiment it was found that when the ammonium molybdate is applied first and then the paranitroaniline, better results are obtained. Also, on waiting for one or two minutes, the reaction is complete and the distinction is then very sharp.

The above certainly seems to be an excellent test for distinguishing paper pulps, and could no doubt be applied to certain other substances as a test for presence of lignin.

NATIONAL CLOAK & SUIT CO. WM. J. SCHEPP
NEW YORK CITY *Chief Chemist and Textile Expert*
September 28, 1915

## THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH

The new professional School of Chemistry of the University of Pittsburgh began its work on September 27, 1915, under the deanship of Dr. Raymond Foss Bacon, Director of the Mellon Institute of Industrial Research. A prescribed four-year undergraduate curriculum leads to the degree of Bachelor of Chemistry; the staff of instruction includes the regular faculty of the University and fellows from the Mellon Institute of Industrial Research who are especially qualified in various theoretical

and technical branches. This combination gives the new school the opportunity to offer not only the usual undergraduate and graduate courses in chemistry and technology, but also specialized work under men who are experts in specific American industries. In addition, thirty special lectures by prominent chemists and technologists in the Pittsburgh district have been arranged for the academic year 1915–16. Attendance at these lectures is required of the student body but they are also open to the public.

The professorate of the new school is constituted as follows: Alexander Silverman, M.S., Professor of Chemistry and Head of the Department of Inorganic, Analytical and Physical Chemistry; David S. Pratt, Ph.D., Professor of Chemistry and Head of the Department of Organic, Sanitary, and Micro-chemistry; Samuel R. Scholes, Ph.D., E. Ward Tillotson, Jr., Ph.D., and Edmund O. Rhodes, M.S., Professors of Applied Chemistry; Benjamin T. Brooks, Ph.D., Professor of Chemical Engineering; William A. Hamor, M.A., Professor of Chemistry; Henry A. Kohman, Ph.D., and Harold Hibbert, Sc.D., Professors of Applied Organic Chemistry; Leonard M. Liddle, Ph.D., and R. Phillips Rose, M.S., Professors of Organic Chemistry; Lester A. Pratt, Ph.D., Professor of Inorganic Chemistry; and C. C. Vogt, Ph.D., Professor of Physical Chemistry. Thirteen assistant professors and ten instructors complete the teaching staff of the school.

## NOTE ON ARTIFICIAL ZEOLITE—PERMUTITE

*Editor of the Journal of Industrial and Engineering Chemistry:*

Having just returned from an extensive tour through Cuba and the Eastern States, I find, on looking through the past numbers of the Journal, in the March number of this year, on page 325, a communication by Mr. Stephen Kocsor: "Preliminary Note on Artificial Zeolite—Permutite."

This note is interesting to me for the reason that for the last two and one-half years I have been, and am still, working along identical lines while Research Chemist of the Kieselguhr Company of America, Van Nuys Building, Los Angeles, California.

During my travels I have freely discussed the results obtained with zeolites thus produced, with a great number of sugar and other chemists whom I have visited professionally during this time.

968 West 42nd Place
Los Angeles, Cal., July 15, 1915

F. R. Bachler

# PERSONAL NOTES

Prof. Julius Stieglitz has been made chairman of the department of chemistry of the University of Chicago to succeed the late Prof. John Ulric Nef.

The One Hundredth Meeting of the Syracuse Section of the A. C. S. was in the form of a banquet held on the evening of October 23rd, at "The Onondaga," Syracuse.

The positions left vacant in the chemical department of Syracuse University by the resignations of Dr. E. H. Archibald and Dr. C. R. Hoover have been filled by Dr. Charles Warren Hill and Prof. Merritt R. Grose.

The October Meeting of the St. Louis Section of the A. C. S. was held on the 11th, with the following program: "The Industrial Utilization of Peat," by Mr. H. E. Wiedemann; "An Apparatus for the Determination of the Degree of Fineness of Paint Pigments," by Mr. E. J. Sheppard, of the National Lead Company.

The American Cyanamid Company announces the opening of its general offices at 200 Fifth Avenue, New York City, on October 1, 1915. The Nashville and Buffalo offices were discontinued on that date.

W. A. Gibb Maitland, Government Geologist and Director of the Geological Survey, Western Australia, has been appointed President of the Royal Society of Western Australia for the Session 1915–1916.

A $500,000 electrochemical plant will be built at Niagara Falls by the E. I. du Pont de Nemours Powder Company, of Wilmington, Del.

The former students of Prof. C. E. A. Winslow have given a dinner in his honor on the occasion of his entrance into his new position of professor of public health at Yale University.

Dr. Walter D. Bonner, formerly assistant professor of chemistry in the School of Mining in Queen's University, has recently been appointed Head of the Department of Chemistry in the University of Utah.

The British Association held its annual series of meetings at Manchester at the beginning of September. The inaugural address entitled "The Common Aims of Science and Humanity" was delivered by the President, Professor Arthur Schuster

Dr. H. H. McGregor, formerly instructor in chemistry in Adelbert College, and recently appointed instructor in biochemistry at the medical school of Western Reserve University, has died of typhoid fever in Toronto, Canada.

Charles Hallet Wing died on September 13th in his eightieth year. In 1870 he became professor of chemistry in Cornell University, from which place he went in 1874 to Boston to accept a like position at the Massachusetts Institute of Technology, where he remained for ten years.

Advance notice has been received of the Joint Meeting of the New York Sections of the American Electrochemical Society and the Illuminating Engineering Society, to be held on Nov. 11, 1915 at the United Engineering Societies Building. The subject for the evening is, "Electrical Phenomena in Vapors and Gases." The following papers will be read: "Unstable States in Arc and Glow," by Walter G. Cady, Wesleyan University; "Gaseous Conductor Light," by D. McFarlan Moore, Edison Lamp Works; "Electric Arc in Complex Vapors," by W. A. Darrah, Mansfield, Ohio. The papers will be illustrated by experiments and lantern slides.

It has been decided that the next meeting of the American Electrochemical Society will be in the Spring in Washington, D. C., with the subject of *Electrochemical Research* as a special order of discussion.

Mr. Lincoln Burrows spoke on "Glycerine" before the October 18th Meeting of the Rochester Section of the A. C. S.

Prof. Albert Victor Bleininger, who has been in charge of the Ceramic Section of the U. S. Bureau of Standards at Pittsburgh since 1912, has been appointed Professor and Head of the Department of Ceramic Engineering of the College of Engineering of the University of Illinois.

The winter meeting of the American Institute of Chemical Engineers will be held in Baltimore, Md., January 12–15, 1916. A number of papers on recent and important developments in some of the chemical industries of the United States are being arranged for. Excursions will be made to a number of the important chemical industries, of which Baltimore is the center. The experimental laboratories of the Johns Hopkins University and the Naval Academy at Annapolis, Md., will be visited.

The following appointments have been made to the faculty of Case School of Applied Science: Melville F. Coolbaugh, South Dakota School of Mines, assistant professor of chemistry; Lawrence G. Wesson, Harvard University, instructor in organic

chemistry; Carl H. Wilson, Harvard University, instructor in chemistry.

Mr. William Roy Mott, of the National Carbon Company, addressed the Cleveland Section of the A. C. S. on "The Use of the Flaming Arc in Paint and Dye Testing," on October 11th.

The October Meeting of the Pittsburgh Section of the A. C. S. was held jointly with the American Electrochemical Society on October 21st. Mr. F. T. Snyder, of the Snyder Electric Furnace Company, Chicago, presented a paper on "Electric Furnaces for High Temperature Industrial Chemical Work."

Dr. Edward Bartow, University of Illinois, spoke on "The Purification of Sewage by Aeration in the Presence of Activated Sludge," before the Chicago Section of the A. C. S., on October 15th. The regular November meeting of the Section will be held on November 12th.

The Bausch & Lomb Optical Company received, at the Panama-Pacific Exposition, four Grand Prix on optical instruments, balopticons, engineering instruments and range finders. The first division, called optical instruments, is comprised of seven classes and covers the company's ophthalmic lenses, microscopes, parabolic and mangin mirrors, field glasses, microtomes and magnifiers. A Medal of Honor was awarded Bausch & Lomb photomicrographic apparatus. Bausch & Lomb-Zeiss photographic lenses received the Gold Medal.

Dr. Frank K. Cameron, of Washington, has severed his connection with the United States Bureau of Soils in order to devote his time exclusively to consulting practice, especially in the field of fertilizers and soil chemistry.

In addition to the regular November Meeting of the Philadelphia Section of the A. C. S., a special joint meeting with the Franklin Institute will be held on November 4th. The program will consist of an illustrated lecture on "The Turpentine Industry in the Southern States," by Dr. Charles H. Herty, President of the American Chemical Society.

Mr. Phillip J. Krell will manage the new plant of the International Oxygen Company now being erected at Verona, Pa. (Pittsburgh district), for the accommodation of its customers in that vicinity.

Dr. Frank K. Cameron gave an illustrated lecture on "The Development of a Dynamic Theory of Soil Fertility," before a joint meeting of the Philadelphia Section of the A. C. S. with the Franklin Institute on October 28th.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

## GEOLOGICAL SURVEY

**Contributions to Economic Geology, 1913. Part II. Mineral Fuels.** Marius R. Campbell and David White. This volume is one of the regular series published annually, being made up of six distinct papers. "The papers included are of two classes: (1) short papers giving comparatively detailed descriptions of occurrences that have economic interest but are not of sufficient importance to warrant a more extended description; (2) preliminary reports on economic investigations, the results of which are to be published later in more detailed form. These papers are such only as have a direct economic bearing, all topics of purely scientific interest being excluded."

The following papers make up the volume:

**Oil Shale of Northwestern Colorado and Northeastern Utah.** E. G. Woodruff and D. T. Day. 23 pp.

**Oil and Gas in the Western Part of the Olympic Peninsula, Washington.** C. T. Lupton. 60 pp.

**The Moorcroft Oil Field, Crook County, Wyoming.** V. H Barnett. 22 pp.

**Possibilities of Oil in the Big Muddy Dome, Converse and Natrona Counties, Wyoming.** V H Barnett. 14 pp.

**Geology and Oil Prospects in Waltham, Priest, Bitterwater, and Peachtree Valleys, California.** R. W. Pack and W. A. English. 42 pp.

**The Coalville Coal Field, Utah.** C. H. Wegermann. 24 pp.

**Analyses of Rocks and Minerals, from the Laboratory of the United States Geological Survey, 1880–1914.** F. W. Clarke. 370 pp. This bulletin summarizes and tabulates approximately 2800 analyses of rocks, clays, soils, meteorites, minerals, etc. The data are arranged principally under the heading of the geographical source of the rock or mineral, thus giving for the various localities the characteristic analyses which have been found by determinations in the Survey's laboratories.

**Nitrate Deposits in Southern Idaho and Eastern Oregon.** G. R. Mansfield. Bulletin 620–B. This is an advance publication of one of the contributions to Economic Geology, 1915. Part I.

The article describes the deposits of nitrate which have recently been discovered and discusses the origin, extent, volume, and utilization of these nitrates. Although the author urges further investigation in the hope that a commercially valuable deposit may be found, he does not consider the outlook very promising at the present time.

**Field Apparatus for Determining Ash in Coal.** C. E. Lesher. Bulletin 621–A. 12 pp. An illustrated description with operating directions are given for a form of portable apparatus which has been designed to meet the needs of field parties of the Geological Survey and which has been in successful use for three years.

**Resins in Paleozoic Plants and in Coals of High Rank.** David White. Professional Paper 85–E. 32 pp. "This paper presents evidence that anthracite and bituminous coals, as well as those of lower rank, originated as peats, and that the plants from which the Paleozoic coals were formed were in part resin-bearing—in fact, the resin-bearing elements in the coal-forming floras of the Carboniferous period, to which the bituminous and high-rank coals of most parts of the world belong, are perhaps as numerous as in the floras from which the coals of later epochs were formed. The author points out the general prominence of resins in the Mesozoic and Tertiary coals of low bituminous and inferior ranks and contributes observations as to the disappearance of these coals in the course of carbonization under regional metamorphism, the resins disappearing at about the stage of carbonization at which the coking quality of the coals is well developed. After reviewing the evidence as to resin and gum secretion in the petrified fragments of Paleozoic plants described by several paleobotanists, he describes, with illustrations of both common and unique materials, the presence of abundant resinous matter in Paleozoic coals of medium bituminous or lower ranks."

**The Fauna of the Batesville Sandstone of Northern Arkansas.** G H Girty Bulletin 593 170 pp., 11 plates

**Geology and Mineral Deposits of the National Mining Dis-**

**trict, Nevada.** WALDEMAR LINDGREN. Bulletin 601. 58 pp., 8 plates, 8 text figures.

SMITHSONIAN INSTITUTION

The following reprints from the 1914 Report of the Smithsonian Institution are now available:

**Modern Views on Constitution of the Atom.** A. S. EVE. Publication 2326. 9 pp.

**Examination of Chinese Bronzes.** JOHN C. FERGUSON. Publication 2347. 6 pp.

**Form and Constitution of the Earth.** LOUIS B. STEWART. Publication 2324. 6 pp.

**Explosives.** EDWARD P. O'HERN. Publication 2331. 26 pp.

**Some Aspects of Industrial Chemistry.** L. H. BAEKELAND. Publication 2330. 25 pp.

**Recent Developments in the Art of Illumination.** PRESTON S. MILLAR. Publication 2350. 18 pp.

DEPARTMENT OF AGRICULTURE

**Prickly-Pears as a Feed for Dairy Cows.** T. E. WOODWARD, W. F. TURNER AND DAVID GRIFFITHS. Journal of Agricultural Research, **4**, 405–50. This includes a considerable number of analyses of feeding materials tested.

**Phosphorus Metabolism and Lambs Fed a Ration of Alfalfa Hay, Corn, and Linseed Meal.** E. L. ROSS, M. H. KEITH AND H. S. GRINDLEY. Journal of Agricultural Research, **4**, 459–74.

COMMERCE REPORTS—SEPTEMBER, 1915

Owing to shortage of the supply of **wood pulp**, efforts are being made to develop its production in New Zealand. (P. 1090.)

The Australian Government has acquired control of the stock of **sugar.** (P. 1096.)

The British **pottery** industry is suffering from lack of a supply of **bone,** formerly obtained from Argentine. (P. 1115.)

A municipal **gas** works at Akkrum, Holland, is now preparing gas from a mixture of two parts coal and one of **peat.** (P. 1151.)

Australian **zinc** concentrates are now being shipped to Galveston *via* the Panama Canal. (P. 1151.)

A large order for **zinc** for Hongkong has been placed in the United States. (P. 1166.)

Bounties are to be paid upon all **zinc** produced in Canada from Canadian ores. (P. 1169.)

The **sewage disposal** plant of Nottingham, England, is being operated with a profit of several thousand dollars per year. (P. 1204.)

Experiments are being conducted on the Pacific coast upon the use of pulverized **coal** as fuel on steamships. (P. 1209.)

Recent rulings of the Steamboat Inspection Service regarding passenger vessels include:

Loaded **shrapnel shells** may not be carried.

**Hydrochloric acid** is subject to the same conditions as sulfuric acid.

Only non-inflammable, non-combustible, non-explosive **metal polishes** may be carried, or used as stores.

**Tanners' oil** of high flash point may be carried.

**Quicklime,** alone or mixed with magnesia, may not be carried.

**Sesquisulfide of phosphorus,** and **red phosphorus** may be carried in iron drums on deck, while **yellow phosphorus** may not be carried.

Moving picture **films** may be carried under the same conditions as celluloid. (P. 1230.)

Prospecting for **petroleum** is being carried on in Zulia, Venezuela. (P. 1235.)

Efforts to discover a source of mineral **phosphates** in New Zealand have not thus far been successful. (P. 1257.)

The present annual profits of some British **dye works** are nearly 50 per cent of the paid up capital. (P. 1261.)

The Brazilian **piassava** fiber industry is described. (Pp. 1262–3.)

The West Indian **lime-juice** industry also produces **calcium citrate** and oil of limes. (P. 1291.)

**Kapok** or "vegetable wool" obtained from a tree of the genus Eriodendron in Ecuador and the Dutch East Indies is used extensively in the United States for mattresses, etc. (P. 1294.)

Among the various substitutes for **absorbent cotton** now being used in Europe, are "lignin" (made of pine cellulose), "cellulose wadding" (made from chemical wood pulp), "bog moss" (*Sphagnum cymbifolium*). (P. 1306.)

The mineral products of Alberta, Canada, include **gold, coal, natural gas, cement, clay products, lime, sand-lime brick** and **stone.** (P. 1312.)

In New South Wales, Australia, a Patents Investigation Committee has been appointed to assist in the development of inventions likely to be of general public utility. (P. 1323.)

The output of **pig-iron** from Penhsihu, China, has increased, the demand being large since it is low in phosphorus and sulfur. (P. 1325.)

With the increased production of lemons in California, it is soon expected to produce all the **lemon oil** and **citrate of lime** required in this country. (P. 1345.)

The **nitrate** industry of Chili shows marked improvement. (P. 1250.)

The Austrian government has taken over entire control of the **petroleum** industry of Galicia. (P. 1353.)

An old **porcelain** plant in Kiangsi, China, is to be conducted as a national model porcelain factory. (P. 1360.)

The mineral resources of Manchuria include **gold, silver, lead,** and tungsten. (P. 1362.)

The **flax fiber** industry of Canada is being revived. (P. 1366.)

A committee has been appointed to improve the quality of the **copra** produced in the Philippines. (P. 1389.)

A marked increase is noted in the imports of American **drugs** into Hongkong. (P. 1393.)

The price of **Epsom salt** in America has increased from $1.10 to over $5.00 per 100 lbs. (P. 1395.)

A plant is being established in Russia for the manufacture of **tanning extracts** from oak and chestnut bark. (P. 1405.)

The **oil** from the **coyol** palm nut found in Central and tropical South America, has the following constants: Sp. gr. 25° = 0.9136; melting point, 25°; "clouding point," 17°; free acid, 1.69; saponification number, 246.2; iodine number, 25.2; Reichert-Meissl number, 5. The oil would be valuable for food products, but its commercial extraction is not profitable, owing to the difficulty of cracking the nuts. (P. 1407.)

The Netherlands Government has assumed charge of all purchase and import of **fertilizers** into Holland. (P. 1417.)

The Swedish **match** industry is suffering from a lack of suitable asp wood, formerly obtained from Russia. (P. 1423.)

A factory to manufacture **paper** from an aquatic plant is being erected at Maracay, Venezuela. (P. 1435.)

New **gold** deposits have been discovered in Thunder Bay District, Ontario. (P. 1492.)

A marked shortage of photographic chemicals is noted in Nottingham, England. (P. 1497.)

The following special supplements, containing statistics and other information, were issued during September:

| | | |
|---|---|---|
| Germany, Frankfurt 6c | Spain 18d | Turkey 18 |
| Roumania 1 | Bahamas 19 | China, Hankow 25 |
| | Martinique 28d | Samoa 63d |

# BOOK REVIEWS

**An Introduction to the Study of Physical Metallurgy.** By WALTER ROSENBAIN, B.A., D.Sc., F.R.S. D. Van Nostrand Co. 6 × 9. 390 pp., illustrated. Price, $3.50 net.

This book is divided into two parts, the first section dealing with the structure and constitution of metals and alloys, the second with the properties of metals as related to their structure and constitution.

Taking up first of all the microscopic examination of metals, the author discusses the preparation of specimens, and the microscope used, then the microstructure of pure metals and alloys. This is followed by the thermal study of metals and alloys, the thermal diagram and its relation to the physical properties. Typical alloy systems are exemplified by the lead-antimony, lead-tin, zinc-aluminum, zinc-copper, tin-copper and certain ternary alloys, followed by the iron–carbon system.

The second part reviews the mechanical testing of metals, the effect of strain on the structure, heat treatment, mechanical treatment and casting, and ends with a discussion of defects and failures.

To review the contents of this book thoroughly would take many pages, because the author has covered the broad field of metallography so thoroughly and so well. This is particularly true of the presentation of the comparatively new ideas on the structure of metals, the effects of strain and of annealing, developed from Beilby's Amorphous Metal Theory. The elongation of the crystals when strained, the production of slip-bands and their nature, the formation of amorphous layers and the hardening of metals by cold work, twin structure, fracture under tensile, shock and alternating stress conditions, and the amorphous cement theory are all most clearly set forth. The criticisms therefore must be on minor points and not on the broad lines of the book.

For example, on page 13, after mentioning the names of the earlier workers, Sorby, Martens, Osmond, Werth, Grenet, Charpy, LeChatelier, Heyn, Wust, Tammann, Andrews, Arnold, Roberts-Austin, Stead, Howe and Sauveur, the author says: "The fact that the present author was privileged to count Roberts-Austen and Osmond among his personal friends and that Arnold and Stead are still actively at work in this field, serves to show how very recent the whole development has been." Besides Arnold and Stead, many of those mentioned are "still actively at work" as current literature in the metallographic field amply proves.

On page 21, in describing the preparation of specimens for polishing, "the necessity of gripping the specimen in the vise" to file, is mentioned. Most people grip the file in the vise and rub the surface of the specimen on it.

On page 31, the reference to etching reagents is too short and might with advantage be expanded.

On page 162, as Ruff's work is mentioned, reference ought also be made to that of Wittorf and of Hanemann.

The photomicrographs are all well chosen and excellently executed, but lose somewhat in not having a title beneath each, rather than having it given only in the list of plates.

In conclusion, the only changes that could be suggested is in the section on the thermal diagram which should contain those diagrams showing partial solubility in the liquid state. A short classification according to solubility in both liquid solid states would help.

The author has succeeded in preparing an excellent book, interesting to the student, valuable to the metallurgist and engineer, and full of ideas for anyone engaged in metallographic research. It is a book that can be recommended to the general reader also, because the style is simple and the ideas are clearly and logically developed and followed. With the growing interest in metallography as a method of testing it will undoubtedly prove very popular.

W. CAMPBELL

**The Chemistry and Technology of Printing Inks.** By NORMAN UNDERWOOD AND THOMAS V. SULLIVAN. New York: D. Van Nostrand Co. 139 pages, 9 illustrations. Price, $3.00 net.

Messrs. Underwood and Sullivan have charge of the Ink-making Division, Bureau of Engraving and Printing, United States Treasury Department, Washington, D. C. This book is an attempt "to give in a brief and practical but yet scientifically correct manner the many facts concerning the raw materials and finished products, used in this industry which they (*i. e.*, the authors) have collected during a number of years of laboratory work and manufacturing experience."

The introduction gives an excellent explanation of the meaning of the many technical terms used. The authors venture the assertion: "A general chemical analysis will not, however, convey any idea of the essential composition of the ink." This is wholly in accord with the opinions of those connected with this industry.

Part I, pp. 15–38, discusses laboratory apparatus, methods of analysis of raw materials and the physical testing of pigments.

In Part II, the manufacture of the various classes of ink-making materials, such as dry colors, oils, etc., is described in detail. The properties of each of these substances as ink-making materials are given very conveniently in tabular form. The constants for raw linseed oil which are given do not agree with those adopted by the American Society for Testing Materials. In giving the specific gravity no temperature is mentioned and the well-known constants of index of refraction, acid number and unsaponifiable matter are not included in the table given.

Part III, pp. 104–132, is devoted to the manufacture of printing ink. No formulae are given and the subject is taken up only very generally. Much attention is given to the making of plate or engraving inks and very little to the manufacture of typographical inks.

There are many mistakes of a kind which are not unusual in a first edition. On page 74 "dilutent" occurs four times; the same mistake was noticed in several other places. "Vermillion" is used repeatedly for "vermilion." On page 97, third paragraph, "there use" should be "their use." On page 44, the fineness of ultramarine blue pigment is given as "very fine impalpable powder."

On page 73, under the heading abrasive qualities and referring to magnetic pigment, it is stated that it is "not abrasive." Since this material is used for sharpening razors one would expect the reverse of this statement. On page 81, third paragraph, "aluminum sulfate" should be "aluminum hydrate."

It is very unfortunate that references to the literature were not put in the book. Only a single reference was found by the reviewer.

The authors hope that the book may "prove valuable and serviceable to the many workers in the art," seems justified yet it is to be hoped that in another edition more extensive material will be included and that the actual manufacture of printing inks will be given more detailed attention.

PHILIP L. DAVIS

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Agriculture: Laboratory Exercises in Principles of Agriculture.** By E. HOPT AND R. R. STAFFORD. 8vo. 192 pp. Price, $0.50. W. M. Welch Mfg. Co., Chicago.

**Alcoholometric Tables.** By SIR EDWARD THORPE. 8vo. Price, $1.10. Longmans, Green & Co., New York.

**Asphalt: Beitraege zur Chemie der Asphalte m. besond. Berueck-sicht. ihrer photochemischen Eigenschaften.** By PAUL GOEDRICH. 8vo. 14 pp. A. Hoelder, Vienna.

**Chemical German.** By FRANCIS C. PHILLIPS 2nd Ed. 252 pp. Price, $2.00. Chemical Publishing Co., Easton

**Chemistry: Cours experimentale de chimie.** By H. GRAND-MONTAGNE. 8vo. 248 pp. Larousse, Paris.

**Chemistry: First Principles of Chemistry.** By R. H. BROWNLEE AND OTHERS. Rev. Ed. 12mo. 526 pp. Price, $1.25. Allyn and Bacon, Boston.

**Chemistry: Laboratory Exercises Arranged to Accompany "First Course in Chemistry."** By W. MCPHERSON AND W. E. HENDERSON. 12mo. 128 pp. Price, $0.60. Ginn & Co., Boston.

**Colloidchemistry: Die Welt der vernachlaessigten Dimensionen.** By WOLFGANG OSTWALD. 8vo. Price, $1.50. Theodor Steinkopff, Dresden.

**Dynamo-Electric Machinery: Specification and Design of Dynamo-Electric Machinery.** By MILES WALKER. 4to. 648 pp. Price, $10.00. Longmans, Green & Co., New York

**Electric Light: De la portée des projecteurs de lumière électrique.** By JEAN REY. 8vo. 150 pp. Berger-Levrault, Paris.

**Electric Measurements and Meter Testing.** By D. P MORETON. 16mo. 328 pp. Price, $1.50. F. J. Drake & Co., Chicago.

**Engineering Mathematics: A Vest-Pocket Handbook of Mathematics for Engineers.** By L. A. WATERBURY. 8vo: 213 pp. Price, $1.50. John Wiley & Sons, New York.

**Field Engineering.** By W. H. SEARLES. 17th Ed. 16mo. 630 pp. Price, $3.00. John Wiley & Sons, New York.

**Food Products: Laboratory Experiments on Food Products.** By E. H. S. BAILEY. 44 pp. Price, $0.25. P. Blakiston's Son & Co., Philadelphia.

**Gas Engineering and Gas Manufacture.** Ed. by C. W. HASTINGS. J. G. Hammond & Co., London.

**Gaseous Combustion at High Pressures.** By W. A. BONE. 4to. 65 pp. Price, $0.65. Wm. Wesley & Sons, London.

**Glycerine: Its Production, Uses and Examination for Chemists.** By S. W. KOPPE. 8vo. 258 pp. Price, $2.00. Scott, Greenwood & Son, London.

**India-Rubber: Die Synthese des Kautschuks.** By R. DITMAR. 8vo. 124 pp. Price, $0.75. Theodor Steinkopff, Dresden.

**Industrial Chemistry: Muspratt's encyclopaedisches Handbuch der technischen Chemie. Vol. 3, Pt. 1, Chemische Technologie organischer Industriezweige.** Ed. by ARTHUR BINZ. 8vo. 515 pp. Price, $6.50. F. Vieweg & Sohn, Braunschweig.

**Iron and Steel: The Canadian Iron and Steel Industry.** By W. J. A. DONALD. 8vo. 376 pp. Price, $2.00. Houghton, Mifflin Co., Boston.

**Mechanics: Cours de mécanique professé à l'Ecole polytechnique.** By LÉON LECORNU. 8vo. 544 pp. Price, $3.75. Gauthier-Villars, Paris.

**Medical Chemistry: A Compend of Medical Chemistry.** By H. LEFFMANN. 6th Ed. 241 pp. Price, $1.00. P. Blakiston's Son & Co., Philadelphia.

**Mineral Industry. Vol. 23 (1914).** Ed. by G. A ROUSH 8vo. 1000 pp. Price, $10.00. McGraw-Hill Book Co., New York.

**Molecules: Studien ueber Molekularstatistik von Emulsionen und deren Zusammenhang mit der Brownschen Bewegung.** By M. SMOULUCHOWOSKI. 8vo. 25 pp. A. Hoelder, Vienna.

**Oil: All About Oil for Engineers.** By A. CREE. 8vo. Price, $0.75. W. Thacker & Co., London.

**Oils: Semi-Annual Report on Essential Oils, Synthetic Perfumes, Etc.** By SCHIMMEL & CO. 110 pp. Schimmel & Co., Miltitz near Leipzig.

**Organic Chemistry for Advanced Students.** Vol. 2. By J. B.-COHEN. 8vo. Price, $4.50. Longmans, Green & Co., New York.

**Organic Chemistry: Laboratory Experiments in Organic Chemistry.** By E. P. COOK. 52 pp. Price, $0.35. P. Blakiston's Son & Co., Philadelphia

**Reed's Handbook to the Examination of Engine-Room Artificers.** By E. R. COLLINGS. New and Rev. Ed. 8vo. 356 pp. Price, $1.25. T. Reed & Co., London.

**Soil Analysis: Eine neue Methode zur mechanischen Bodenanalyse.** By SVEN ODEN 8vo. 55 pp. Price, $0.75. Verlag fuer Fachliteratur, Berlin.

**Steam Boiler Economy.** By W. KENT. 2nd Ed. 8vo. 717 pp. Price, $4.50. John Wiley & Sons, New York.

**Steam Engine: Dampfmaschine oder Elektromotor.** By F. BARTH. 8vo. 64 pp. Price, $0.50. R. Oldenbourg, Munich.

**Storage Batteries: A List of References 1900-1915.** By G. S. MAYNARD. 8vo. 37 pp. New York Public Library, New York.

**Turbine Regulator: Beitrag zur Frage der Stabilitaetsbedingungen der Turbinenregler.** By H BAUDISCH 8vo. Verlag fuer Fachliteratur, Berlin.

**Ultramarine: Ueber natuerliches und kuenstliches Ultramarin.** By C. DOELTER. 8vo. A. Hoelder, Vienna.

## RECENT JOURNAL ARTICLES

**Agricultural Chemists: Journal of the Association of Official Agricultural Chemists.** New Journal. Published by Williams & Wilkins Co., Baltimore, for the Association.

**Air and Steam as Atomizing Agents.** By R. A. BULL. *Iron Trade Review*, Vol. 57 (1915), No. 14, pp. 626–629.

**Alcohol: Die Bestimmung von Alkohol in Aether.** By P. SZEBERÉNYI. *Zeitschrift fuer analytische Chemie*, Vol. 45 (1915), No. 8, pp. 409–411.

**Aluminium-Bestimmung in Silikaten.** By EMMERICH SELCH. *Zeitschrift fuer analytische Chemie*, Vol. 45 (1915), No. 8, pp. 395–403.

**Aluminum Precipitation at the Mill of the Butters Divisadero Company.** By E. M. HAMILTON AND P. H. CRAWFORD. *Mining and Scientific Press*, Vol. 111 (1915), No. 11, pp. 387–391.

**Ammonia Compressor Efficiency.** By CHARLES JOHNSSON. *Refrigerating World*, Vol. 49 (1915), No. 8, pp. 25–26.

**Benzol: Unterscheidung von Benzin und Benzol.** By H. MIX. *Kolloid-Zeitschrift*, Vol. 17 (1915), No. 1, pp. 7–9.

**Bronze: Ueber elektrolytische Bronzefaellung.** By W. D. TREADWELL AND E. BECKH. *Zeitschrift fuer Elektrochemie*, Vol. 21 (1915), No. 15/16, pp. 374–381.

**Cellulose: Experimental Work on Soda Cellulose.** By SIDNEY D. WELLS. *Paper*, Vol. 17 (1915), No. 4, pp. 14–15.

**Coal Tar: Use of Coal Tar in Flotation.** By W. A. MUELLER. *Engineering and Mining Journal*, Vol. 100 (1915), No. 15, pp. 591–593.

**Corrosion: Influence of Different Elements on the Corrosion of Iron.** By L. C. WILSON. *Engineering Magazine*, Vol. 50 (1915), No. 1, pp. 78–86.

**Flotation: What is Flotation?** By T. A. RICKARD. *Mining and Scientific Press*, Vo. 111 (1915), No. 11, pp. 383–386.

**Gas *vs.* Electrically Heated Ovens.** By G. H. TROUT. *Iron Trade Review*, Vol. 57 (1915), No. 12, p. 526.

**Gas Producers: Factors Governing Gas Producer Practice.** By FRANZ DENK. *Steel and Iron*, Vol. 49 (1915), No. 26, pp. 911–914.

**Gases: The Kinetic Theory of Gases.** By SAUL DUSHMAN. *General Electric Review*, Vol. 18 (1915), No. 10, pp. 952–958.

**Gold Milling in California.** By L. A. PALMER. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 10, pp. 617–624.

**Hydrogen: Bestimmung des Wasserstoffs in Gasgemengen durch katalytische Absorption.** By E. BOSSHARD AND E. FISCHLI. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 70, pp. 365–366.

**Hydroquinone: Die Sulfurierung des Hydrochinons.** By JOHANN PINNOW. *Zeitschrift fuer Elektrochemie*, Vol. 21 (1915), No. 15/16, pp. 380–388.

**India Rubber: Arbeiten ueber Kautschuk und Guttapercha.** By G. H. HILLEN. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 66, pp. 349–354.

**Insulating Materials: The Volume Resistivity and Surface Resistivity of Insulating Materials.** By H. L. CURTIS. *General Electric Review*, Vol. 18 (1915), No. 10, pp. 996–1001.

**Kilns: Setting Down Draft Kilns.** By A. F. GREAVES-WALKER. *Brick and Clay Record*, Vol. 47 (1915), No. 7, pp. 501–505.

**Leather: Ueber ein Neutralfettverbot in der Lederindustrie.** By W. FAHRION. *Chemische Revue ueber die Fett- und Harz-Industrie*, Vol. 22 (1915), No. 9, pp. 77–80.

**Oil Engine for Ice Plant Service.** By L. K. DOELLING. *Ice and Refrigeration*, Vol. 49 (1915), No. 4, pp. 154–162.

**Paper Fiber Analysis.** By MAX CLINE. *Paper*, Vol. 17 (1915), No. 3, pp. 19–21

**Petroleum: Beitrag zur Untersuchung und Beurteilung des zu Leuchtzwecken dienenden Petroleums.** By R JUNGKUNZ. *Chemiker-Zeitung*, Vol. 39 (1915), No. 102, pp. 641–642.

**Portland Cement: Controlling the Raw Mix in the Manufacture of Portland Cement.** By SAMUEL MCANALLY. *Concrete-Cement Age*, Vol. 7 (1915), No. 3, pp. 30–33.

**Rare Earths: Die seltenen Erden in der Therapie.** By C. R. BOHM. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 64, pp. 346–348.

# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. Parker
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**Compressing, Drying, and Transferring Chlorin Gas. J. W. Aylsworth, April 6, 1915. U. S. Pat. 1,134,432.** Alternate volumes of chlorin gas and sulfuric acid are caused to continuously enter a helical pipe. The pipe is rotated thus transferring the acid and gas compressed thereby into a receiver. The intimate contact between the acid and gas dries the gas and the acid is finally separated from the dried gas.

**Converting Meadow or Swamp Land into Fertilizer. B. Reichelt, April 6, 1915. U. S. Pat. 1,134,760.** Meadow or swamp land material containing potash is converted into fertilizer by heating the material to a temperature sufficient to dry it and to drive off the potash therefrom. The dried material is then ground and finally the potash is re-mixed with the ground material.

**Nitrogen and Potash Mixture. S. W. Sinsheimer, April 6, 1915. U. S. Pat. 1,134,921.** The product is a fertilizing agent consisting of the residue of waste liquid after the separation of sugar from molasses which has been treated with carbon dioxid and evaporated at a low temperature to produce a concentrated product.

**Preventing Escape of Sulfur Dioxid in Smelting Sulfid Ores. W. A. Hall, April 6, 1915. U. S. Pat. 1,134,846.** A reducing flame together with steam is introduced into the upper level of the furnace at a point near the normal charge level therein and under conditions capable of reducing a part at least of the $SO_2$ in the exit gases and separating the sulfur from the gases.

**Producing Hydroxids of Metals by Means of Ammonia. H. A. Frasch, April 13, 1915. U. S. Pat. 1,135,785.** Nickel oxid is precipitated from a solution of nickel ammonium chlorid by boiling in the presence of a solution of ammonium chlorid until the nickel oxid is precipitated, while maintaining the solution alkaline with ammonia.

**Treatment of Alunite, Etc. C. H. MacDowell, April 20, 1915. U. S. Pat. 1,136,549.** Alunite is calcined for the purpose of driving off anhydrid and sulfuric anhydrid. The product is heated to a temperature sufficient to volatilize and drive off potash and the exit of the volatilized potash from the charge is expedited by carrying it off in a gaseous current.

**Continuous Distillation and Rectification of Alcoholic Liquids. V. Slavicek, April 20, 1915. U. S. Pat. 1,136,559.** The alcoholic raw vapor is divided into portions. The non-cooled phlegm of one portion of the head product is purified and immediately introduced at the beginning of the rectification into the alcoholic raw vapor of the second portion.

**Coagulant for Water Purification. A. Jacobson, April 27, 1915. U. S. Pat. 1,137,005.** The coagulant is produced by passing an aqueous solution of sulfate of aluminum over metallic iron so that a part of the iron is dissolved to form iron sulfate and sulfate of aluminum is reduced to a soluble basic sulfate of aluminum.

**Rendering Phosphoric Acid Available. W. S. Landis, April 27, 1915. U. S. Pat. 1,137,065.** A mixture of finely divided phosphate rock, an alkali metal salt and carbon is heated to a sufficient temperature to eliminate the acid radical of the salt. The mixture is then subjected to a higher temperature sufficient to cause an incipient fusing or clinkering of the mixture.

**Carbonitrids. S. Peacock, April 27, 1915. U. S. Pat. 1,137,524.** The process consists in heating in the presence of nitrogen an oxid of an element having metallic properties with sufficient carbon and to a temperature sufficient to produce carbonitrid while preventing the partial pressures of the gaseous products from rising sufficiently to interfere with the reaction.

**Alkali-Soluble Alumina. P. R. Hershman, April 27, 1915. U. S. Pat. 1,137,617.** Alumina in admixture with carbon is heated in the presence of a non-nitrifying atmosphere, to a temperature sufficient to make it soluble in alkali.

**Recovering Soda Content of Waste Liquor. H. K. Moore, May 4, 1915. U. S. Pat. 1,137,779.** The lignin is utilized in making steam which may be employed in the digestion of the raw wood. Multiple-effect evaporators are used in concentrating the lignin to approximately 355 Bé. and the residuum is mixed with sulfate of soda and a carrier of carbonaceous material such as sawdust, pulverized bark, peat, coke, or the like. The mixture is dried, burned in a smelting furnace and the soda recovered.

**Acid Mono-Calcium Phosphate. Robert Stewart, May 4, 1915. U. S. Pat. 1,137,806.** Phosphate rock is fed by the conveyor 10 into the upper end of the tube furnace 5, heated by the burner 14 and subjected to the action of steam and smelter smoke introduced through the pipes 12 and 13, respectively. The reaction results in the production of acid mono-calcium phosphate and a solution of acid calcium sulfite.

**Treating Aluminate Solutions. H. Howard, May 4, 1915. U. S. Pat. 1,137,860.** Silica is removed from aluminate solutions by subjecting the hot aluminate solution, at a concentration not exceeding 300 Bé. to the action of the residues from the decomposition of bauxite by alkali.

**Reducing Waste Sulfite Liquor to a Powder. F. H. Kennard, May 4, 1915. U. S. Pat. 1,138,118.** The waste sulfite liquor is first concentrated to a viscous state in a vacuum. The viscous material is then applied in a vacuum, in a thin sheet, onto a heated surface and retained thereon until the viscous material is evaporated to dryness.

**Treating Hydrocarbon Oils. C. H. Washburn, May 4, 1915. U. S. Pat. 1,138,266.** Petroleum oils of from 260 to 488 Bé. are transformed into a product not exceeding 520 Bé. by passing the oil and water in liquid form into a retort where they are converted into vapor, and leading the vapor to a condenser, the terminal of which is closed to create a back pressure, thereby condensing the vapor at a pressure of from three to five atmospheres maintained throughout the distillation and condensation.

**Drying Sodium-Bisulfite Crystals. H. Howard, May 11, 1915. U. S. Pat. 1,138,658.** Wet sulfite crystals are subjected to a current of hot sulfur dioxid gas.

**Nitroglycerin. R. Weyel, May 11, 1915. U. S. Pat. 1,138,917.** The separation of a mixture of liquids, containing nitroglycerin and an acid is facilitated by generating silicon fluorid in the liquids by the addition of a fluorid and an insoluble siliceous compound.

**Explosive. G. Burgschmiet, May 11, 1915. U. S. Pat. 1,139,339.** The composition comprises essentially about 80 per cent of ammonium nitrate, about 18 per cent of dinitrotoluene and about 2 per cent charcoal and wood meal.

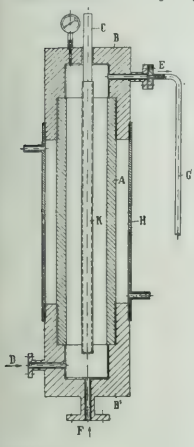
**Wood-Preservative. J. A. DeCew, May 18, 1915. U. S. Pat. 1,140,127.** The composition comprises a mixture of waste sulfite liquor, creosote oil, and chlorid of zinc.

## BRITISH PATENTS

By D. Geddes Anderson
Chemical Engineer and Patent Chemist, Glasgow, Scotland

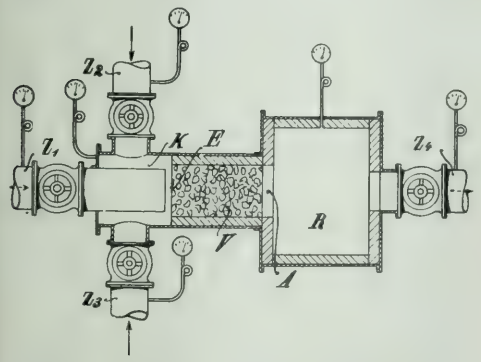
The following abstracts are taken direct from the patent specifications as soon as these are published by the British Patent Office. The date given at the end of the abstract is the date of acceptance.

**Manufacture of Hydrogen Peroxide. Henkel and Cie, Nov. 18, 1914. Brit. Pat. 22,714.** A is a tube of suitable metal coated inside with a thin layer of cathode material, such as silver amalgam and copper amalgam. The electrolyte is pumped in at D and escapes at E, and oxygen is admitted at F. C is the anode and is covered with the diaphragm tube K.—June 17, 1915.




**Production of Esters of the Tertiary Alcohols. Neumann and Co., Chemische Fabrik G. M. B. H and J. Zeltner, Nov. 5, 1913. Brit. Pat. 25,262.** Organic acid chlorides, with the exception of the chlorides of carbonic acid and their derivatives are caused to react with non-substituted aliphatic tertiary alcohols in the presence of tertiary bases, *e. g.*, 64 grams of valeric chloride are added to 44 grams tertiary amyl alcohol in 55 grams pyridine. After standing 24 hours, 100 cc. water and 100 cc. hydrochloric acid are added and the tertiary amyl valeriate is distilled *in vacuo*.—July 1, 1915.

**Production of Nitrogen and Oxygen Compounds. C. Krauss and P. Staehelin, Nov. 18, 1913. Brit. Pat. 26,499.** Liquid or gaseous fuel is burned without flame at high pressure in an




atmosphere of nitrogen and oxygen. The combustion chamber is filled with a granular material coated with substances such as oxides of chromium, titanium or vanadium, which facilitate the combination of nitrogen and oxygen.—July 8, 1915.

**Plastic Compositions. E. Krause and H. Blucher, Jan. 1, 1914. Brit. Pat. 76.** The plastic material is made by treating the albuminous and cellulosic residues from the manufacture of yeast extracts or preparations, with formaldehyde. The residues obtained from yeast in the manufacture of preparations of the nature of meat extract are preferably employed.—July 29, 1915.

**Rubber Substitute. J. Baier and A. G. M. Weale, Jan. 15, 1914. Brit. Pat. 1,171.** Animal tissue is dissolved in zinc chloride and the thick jelly obtained is mixed with a starchy material such as finely ground tapioca. The thick dough so prepared is mixed with rubber solution, or with a saturated solution of resin in methylated spirit.—July 29, 1915.

**Varnish. E. Girzik, Jan. 20, 1914. Brit. Pat. 1,575.** Process relates to the manufacture of varnish from semi-drying oils such as train oil. The free fatty acids in the oil are removed by adding a suitable quantity of soda lye, and allowing to stand in the cold for several days. The soap is separated and the oil subjected to a boiling or polymerization process.—July 29, 1915.

**Extracting Sulfurous Acid and Oxides from Sulfates. A. Bambach, Feb. 6, 1914. Brit. Pat. 3,174.** The sulfates, such as calcium and barium sulfates, are introduced into a shaft furnace in a fragmentary state and heated with a flame from a gas and air mixture. The operation is finished by feeding the flame with excess of air.—July 29, 1915.

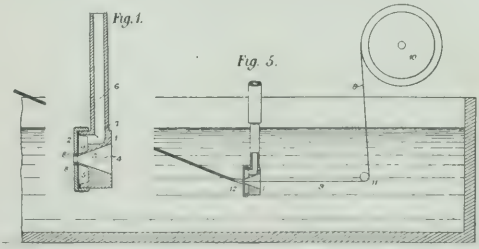
**Coating Articles with Aluminum. W. Krumbhaar, Feb. 12, 1914. Brit. Pat. 3,713.** The article to be treated is first given a coat of lacquer, and when this coat is perfectly dry, finely divided aluminum powder is rubbed in.—July 1, 1915.

**Manufacture of Light Hydrocarbons from Heavy Hydrocarbons. F. Bergius, Feb. 21, 1914. Brit. Pat. 4,574.** The hydrocarbons, previous to distillation, are heated in the presence of hydrogen under a pressure of 100 atmospheres. The hydrogen reacts and converts all non-saturated compounds into saturated compounds. The petroleum so treated is then distilled and it is found that the proportion of light constituents is very much increased.—July 8, 1915.

**Manufacture of Sulfate of Ammonia, and the Purification of Coal Gas. J. Mackenzie, April 23, 1914. Brit. Pat. 10,059.** The gas, freed from tar, is passed into a moist atmosphere of nitrous acid at 200° F. The sulfur compounds contained in the coal gas are oxidized and combine with the ammonia to give sulfate of ammonia. The excess of nitrous acid is absorbed in sulfuric acid.—July 23, 1915.

**Carbon Electrodes for Galvanic Cells. V. Scholz, April 24, 1914. Brit. Pat. 10,171.** Carbon powder in the form of colloidal graphite is employed in the formation of the electrode. The voltage is rendered more constant by using the graphite in this form.—July 8, 1915.

**Manufacture of Tubular Threads from Solutions of Cellulose. Courtnaulds, Ltd., and L. P. Wilson, July 23, 1914. Brit. Pat. 17,495.** A jet as shown in Fig. 1 is used, and is immersed in a coagulating bath. The liquid of the bath has access to both the




interior and exterior surfaces of the thread being formed. Compound threads can also be formed by projecting a solution of viscose through the orifice of the jet while a free formed thread of suitable textile fiber is introduced into the interior of the tabular thread as in Fig. 5.—July 23, 1915.

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON OCTOBER 20TH. (See this issue, page 997)

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lime, gray | 100 Lbs. | 4.00 | @ | 4.05 |
| Alum, lump | 100 Lbs. | 5.25 | @ | 5.50 |
| Aluminum Sulfate, high-grade | 100 Lbs. | 2.25 | @ | 2.75 |
| Ammonium Carbonate, domestic | Lb. | 8 1/2 | @ | 9 1/2 |
| Ammonium Chloride, gray | Lb. | 8.25 | @ | 8.50 |
| Ammonium Phosphate, commercial, 98–100% | Lb. | 10 | @ | 10 1/2 |
| Aqua Ammonium, 16°, drums | Lb | 2 1/4 | @ | 2 1/2 |
| Arsenic, white | Lb. | 3 3/4 | @ | 4 |
| Barium Chloride | Ton | 90.00 | @ | 100.00 |
| Barium Nitrate | Lb. | 15 | @ | 16 |
| Barytes, prime white, foreign | Ton | 19.00 | @ | 23.00 |
| Bleaching Powder, 35 per cent | 100 Lbs. | 3.50 | @ | 4.00 |
| Blue Vitriol | Lb. | 6 1/2 | @ | 7 |
| Borax, crystals, in bags | Lb. | 5 1/2 | @ | 6 |
| Boric Acid, powdered crystals | Lb. | 10 | @ | 10 1/4 |
| Brimstone, crude, domestic | Long Ton | 22.00 | @ | 22.50 |
| Bromine, technical, bulk | Lb. | 1.50 | @ | 1.75 |
| Calcium Chloride, lump | Ton | — | @ | 11.78 |
| Calcium Chloride, granulated | Ton | — | @ | 14.78 |
| Caustic Soda, 70 @ 76 per cent | 100 Lbs. | 5.25 | @ | 5.50 |
| Caustic Soda, powdered or granulated, 76 per cent | 100 Lbs. | 5.50 | @ | 5.75 |
| Chalk, light precipitated | Lb. | 4 3/4 | @ | 5 1/2 |
| China Clay, imported | Ton | 20.00 | @ | 25.00 |
| Feldspar | Ton | 8.00 | @ | 12.00 |
| Fuller's Earth, foreign, powdered | 100 Lbs. | 80 | @ | 1.00 |
| Glauber's Salt, in bbls. | 100 Lbs. | 60 | @ | 75 |
| Green Vitriol, bulk | 100 Lbs. | 70 | @ | 80 |
| Hydrochloric Acid, commercial, 18° | 100 Lbs. | 1.75 | @ | 2.00 |
| Hydrochloric Acid, C. P., conc., 22° | 100 Lbs. | 2.25 | @ | 2.50 |
| Iodine, resublimed | Lb. | 4.30 | @ | 4.35 |
| Lead Acetate, white crystals | Lb. | 11 5/8 | @ | 12 1/8 |
| Lead Nitrate | Lb. | 11 1/2 | @ | 12 |
| Litharge, American | Lb. | 6 1/4 | @ | — |
| Lithium Carbonate | Lb. | 97 | @ | 1.00 |
| Magnesium Carbonate | Lb. | 5 1/2 | @ | — |
| Magnesite, "Calcined" | Ton | 34.00 | @ | 36.00 |
| Mercuric Chloride, commercial | Lb. | 1.50 | @ | — |
| Nitric Acid, 68 per cent, sp. gr. 1.42 | Lb. | | nominal | |
| Nitric Acid, fuming | Lb. | | nominal | |
| Phosphoric Acid, sp. gr. 1.750 | Lb. | 28 | @ | 31 |
| Phosphorus | Lb. | 40 | @ | 1.00 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate, casks | Lb. | 21 | @ | 22 |
| Potassium Bromide | Lb. | 2.50 | @ | 2.51 |
| Potassium Carbonate, calcined, 80 @ 85% | 100 Lbs. | 27 | @ | 29 |
| Potassium Chlorate, crystals, spot | Lb. | 38 | @ | 42 |
| Potassium Cyanide, bulk, 98–99 per cent | Lb. | 28 | @ | 32 |
| Potassium Hydroxide | Lb. | 37 | @ | 40 |
| Potassium Iodide, bulk | Lb. | 3.70 | @ | 3.75 |
| Potassium Nitrate | Lb. | 19 | @ | 20 |
| Potassium Permanganate, bulk | Lb. | 1.25 | @ | — |
| Quicksilver, flask, 75 lbs. | | 93.00 | @ | 95.00 |
| Red Lead, American, dry | Lb. | 6 1/2 | @ | — |
| Salt Cake, glass makers' | 100 Lbs. | 55 | @ | 65 |
| Silver Nitrate | Oz. | 31 3/4 | @ | 33 3/4 |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash, 48 per cent | 100 Lbs. | 80 | @ | 90 |
| Sodium Acetate | Lb. | 5 | @ | 6 |
| Sodium Bicarbonate, domestic | 100 Lbs. | 1.00 | @ | 1.10 |
| Sodium Bicarbonate, English | Lb. | 3 1/2 | @ | 3 5/8 |
| Sodium Bichromate | Lb. | 15 1/2 | @ | 16 |
| Sodium Carbonate, dry | 100 Lbs. | 1.10 | @ | — |
| Sodium Chlorate | Lb. | 38 | @ | 40 |
| Sodium Fluoride, commercial | Lb. | 12 | @ | — |
| Sodium Hydroxide, 60 per cent | 100 Lbs. | | 2.25 | |
| Sodium Hyposulfite | 100 Lbs. | 2.25 | @ | 2.50 |
| Sodium Nitrate, 95 per cent, spot | 100 Lbs. | 2.95 | @ | 3.00 |
| Sodium Silicate, liquid | 100 Lbs. | 85 | @ | 1.10 |
| Sodium Sulfide, 30%, crystals, in bbls. | Lb. | 2 | @ | 2 1/2 |
| Sodium Sulfite, crystals | Lb. | 2 1/2 | @ | 2 5/8 |
| Strontium Nitrate | Lb. | 18 | @ | 19 |
| Sulfur, flowers, sublimed | 100 Lbs. | 2.20 | @ | 2.60 |
| Sulfur, roll | 100 Lbs. | 1.80 | @ | 2.15 |
| Sulfuric Acid, chamber, 60° | 100 Lbs. | 1.00 | @ | 1.25 |
| Sulfuric Acid, conc., sp. gr. 1.842 | 100 Lbs. | 1.75 | @ | 2.50 |
| Sulfuric Acid, oleum (fuming) | 100 Lbs. | 1.75 | @ | 2.50 |
| Talc, American | Ton | 9.00 | @ | 13.00 |
| Terra Alba, American, No. 1 | 100 Lbs. | 75 | @ | 80 |
| Tin Bichloride, 50° | Lb. | 10 | @ | 10 1/2 |
| Tin Oxide | Lb. | 38 | @ | 40 |
| White Lead, American, dry | Lb. | 5 1/2 | @ | |
| Zinc Carbonate | Lb. | 12 | @ | 13 |
| Zinc Chloride, commercial | Lb. | 8 | @ | 8 1/2 |
| Zinc Oxide, American process | Lb. | 8 | @ | 8 1/4 |
| Zinc Sulfate | Lb. | 6 1/2 | @ | 7 |

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid, C. P., in bbls. | Lb. | 1.10 | @ | 1.15 |
| Acetic Acid, 28 per cent, in bbls. | 100 Lbs. | 3.00 | @ | 3.25 |
| Acetic Acid, glacial, 99 1/2%, in carboys | Lb. | 21 1/2 | @ | 25 |
| Acetone, drums | Lb. | 28 1/2 | @ | 30 |
| Alcohol, denatured, 180 proof | Gal. | 39 | @ | 40 |
| Alcohol, grain, 188 proof | Gal. | 2.60 | @ | — |
| Alcohol, wood, 95 per cent, refined | Gal. | 45 | @ | 47 |
| Amyl Acetate | Gal. | 3.00 | @ | 3.25 |
| Aniline Oil | Lb. | 1.00 | @ | 1.35 |
| Benzoic Acid, ex-toluol | Lb. | 3.25 | @ | 3.30 |
| Benzol, 90 per cent | Gal. | 80 | @ | 90 |
| Camphor, refined in bulk, bbls. | Lb. | 43 | @ | — |
| Carbolic Acid, U. S. P., crystals, drums | Lb. | 1.70 | @ | 1.75 |
| Carbon Bisulfide | Lb. | 6 1/2 | @ | 7 1/2 |
| Carbon Tetrachloride, drums, 100 gals. | Lb. | 17 | @ | 18 |
| Chloroform | Lb. | 35 | @ | — |
| Citric Acid, domestic, crystals | Lb. | 55 | @ | 55 1/2 |
| Cresol, U. S. P. | Gal. | 1.15 | @ | 1.25 |
| Dextrine, corn (carloads, bags) | 100 Lbs. | 2.80 | @ | — |
| Dextrine, imported potato | Lb. | 10 | @ | 12 |
| Ether, U. S. P., 1900 | Lb. | 15 | @ | 20 |
| Formaldehyde, 40 per cent | Lb. | 9 1/2 | @ | 10 1/2 |
| Glycerine, dynamite, drums included | Lb. | 57 | @ | 60 |
| Oxalic Acid, in casks | Lb. | 45 | @ | 46 |
| Pyrogallic Acid, resublimed bulk | Lb. | 1.45 | @ | 1.55 |
| Salicylic Acid | Lb. | 3.50 | @ | 3.75 |
| Starch, cassava | Lb. | 3 1/2 | @ | 4 1/8 |
| Starch, corn (carloads, bags) | 100 Lbs. | — | @ | 2.25 |
| Starch, potato | Lb. | 6 3/4 | @ | 7 |
| Starch, rice | Lb. | 7 | @ | 8 |
| Starch, sago | Lb. | 3 | @ | 3 1/2 |
| Starch, wheat | Lb. | 5 | @ | 5 1/2 |
| Tannic Acid, commercial | Lb. | 75 | @ | 76 |
| Tartaric Acid, crystals | Lb. | 47 | @ | 47 1/2 |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax, pure, white | Lb. | 45 | @ | 52 |
| Black Mineral Oil, 29 gravity | Gal. | 12 1/2 | @ | 13 |
| Castor Oil, No. 3 | Lb. | 9 3/4 | @ | 10 1/4 |
| Ceresin, yellow | Lb. | 10 | @ | 14 |
| Corn Oil | 100 Lbs. | 7.75 | @ | 7.85 |
| Cottonseed Oil, crude, f. o. b. mill | Gal. | 52 | @ | 53 |
| Cottonseed Oil, p. s. y. | Lb. | 7 5/8 | @ | 7 3/4 |
| Creosote, beechwood | Lb. | 2.50 | @ | 3.50 |
| Cylinder Oil, light, filtered | Gal. | 20 | @ | 25 |
| Fusel Oil, crude | Lb. | 2.65 | @ | 2.75 |
| Japan Wax | Lb. | 12 3/4 | @ | 13 |
| Lard Oil, prime winter | Gal. | 86 | @ | 90 |
| Linseed Oil, raw (car lots) | Gal. | 58 | @ | — |
| Menhaden Oil, crude | Gal. | | nominal | |
| Naphtha, 68 @ 72° | Gal. | 22 | @ | 24 |
| Neat's-foot Oil, 20° | Gal. | 92 | @ | 94 |
| Paraffine, crude, 120 & 122 m. p. | Lb. | 2 1/2 | @ | 3 |
| Paraffine Oil, high viscosity | Gal. | 23 | @ | 24 |
| Rosin, "F" Grade, 280 lbs. | Bbl. | 4.15 | @ | — |
| Rosin Oil, first run | Gal. | — | @ | 25 |
| Shellac, T. N. | Lb. | 15 | @ | 15 1/2 |
| Spermaceti, cake | Lb. | | 25 | |
| Sperm Oil, bleached winter, 38° | Gal. | 70 | @ | — |
| Spindle Oil, No. 200 | Gal. | 18 | @ | 19 |
| Stearic Acid, double-pressed | Lb. | 13 | @ | 13 1/2 |
| Tallow, acidless | Gal. | 64 | @ | 65 |
| Tar Oil, distilled | Gal. | 30 | @ | 31 |
| Turpentine, spirits of | Gal. | 42 | @ | 44 |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum, No. 1, ingots | Lb. | 50 | @ | 55 |
| Antimony, Hallets' | Lb. | | nominal | |
| Bismuth, New York | Lb. | | 3.00 | |
| Copper, electrolytic | Lb. | 17 3/4 | @ | 18 |
| Copper, lake | Lb. | 17 3/4 | @ | 18 |
| Lead, N. Y. | 100 Lbs. | | 4.50 | |
| Nickel, electrolytic | Lb. | 50 | @ | — |
| Nickel, shot and ingots | Lb. | 45 | @ | — |
| Platinum, refined | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | | 49 3/4 | |
| Tin | 100 Lbs. | 33.50 | @ | — |
| Zinc, N. Y. | Lb. | | 13 1/2 | |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | 100 Lbs. | | 3.40 | |
| Blood, dried | Unit | | 2.85 | |
| Bone, 4 1/2 and 50, ground, raw | Ton | | 33.00 | |
| Calcium Cyanamid | Unit of Ammonia | | 2.35 | |
| Calcium Nitrate, Norwegian | 100 Lbs. | | — | |
| Castor Meal | Unit | | — | |
| Fish Scrap, domestic, dried, f. o. b. works | Unit | 3.25 | @ | 10 |
| Phosphate, acid | Unit | 75 | @ | 80 |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble, 68 per cent | Ton | 2.75 | @ | 3.00 |
| Tennessee, 70–80 per cent | Ton | 5.00 | @ | 5.50 |
| Potassium "muriate," basis 80 per cent | Ton | 245.00 | @ | 250.00 |
| Pyrites, furnace size, mported | Unit | — | @ | 13 |
| Tankage, high-grade; f. o. b. Chicago | Unit | 2.30 | & | 10 |

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# EDITORIALS

## CHEMICAL INDUSTRY AND THE UNIVERSITY

It seems quite proper that a representative of the mechanical engineering profession should be heard on the subject of the development of chemical industry, because, in the ordinary course of events, the mechanical engineer must follow the chemist, to provide the means for doing on a suitably large scale what has been found chemically necessary. A chemical industry centers in a factory plant, the machinery and mechanical equipment of which constitute the means whereby chemistry is transformed into chemical industry. The test tube becomes a huge tank; the Bunsen burner a furnace fire or a steam boiler; the filter paper and glass funnel, a pump-operated filter press; the hand mortar a power-driven crusher and grinder; the rubber hose a complicated system of piping; and the movements of the hand are replaced by a power plant with a transmission system. The chemical industries are distinguished from the other allied manufacturing industries by the sort of processes used to convert raw materials into finished products. These processes are partly chemical in nature, never wholly so, and frequently are chemical to only a minor degree, the rest being purely mechanical, thermal or perhaps hydraulic. Most of the apparatus for the execution of these processes is practically standardized, being made and sold in a variety of forms in standard sizes for other purposes than purely chemical ones, but, as a rule, each establishment must, and does, have some special equipment peculiar to its own processes and not used elsewhere. Discussions of the equipment of chemical factories or their processes tend to revolve about these special parts that are purely chemical, or peculiar to only one branch of the chemical industry, and ignore the fact, so easily established, that, taking the chemical industries as a whole, their equipment is largely made up of more or less standard machinery or mechanical appliances. The significance of this is especially great in any investigation of progress in the chemical industries, whether the object be to discover the cause of lack of progress, or, assuming the cause to be established, to discover a remedy.

Any lack of development in the chemical industries in America cannot be traced to lack of suitable standard machinery of the sort that must necessarily make up so large and important a part of any manufacturing establishment, because such American machinery enjoys a world-wide reputation as a class, second to that of no other nation. This includes all equipment and methods for generating or transmitting power; for combustion of fuels; for absorption, exchange and dissipation of heat, including refrigeration; for changing the physical state of, or moving, transporting, mixing and separating solids, liquids and gases; for crushing, pulverizing, consolidating, pressing, molding or cutting solids, and many others equally fundamental in importance and common in use. Improvements in this sort of equipment in quality, cost, capacity, or efficiency, arising from researches on their basic processes, on the principles of design, or on the use of new materials, are all available to the chemical industries, provided first, that they are known, and second, that they are adopted and intelligently installed in coöperation with the other equipment of the plant.

This citation will serve to show that the welfare of chemical industries, while of course fundamentally resting on a chemical basis, is not exclusively a chemical question, any more than it is exclusively an engineering, or in general a technological question. Contributions to chemical industry along such general engineering lines may properly be classed as indirect. This indirect class is a very large one and includes activity in all the basic sciences, in economics, sociology and law, and in all related industries or industry in general. It is very easy for one vitally concerned in the chemical industries, or one branch in particular, to forget these indirect yet powerful aids, and to be led into impatient complaint because of a lack of specific direct contributions to his own immediate needs. These indirect contributions are just as necessary in their way as a healthy body is to a successful lawyer, who, however, may properly be expected to know some law.

We of the modern university are students of the industries, and of the conditions that concern their general, as well as their specific welfare—students, not in the old absorptive sense, but in the new reactionary sense. The university of to-day is not a safe-depository of learning nor a cold storage warehouse of facts and principles to be carefully guarded from the world for fear someone may use them. It is, on the contrary, the digestive tract of the community, receiving all sorts of mental food, rejecting the bad, and transforming the good into those forms of energy that can be given out as new sources of vitality to all forms of activity that may be suffering from the common complaint of general debility.

Industrially, the university recognizes the primary wealth-producing industries of mining, agriculture, forestry and fisheries; the secondary producing industries of the manufactures, of which the chemical industries are but a part; and, finally, the industries of transportation and communication, all associated with commerce, merchandizing and, banking. Our organization does not follow just these lines of division but is arranged on the divisions of typical basic studies, or the fundamental sciences, any one of which may concern itself with several or all of the industrial applications. This is one reason why the contributions of the university are not more often recognized by the industries concerned, as so many of them are indirect, bear an unfamiliar label, and require interpretation and adaptation to become directly available. Even this function of interpretation and adaptation of its general contributions to industrial use is

being fulfilled by the newer elements of the university organization through its engineering division in general and more specifically, for the chemical industries, by its chemical engineering department.

Those members of the university staff that are charged with industrial responsibility are not merely students, but are really participators and direct contributors, to a degree that is limited, not by any lack of interest, ability or energy, but solely by available time and money. It is freely admitted that the direct contributions to the advance of the chemical industries in America by the university have, up to the present, not been what they should be, but it can be proved that the fault is only one of degree and not of kind. Everything that should, or could, reasonably be expected, in both the direct or indirect classes, is being done to some degree, and the problem is one of ways and means of increase of activity of the same sort, rather than one of creation of a new kind. However great the indirect contributions may be, they will never serve so useful a purpose, nor receive so much recognition, nor warrant so much support, as an even moderate increase in direct contributions made in a form directly available for immediate use, and requiring no explanations or interpretations to manufacturers concerned, for an appreciation of value.

The most immediately available, and hence useful and valuable contribution that any one can make to the chemical industries, is new apparatus, mechanical equipment, or machinery, of proved capability to produce new and valuable results in lessening costs of present procedure, in making new products from the same materials, or the same products from different materials, or combining all three—new products, new materials, and reduced costs. Next in direct order of immediate value, come new processes, which, however, must be incorporated into apparatus before becoming usable.

No improvement in either apparatus or processes can be attained withcut an initial step of conception of need on the one hand, or of possibility on the other, and in point of time either may lead the other. Recognition of defects or needs may be a part of common experience, or such may be the result of the critical searching by test and computation that should characterize the work of the engineers of the apparatus manufacturer, and of the chemical factory using the apparatus. As a matter of fact both of these interests are so occupied with routine and so inclined to rest on the tradition of old practice that an outside man, continuously engaged in investigating faults in all classes of apparatus, can find things worth improving in almost any plant that the regular staff often regard as sacredly perfect. This initial step of fault discovery by investigation and comparison is one of the regular contributions of the university staff engineer that his independence of thought, breadth of interests and soundness of scientific training particularly fit him to perform, and that he does perform well. This requires, however, sufficient freedom from the university routine to permit travel for inspection or tests, and an invitation and welcome by the manufacturers.

The conception of a remedy for a discovered fault or need, or the conception of an improvement even when no need has been particularly felt or fault admitted, is the second step, the result of which is an idea, a scheme, a promising possibility. Such a conception may come to the factory man either producing or using the apparatus, or to an independent individual, or to one of the regular university staff constantly engaged in studying practices and comparing with possibilities. It is often in the form of a patentable invention though just as often it is not. This conception may be concerned with either a design form for a piece of apparatus, or with a method or process for which apparatus must later be designed. In any case, its value remains a matter of speculation until apparatus is constructed and tried to prove the soundness of the idea at least qualitatively. This step of experimental construction is the first in the series generally termed *development*. It necessarily costs money, and often a large sum, the investment of which is in the nature of a pure speculation, and hence subject to many limitations, especially when associated, as is usually the case, with the question of legal property rights in the invention involved originally, or to be developed.

It is right here that the real barrier to great and material advancement in the chemical factory is usually to be found; this is the neck of the bottle which restricts the flow. Any number of splendid ideas have never been admitted to this first development step of experimental construction to demonstrate their soundness and the possibilities of success, or having been permitted one trial, have been rejected and development stopped through mistakes due to lack of skill rather than to wrong ideas, and just as many bad ideas, that were never worth it, have received experimental trials. As a result the world is full of disgruntled inventors, manufacturers, promotors and bankers, to whom a new idea of this sort is a thing shunned, instead of sought. Here the staff of the research laboratory of the university can, and to some extent does, contribute most valuable aid in sifting the promising from the hopeless, and in studying out the cheapest, best and most convincing experimental construction and demonstration. Especially effective is such coöperation when shop and engineering research laboratory facilities are available, so the whole procedure can be kept well in hand during this anxious time of perplexities and trouble. At the present time, this sort of work, which is a clearing-house operation, equalizing the debits and credits of the men of ideas and the industry concerned, and which should be undertaken on a large scale with financial support to the full extent, is now, however, being carried out on only a small scale, supported more by enthusiasm than by money or industrial appreciation.

This first step in experimental development ends with a demonstration of the soundness of the idea qualitatively, or of the bare possibility of the desired result, but still leaves open the commercial value.

Proof of commercial value requires further and larger-scale demonstration on apparatus carefully designed in either full commercial size, or truly proportioned models of smaller size, but still large enough to permit tests for reliable data. This is usually an expensive procedure to be undertaken as a true investment on the prospect of financial returns to follow adoption and use. While in most cases it is a proper thing for an engineering research and development laboratory, it usually involves larger equipment than any existing university laboratory can care for, and in some cases, due to the nature or the size of the equipment, must be carried out in a commercial establishment. Such commercial demonstrations, being financial enterprises of direct concern to the industries, must have industrial support, even if the work is done by the university staff, but in every case this staff can render valuable assistance by bringing to bear its broader scientific and engineering judgment unhampered by commercial traditions and jealousies. At the present time some work of this kind is being undertaken and carried through, limited only by the number of available men and facilities on the one hand, or, on the other, by the willingness or unwillingness of the industrial interests to use what is to be had.

The last step in the development of new apparatus for the industries is that of commercial perfection and installation, all of which culminates in a working plant, in which the perfected apparatus is correctly associated with the existing apparatus in an old plant, or in a complete new plant with standard equipment selected so as to coöperate best with it for proper results in quality or product and economy of production. In this last stage the university laboratory can play no part, but its staff can, and at present does to a limited degree, partly in the designing of the final form of the apparatus, partly in the selection of the standard equipment to be associated with it and in planning the connections and controls, and finally in testing for full scale performance data, publication of which creates an industrial document, a record of results achieved, and a standard by which further suggestions for improvement must be judged. Such test results of complete plants and the division of performance factors between the several units, is almost wholly lacking for the factories of the chemical industries, though quite common and even standard practice for other kinds of establishments, notably central power stations, shops and many of the non-chemical manufactures.

In conclusion it is believed that any correct analysis of the relations between the university and the chemical industries will show that the industries are receiving from the university the right kind of both direct and indirect contributions, though to an inadequate degree, limited only by financial support, and this limit, it would appear, could be removed by the industries themselves, by contributions in the reverse direction from them to the university.

CHARLES E. LUCKE[1]

# ORIGINAL PAPERS

## THE UTILIZATION OF AROMATIC HYDROCARBONS DERIVED FROM CRACKED PETROLEUM[1]

By W. F. RITTMAN

Received October 10, 1915

In the course of the commercial development of the vapor-phase cracking process for the production of benzene and toluene from petroleum, numerous chemical problems have arisen. One of the most important is the utilization of the products obtained, since these necessarily differ from those derived from coal. The idea is widely prevalent that petroleum-derived products are inferior and a principal object of the present work has been to show that this prejudice is due entirely to a lack of knowledge concerning proper methods of utilization.

The immediate cause for the present work has been the necessity of demonstrating that petroleum-derived toluene can be successfully converted into trinitrotoluene in a commercially practicable manner.

### DIFFERENCES BETWEEN COAL-DERIVED AND PETROLEUM-DERIVED HYDROCARBON MIXTURES

A brief consideration of the sources and methods of production of the two types of commercial hydrocarbon mixtures serves to indicate the nature of the present problem.

The coal-derived products are the results of decomposition of the original material at high temperatures, which fact influences to a large degree the composition of these mixtures. The aromatics are associated with varying quantities of such impurities as sulfur, oxygen, and nitrogen bodies, as well as non-aromatic hydrocarbons of various degrees of unsaturation. Condensable paraffins are not, however, stable at the temperatures which occur during the destructive distillation of coal and these hydrocarbons are, therefore, absent from products derived from this source. It follows, therefore, that aromatic products obtained from coal contain objectionable impurities, from which, however, they may be freed if subjected to treatment by proper physical and chemical processes. On the other hand, the cracking of petroleum yields aromatics which are entirely free from oxygen-containing impurities and which at worst carry only minute quantities of sulfur and nitrogen bodies. The chief and practically the only impurities are olefins and paraffins. These paraffins are necessarily present because maximum yields of toluene and benzene cannot be obtained under conditions which entirely break down these saturated compounds and, furthermore, it is difficult or even impossible to get rid of them completely. Methods of fractional distillation do not effect complete separation and chemical methods are ineffective, since the aromatics are more reactive than the paraffins.

Thus, in attacking the present problem it has been

[1] Published with the permission of the Director of the Bureau of Mines.

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granted that it may be difficult or even impossible to obtain pure aromatics from cracked petroleum. Experiments have, therefore, aimed at devising methods of utilization suitable for the impure products and it now appears that these methods have commercial advantages over those in use for coal-derived products, although the latter substances cannot be treated in the same way as the petroleum products since the sulfur, oxygen, and nitrogen bodies are not chemically inactive, as are the paraffin hydrocarbons.

## METHODS OF PREPARATION AND PROPERTIES OF THE NITROTOLUENES

Trinitrotoluene is obtained from toluene by a process of nitration occurring in three successive stages and involving the intermediate formation of mononitrotoluene and dinitrotoluene.

(1) $C_7H_8 + HNO_3 \rightleftarrows C_7H_7(NO_2) + H_2O$
Toluene — Mononitrotoluene

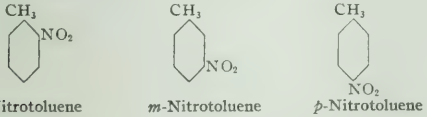
(2) $C_7H_7(NO_2) + HNO_3 \rightleftarrows C_7H_6(NO_2)_2 + H_2O$
Mononitrotoluene — Dinitrotoluene

(3) $C_7H_6(NO_2)_2 + HNO_3 \rightleftarrows C_7H_5(NO_2)_3 + H_2O$
Dinitrotoluene — Trinitrotoluene

The extent to which the nitration may proceed to any one of the above stages is controlled by conditions of treatment and particularly by the factor of acid concentration. This can be regulated by adjustment of the quantity of nitric acid employed and also by varying the amount of sulfuric acid mixed with the nitric to take up and render inactive the water which is one of the reaction products.

### PROPERTIES OF THE NITROTOLUENES

MONONITROTOLUENE, $C_7H_7NO_2$, exists in three isomeric forms, ortho- meta- and para:



*o*-Nitrotoluene *m*-Nitrotoluene *p*-Nitrotoluene

The physical properties of these compounds are indicated below:

| Mononitrotoluene | Melting Point | Boiling Point | Specific Gravity |
|---|---|---|---|
| Ortho..... | —10.5° | 218° | 1.168(15°/15°) |
| Meta..... | 16.0° | 231° | 1.168(15°/15°) |
| Para..... | 54.0° | 238° | 1.231(54°/4°) |

Direct nitration of toluene yields a mixture of the three isomers, which, however, contains little of the meta product. This is in accord with the law of substitution in the benzene ring, the methyl group being one which controls the ortho and para positions.

DINITROTOLUENE exists in six possible isomeric forms, all solids. These are designated by numbers, the position occupied by the methyl group being No. 1.

| Dinitrotoluene | 2:4 | 3:4 | 2:3 | 2:6 | 3:5 | 2:5 |
|---|---|---|---|---|---|---|
| Melting point..... | 70.5° | 60.0° | 63.0° | 61.0° | 93.0° | 52.5° |

The dinitrotoluene produced by the nitration of toluene or of the commercial mixture of *o*- and *p*-nitrotoluenes consists chiefly of the 2:4 and 2:6 products.

TRINITROTOLUENE is theoretically capable of existing in six isomeric forms. Of these the 2:4:6, the 2:3:4 and 2:4:5 compounds have been prepared. The 2:4:6, or "symmetrical" compound, is the best known and is by far the chief constituent of the commercial product.

| Trinitrotoluene | 2:4:6 | 2:3:4 | 2:4:5 |
|---|---|---|---|
| Melting point ..... | 80.6° | 112.0° | 104.0° |

Pure nitrotoluene is a white solid of absolutely neutral reaction and of unusual stability. The commercial product is generally pale yellow. Trinitrotoluene is very slightly soluble in water, either hot or cold. It is sparingly soluble in cold alcohol, but readily in hot, this solvent being one commonly used for the process of recrystallization.

Trinitrotoluene is by far the most valuable explosive now used in military service for bursting charges. The substance may be manufactured with comparative safety and is free from danger of deterioration. It is non-acid and does not act upon metals with which it may come in contact. The lowness of its melting point makes easy the filling of shells and containers, which is accomplished by the simple process of pouring the molten explosive. Trinitrotoluene is sufficiently inert so that the possibility of accidental explosion through concussion is practically nil. It is stated that a shell filled with it may be made to penetrate steel plates without setting off the explosive through the shock. Detonation is accomplished after penetration by means of a time fuse.

### COMMERCIAL PREPARATION OF TRINITROTOLUENE

The commercial preparation of trinitrotoluene is accomplished in either of two general ways: (1) The process may be completed in one stage, or (2) it may be accomplished in several successive stages. In any event, it has been found commercially undesirable, in this country at least, to purify the final product by any process of crystallization or washing which involves the use of organic solvents. The purity of trinitrotoluene is generally determined by its melting point and present specifications place this at 75° C., which is about 5° below the melting point of the pure compound. It has been found possible to attain the desired degree of purity by a simple process of water washing, providing conditions of preparation are right.

THE SINGLE STAGE PROCESS of nitration is of course simple in operation and requires a minimum of plant equipment. It has the decided disadvantage, however, of being uneconomical in acid consumption. The process requires a considerable concentration of acid at the end of the reaction and the resulting spent acid cannot be utilized in the single stage method, although its strength is considerably greater than would be necessary in the earlier stages of the other general process.

PROCESSES INVOLVING SEVERAL STAGES, with complete or partial purification of intermediate products are, of course, expensive as regards costs of labor and plant equipment. They do, however, permit economic utilization of acid, since the spent acid from the final stage may be employed in an earlier stage of the next

cycle, obviating the necessity of discarding any but a thoroughly exhausted waste acid. In addition, as has been shown by the results of the present experiments, the polystage process permits the use of a less expensively purified raw material.

The preparation of trinitrotoluene involves the removal of water-insoluble impurities from the final product or from some one of the other substances, dinitrotoluene, mononitrotoluene, or toluene. Processes involving the use of coal-derived toluene have been dependent upon the purification of the initial substance. In the past, when specifications were more exacting, and especially abroad, crystallization of the final product has been resorted to but this is not practicable under present conditions. The purification of dinitrotoluene involves the same methods as need be applied to trinitrotoluene and that possible medium for purification is likewise eliminated.

## SCOPE AND PLAN OF PRESENT WORK

The present work has been based upon the device of purifying the mono-substitution product. The whole proposition may be stated concisely as follows:

The preparation of satisfactory trinitrotoluene involves a purification from water-insoluble impurities of one of the four substances: toluene, mononitrotoluene, dinitrotoluene or trinitrotoluene. Both toluene and mononitrotoluene are liquids having boiling points sufficiently low that their distillation is a matter involving no inherent difficulty. The purification of dinitrotoluene and trinitrotoluene can be accomplished only through commercially impracticable processes of crystallization or washing which involve the use of organic solvents.

Toluene derived from petroleum cannot be brought to a state of complete purity readily by any methods now known, but by means of simple processes of fractionation it is possible to obtain, from cracked petroleum, toluene with no impurities save paraffin and olefin bodies. The olefins may be removed by extraction with sulfuric acid, and the resulting mixture, when nitrated under proper conditions of acid concentration, yields mononitrotoluene contaminated with the original paraffins, with resinous bodies formed by the action of the acid, and possibly with a small quantity of dinitrotoluene.

Mononitrotoluene boils between 218° C. and 238° C., the paraffins in the neighborhood of 110° and the resins, etc., at temperatures above 300° C. Hence, a simple distillation, preferably *in vacuo* or with steam, gives an easy and practically complete separation of mononitrotoluene from the low boiling paraffins and the high boiling resins.

Since no water-insoluble impurities are present in the mononitrotoluene it may be converted readily into trinitrotoluene by commercially practicable methods.

## EXPERIMENTAL

Samples of toluene were obtained which had been prepared by simple distillation and redistillation of cracked petroleum from the commercial furnaces employed in the Bureau of Mines vapor-phase cracking process.

MONONITROTOLUENE—The first section of the work involved the preparation of pure mononitrotoluene and this process was studied in detail. Large quantities were not used, but data were obtained which can be applied with some exactness to commercial work. It was shown conclusively that no difficulties need be encountered in large scale operations. The mononitrotoluene prepared was analyzed carefully for its purity, as indicated by nitrogen content. Yields were also measured, although no emphasis is laid on these since the scale of operation made them necessarily low.

TRINITROTOLUENE—The analyses of the mono product indicated that it was almost chemically pure but it was thought desirable to actually convert it into the higher substituted compound. Samples of trinitrotoluene were therefore prepared; these, when washed with water, showed melting points of 75° and above. In the course of these preparations valuable indications were obtained as to advantageous methods of procedure for large scale operations, although no final details were worked out.

NITROBENZENE—Finally a simple experiment was performed to verify the obvious conclusion that benzene mixtures would behave in a manner identical with those containing toluene. Nitrobenzene was prepared by the method used for mononitrotoluene. The resulting product was tested by conversion into aniline by the method outlined by Gattermann.[1] This section of the work was purely qualitative and no figures were obtained, but it may be stated that the preparations involved no difficulty and that the behavior of the benzene product was identical with that of the toluene.

ORIGINAL MATERIALS—The original materials were toluene fractions obtained from petroleum cracked by the Bureau of Mines vapor-phase process. The oils were distilled in commercial Badger stills. Analyses of the products yielded the following figures:

| | Sample No. 1 | Sample No. 2 |
|---|---|---|
| Distillation range | 109°–115° | |
| Specific gravity (15°/15°) | 0.832 | 0.823 |
| Toluene content (on basis of sp. gr.)(a) | 72.9 per cent | 66.4 per cent |

(a) Rittman, Twomey and Egloff, *Met. Chem. Eng.*, **13** (1915), 682.

PREPARATION OF MONONITROTOLUENE—The method employed for the preparation of mononitrotoluene was that of Schultz and Flachslander:[2]

The nitration is conducted in a wide-mouthed, round-bottomed flask fitted with a thermometer (bulb immersed in the liquid) and with a short condenser, through which is passed a motor-driven stirrer. The nitrating acid is introduced through the condenser, being run in from a dropping funnel.

For each 100 grams of toluene a mixture of 110 grams of nitric acid (sp. gr. 1.456) and 143 grams of sulfuric acid (sp. gr. 1.84) is required (the mixture made up in these proportions is hereafter designated as "mixed acid"). In the process of nitration the cold mixed acid is run in slowly from the dropping funnel. During the main course of the reaction the temperature is not allowed to rise above from 45° to 55°. At the end, when the concentration of excess acid is small, the mix-

[1] "Practical Methods of Organic Chemistry," second English from fourth German edition, 1907, p. 188.

[2] *J. prakt. Chem.*, [2] **66** (1902), 156.

ture is heated to 100° in order to complete the nitration. It is claimed that by this method it is possible to obtain a yield which is 95 per cent of the theoretical.

After completing the process of nitration the mixture is cooled and then washed with water to remove the remaining acid. The resulting oil is dried and distilled *in vacuo*. The use of vacuum or steam in the distillation does not permit the obtaining of actual boiling points but there is no necessity for this. A low boiling fraction comes over first, which includes the paraffins and any small residue of unnitrated toluene. The thermometer then starts to rise rapidly and at this point the receiver is changed. After the collection of a large fraction the temperature begins another sharp rise and the distillation is then stopped. The residue consists of resins and any di- or trinitrotoluene which may have been formed.

The experiments with mononitrotoluene were conducted to ascertain:

1—The effects of various methods of preliminary deolefinization;

2—The effect of variation in the quantity of nitrating acid upon the degree of purity;

3—The quantitative yields of the samples of mononitrotoluene obtained.

Details of these experiments are given in Table I. In Experiment 2, the sample of the toluene mixture was deolefinized by treatment with quantities of treatment with sulfuric acid. This is, however, undesirable from a commercial point of view. Mechanical difficulties arise on account of the formation of emulsions and, in addition, this treatment is unnecessary since the acid removed is immediately added again when the nitrating "mixed acid" is run in.

The next best yield was obtained when there was no preliminary treatment and this result furnished the key to a solution of this phase of the problem. The quantity of mixed acid used was calculated for 100 grams of actual toluene and as this amount of aromatic hydrocarbon was not present there was some conversion to dinitrotoluene, which substance is in the present course of procedure lost in the residue after distillation. When the preliminary deolefinization was omitted some of the nitric acid was taken up by the unsaturated bodies and the excess reduced, which resulted in an increased yield of mononitrotoluene. From a commercial point of view this is an undesirable mode of procedure since it involves allowing expensive nitric acid to do work which may be performed equally well by cheap sulfuric. It is obvious, however, that the magnitude of the yield is controlled by this factor of acid concentration and it appears that an excess is undesirable from the

TABLE I—MONONITROTOLUENE FROM TOLUENE (*100 Gram Sample—Toluene Content as Given*)
The Preliminary Treatments for Removal of Olefins Are Described in the Text

| Type of Nitration | Exp. No. | Mixed Acid Grams | Toluene used Grams | Yield of crude mononitrotoluene Grams | Yield of Purified (Distilled) Mononitrotoluene: Grams Yield Actual | Theoretical | Per Cent Nitrogen(a) Actual | Theoretical | Actual Per Cent Yield | Purity |
|---|---|---|---|---|---|---|---|---|---|---|
| Olefins Present | 1 | 253 | 72.9 | 95.0 | 79.0 | 108.5 | 10.16 | 10.21 | 72.7 | 99.5 |
| Olefins Removed, sample washed and redistilled | 2 | 253 | 97.0 | 127.0 | 104.5 | 144.5 | 10.19 | 10.21 | 73.2 | 99.8 |
| Olefins Removed, no washing or redistillation | 3*a* | 253 | 88.5 | 127.0 | 86.4 | 131.8 | 10.19 | 10.21 | 66.6 | 99.8 |
| | 3*b* | 253 | 79.2 | 126.0 | 76.8 | 118.0 | 10.17 | 10.21 | 65.3 | 99.6 |
| Same as Experiment 3 | 4*a* | 200 | 79.2 | 126.0 | 90.7 | 118.0 | ... | 10.21 | 77.3 | .... |
| | 4*b* | 200 | 76.2 | 120.0 | 90.0 | 115.3 | 10.04 | 10.21 | 79.3 | 98.5 |
| Same as Experiment 3, but different sample | 5*a* | 180 | 68.8 | 126.0 | 84.4 | 102.5 | ... | 10.21 | 82.2 | .... |
| | 5*b* | 180 | 68.8 | 128.0 | 82.6 | ... | ... | 10.21 | 80.7 | .... |

(*a*) Nitrogen determinations were made under the direction of Mr. W. C. Cope of the Explosives Laboratory of the Bureau of Mines. Analyses were made by Mr. Cope's modification of the Kjeldahl method, which has been devised for nitro-substitution products. (Description about to be published.) The modification is characterized by a preliminary 12-hour cold digestion of the unknown substance with sulfuric acid, salicylic acid and zinc dust.

10 and 5 per cent of its volume of ordinary concentrated sulfuric acid. The product was washed with water and alkali, dried and redistilled. A fraction was collected, boiling between 105° and 110°. This represented 75.2 per cent of the original and, on the approximately correct assumption that no toluene was lost in the preliminary treatment, it contained 97 per cent of actual toluene.

In Experiment 3 the sample of the toluene mixture was deolefinized as in Experiment 2, but the resulting mixture was nitrated immediately after drawing off the second lot of acid sludge.

Experiments 1, 2 and 3 established without any possible doubt the fact that by the simple process of nitration to the mono-stage, with subsequent distillation, it is possible to get rid of the impurities which are associated with aromatic hydrocarbons produced by the cracking of petroleum. The products obtained are pure within the limits of errors of analysis.

Correct indications as to the desirable method of preliminary treatment were obtained only by careful interpretation of results. It appears on superficial examination of the data obtained that the most desirable method on the basis of percentage yield is that which involves purification after the preliminary point of view of yield of the desired product as well as cost of wasted nitric acid. The conditions of preliminary treatment seem to have no effect upon the purity of the product, the general method of procedure being such as to fix this at a high mark.

On the basis of general considerations of expense and convenience the process involving a simple refining with sulfuric acid and no intermediate washing before nitration seemed most desirable, even in face of the fact that it seemed to give lower yields than either of the two other methods. This low yield appeared to be explainable on the basis of excess of nitrating acid and Experiments 4*a* and *b* were therefore conducted to demonstrate whether or not this was the case. The indications furnished by these two experiments were clear-cut and satisfactory. To show that there was nothing accidental about them, and that they were not characteristic of the particular sample of toluene mixture used as original material, some supplementary preparations (Experiments 5*a* and *b*) were made, using a second sample of toluene, which had a lower content of the aromatic hydrocarbon. The quantity of acid used was equivalent to that needed for 71 grams of toluene, so that a 3 per cent excess was present.

## CONCLUSIONS REGARDING THE PREPARATION OF MONONITROTOLUENE

1—Mononitrotoluene of a high degree of purity may be prepared from the paraffin-olefin-toluene mixtures obtained by the simple distillation of cracked petroleum. The purity of the nitro-product and, consequently, its utility for the preparation of water-washed trinitrotoluene, is fixed by the general method of treatment, which ensures a very sharp separation of mononitrotoluene from the impurities associated with it.

2—It is desirable to remove olefins by a preliminary extraction with sulfuric acid. Otherwise they consume expensive nitric acid and incidentally develop so much heat that the process of nitration is difficult to regulate. No washing is necessary between the processes of deolefinization and nitration since such a treatment removes acid which must be added again as soon as nitration is begun.

3—The quantity of nitrating acid mixture should be based approximately on the actual toluene in the mixture to be treated and not on the total quantity of the latter. An excess of acid causes the formation of dinitrotoluene, which under present conditions is an undesirable occurrence.

## PREPARATION OF TRINITROTOLUENE

Experiments on the preparation of trinitrotoluene were not conducted for the purpose of modifying or improving any of the numerous methods which have already been proposed. The work done was for the simple purpose of obtaining absolute verification of the results obtained by the analyses of the samples of mononitrotoluene prepared by the method indicated above. The fact to be established was that the fraction of a per cent of impurities included in the mononitro product did not in any unexpected way interfere with its transformation into water-washed trinitrotoluene of a satisfactory degree of purity.

Preliminary experiments were performed according to various sets of directions found in the literature, but the products obtained invariably melted below the required mark of 75° C. A satisfactory product could always be obtained by a simple crystallization from alcohol but this fact was of little significance.

It finally appeared necessary to concentrate on the details of some specific method and for this purpose the poly-stage process employed by one of the large explosives companies in this country was selected as most promising. Translated into terms of quantities usable in the laboratory the method of procedure is as follows:

FIRST STAGE—*Transformation of mononitrotoluene into dinitrotoluene*

| | |
|---|---|
| Amount of mononitrotoluene | 50 g. |
| Acid concentration | 107.6 g. of a mixture of 1 part by weight of $HNO_3$ (sp. gr. 1.5) and 2 parts $H_2SO_4$ (sp. gr. 1.84) |
| Temperature during addition of acid | 88.0° C. |
| Time of heating | ½ hour at 88.0° C. |

The mixture is then cooled and the spent acid drawn off.

SECOND STAGE—*Transformation of unpurified dinitrotoluene into trinitrotoluene.*

| | |
|---|---|
| Acid concentration | 67 g. of "oleum" (fuming sulfuric acid containing an excess of 20 per cent of $SO_3$ over ordinary conc. $H_2SO_4$). 42 g. of nitric acid (sp. gr. 1.5) |
| Temperature during addition of acid | Below 88.0° C. |
| Heating | 1 hour at 88.0° 1½ hours at 100° |

The mixture is then cooled and the acid drawn off. The remaining product is washed several times with hot water, being stirred with the latter while in a molten condition. It is finally dried.

The first experiments were performed using the quantities of acids specified in these directions but with modifications in the time and degree of heating (Nos. 1 to 4, Table II):

TABLE II—TRINITROTOLUENE FROM MONONITROTOLUENE

| First Stage: Mono- to Di-nitrotoluene, Acid specified | | | Second Stage: Di- to Trinitrotoluene, Acid in Excess of Amount Specified | | | | | | | Yield | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. No. | Heated Hrs. | Temp. °C. | Excess Acid | 95 | Hours heated at Temperatures (° C.) 100 | 110 | 115 | 120 | 130 | In grams | Melting point (a) °C. |
| 1 | 1 | 88 | 0 | 1 | 1½ | 0 | 0 | 0 | 0 | 64 | 57 –72 |
| 2 | 1 | 88 | 0 | 1 | 1 | 0 | ½ | 0 | 0 | 61 | 58 –69 |
| 3 | 1 | 88 | 0 | 1 | 1½ | 1 | 0 | 1½ | 1½ | 61 | 55 –72 |
| 4 | ½ | 115 | 0 | 1 | 0 | 0 | 0 | 1½ | 0 | 60 | 69 –77 |
| 5 | ½ | 115 | 25 | 1 | 1½ | 1 | 0 | 1½ | 0 | 60 | 73.5–77.5 |
| 6 | ½ | 115 | 25 | 1 | 0 | 0 | 0 | 1½ | 0 | 58 | 75 –79 |
| 7 | 1 | 115 | 50 | 1 | 1½ | 0 | 0 | 0 | 0 | 60 | 74 –80 |
| 8 | 1 | 115 | 50 | 1 | 1½ | 0 | 0 | 0 | 0 | 56 | 75.5 79.5 |
| 9 | 1 | 115 | 50 | 1 | 4 | 0 | 0 | 0 | 0 | 60 | 75.5–79 |
| 10 | ½ | 115 | 50 | 1 | 0 | 0 | 0 | 1½ | 0 | 60 | 78 –79.5 |

(a) Melting points were determined under the direction of Mr. Cope in the Explosives Laboratory of the Bureau of Mines. Thermometers were carefully standardized. The apparatus was that described by Mulliken, "A Method for the Identification of Pure Organic Compounds," Vol. I (1908), p. 218.

This series of experiments was instructive, since it appeared that no improvement could be secured through increasing time of heating and temperature in the second stage of the process. A marked improvement, however, appeared by the modification of treatment in the first stage. Heating for one-half hour at 115° instead of an hour at 88° resulted in an increase of about 10° in the melting point of the product.

The next series of experiments involved a 25 per cent increase in the amount of acid used for the second stage of the nitration (Nos. 5 and 6, Table II). An improvement was shown here, the product obtained in one case being just above the satisfactory degree of purity.

From a commercial point of view there seems to be no inherent objection to the employment of a considerable excess of acid at the second stage of the reaction, since the spent acid may be utilized in an earlier stage in the next cycle. Hence, instead of proceeding with experiments involving a 25 per cent excess of acid, the quantity was increased to a 50 per cent excess and a third series of preparations made (Nos. 7–10, Table II). Three of these four experiments yielded satisfactory products and there seemed to be no doubt but that with the higher concentration of acid there was little difficulty in producing a trinitrotoluene of a satisfactory degree of purity. The yields were all in the neighborhood of 60 grams, which is about 70 per cent of the theoretically possible amount. This is, of course, low, for commercial work, but conditions here were less favorable than they would be on a large scale and, at best, the work has only remotely approached completion in the matter of determining optimum conditions for the process of nitration. Here as well as in the earlier

part of the work, attention was given only to the establishment of general principles and no attempt was made to learn details.

### CONCLUSIONS REGARDING THE PREPARATION OF TRINITROTOLUENE

1—Trinitrotoluene, of a satisfactory degree of purity, may be prepared from the mononitrotoluene obtained by the nitration of the toluene-paraffin-olefin mixtures produced by the fractionation of "cracked" petroleum.

2—From the laboratory point of view, at least, the poly-stage process seems best. The transformation from mono- to di-product should involve a fair degree of heating and a moderate concentration of acid. The final stage of the nitration should be conducted with a considerable excess of strong acid, which acid need not be wasted since when drawn off it may be used in an earlier stage of the next cycle of nitration.

### GENERAL SUMMARY

I—The aromatic hydrocarbons produced by the "cracking" of petroleum may be utilized for the preparation of nitro-products without being brought to a high degree of purity. The foreign substances not easily removable are paraffins and these are not affected by reagents of sufficient vigor to transform the aromatics quantitatively into mono-nitro products. These compounds may be separated in a high degree of purity by a simple process of distillation.

II—The mononitrotoluene prepared by the method indicated may be readily converted into trinitrotoluene which, when washed with hot water, satisfies the ordinary commercial specification of a melting point of 75° C.

CHEMICAL SECTION OF THE PETROLEUM DIVISION
U. S. BUREAU OF MINES

## THERMAL REACTIONS OF AROMATIC HYDROCARBONS IN THE VAPOR PHASE[1]

By W. F. Rittman, O. Byron and G. Egloff

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In connection with the phenomena of thermal decomposition or "cracking" of hydrocarbons a study has been outlined for the purpose of obtaining comprehensive data regarding the whole field. A first series of experiments[2] dealt with the production of gas and determined the influence of temperature, pressure and concentration on the yield and composition of the product. Another series of experiments[3] dealt with liquid reaction products and indicated conditions favorable for the production of (1) open-chain hydrocarbons and (2) aromatic hydrocarbons; it was shown that the temperature range may be divided roughly as follows with regard to the products of the cracking reaction: up to about 600° C. the formation of low-gravity hydrocarbons of the open chain class is favored; from 600° to 800° aromatic compounds are produced in large quantity; above 800° the maximum products are carbon and gas.

From both a scientific and a commercial point of view the differences among various aromatic hydrocarbons are of almost, if not quite, as great importance as the differences among classes. The present series of experiments has, therefore, been conducted for the purpose of establishing facts concerning the influence of conditions of temperature and pressure on inter-aromatic reactions. Four typical monocyclic hydrocarbons—cymene, xylene, toluene and benzene—were subjected to cracking, each at three different temperatures and at each temperature under four pressures. Some work has been done also with the solid hydrocarbons naphthalene and anthracene, but on account of experimental difficulties, the results obtained are only qualitative.

From the results of the study of reaction products, indications have been obtained which may be summarized in the following general way:

1—(*a*) The course of the reaction is in the direction of decrease in size of molecule when the degree of saturation is unchanged.

(*b*) Reactions may occur in the direction of de-hydrogenation either with increase or with decrease in size of molecule.

2—Reverse reactions occur in practically negligible amount.

### HISTORICAL

More or less work seems to have been done by previous investigators on the problem of thermal reactions of aromatic compounds but in no case has a systematic study been made. The information desired at present concerns the influence of conditions of temperature and pressure upon quantitative and qualitative relations among end products and this is not adequately supplied by the literature.

The classic researches of Bertholet[1] have furnished a foundation for our knowledge in this general field. His series of thermal reactions is comprehensive and the results obtained are valuable, though not such as to supply the needs of the present case.

Ferko[2] furnished some valuable information, particularly with regard to the direction of reactions. He passed the vapors of several hydrocarbons, either pure, or mixed with ethylene gas, through an iron tube heated over a 40 cm. length in a gas furnace. The products were condensed and their composition studied. The more important of the results obtained are summarized in Table I. Without attempting a

TABLE I—SUMMARY OF RESULTS OBTAINED BY FERKO

| | | Reaction Products Percentages of Original Material | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Original Material Hydrocarbon | Quantity Grams | Benzene | Toluene | Styrolene | Ethyl benzene | Dinaphthalene | Diphenyl | Naphthalene | Phenanthrene | Anthracene |
| Benzene and ethylene | 1320 | 6.0 | 0.0 | 1.3 | 0.0 | 0.0 | 22.7 | 0.0 | 0.8 | 1.1 |
| Toluene | 1300 | 11.5 | 13.8 | 0.5 | 0.0 | 0.0 | 2.1 | 3.0 | 1.1 | 1.0 |
| Toluene and ethylene | 1300 | 15.4 | 12.3 | 0.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.5 |
| Naphthalene and ethylene | 900 | 0.0 | 0.0 | 0.0 | 0.0 | 13.3 | 0.0 | 44.5 | 0.1 | 0.0 |
| Ethyl benzene | 500 | 15.0 | 1.0 | 2.0 | 4.0 | 0.0 | 0.6 | 2.2 | 2.6 | 0.4 |

detailed study of this table it may be seen that no reaction products are obtained which are not in the order of decrease of saturation, or of molecular weight

[1] Published with the permission of the Director of the Bureau of Mines.
[2] Rittman and Whitaker, THIS JOURNAL, **6** (1914), 383 and 472.
[3] Rittman, *Ibid.*, **7** (1915), 945.

[1] *Ann. chim. phys.*, [4] **9** (1866), 445; **12** (1867), 5; **16** (1869), 143.
[2] *Ber.*, **20** (1887), 660.

if saturation remains unchanged. Thus benzene yields no toluene nor any other compound of equal saturation or of greater molecular weight. Naphthalene yields neither benzene nor toluene. From ethyl benzene, however, it is possible to obtain toluene, benzene and compounds of lower saturation. The work of Ferko seems to have been the most valuable of all hitherto done in this field but it gives little attention to the influence of temperature and none to that of pressure.

Haber[1] studied the thermal reactions of various substances, among them benzene, at temperatures ranging between 600–800° C. and 900–1000° C. One of his observations is contrary to the results of the present experiments. He states that although benzene goes readily to diphenyl it does not form naphthalene.

McKee[2] has, as a result of some qualitative experiments, concluded that the order of hydrocarbon decomposition is: higher paraffins ⟶ lower paraffins ⟶ olefins ⟶ acetylenes ⟶ benzene and homologs ⟶ diphenyl ⟶ naphthalene, etc., ⟶ tarry matter ⟶ carbon and gas. In his experiments benzene was passed through a hot copper tube and the degree of decomposition determined by change in specific gravity of the product. No analysis or separation seems to have been attempted upon the latter.

Smith and Lewcock[3] passed benzene through an iron tube and at 800° C. obtained a 25 per cent yield of diphenyl. They were not, however, able to reverse the reaction, which inability they attributed to experimental difficulties. They observed that the quantity of diphenyl produced increased with the rate of feed, which indicates that this is not an equilibrium product, but simply one which is intermediate.

## THEORETICAL

GENERAL CONSIDERATIONS—In the present as well as in the earlier series of experiments cracking was produced in a system having a single (gaseous) phase. The characteristics and advantages of this method of procedure have been already discussed in detail.[4] It is sufficient in the present connection to recall the fact that the basic reason for the employment of the one-phase system is that it permits the independent regulation of the two factors of temperature and pressure. In any two-phase system each of these is a function of the other. There are numerous other advantages but these have received adequate discussion in earlier connections.

EQUILIBRIUM RELATIONS—In each of the two preceding communications applications have been given of the Nernst approximation formula for equilibrium constants. The use of this expression is particularly helpful in connection with the present series of experiments as the reactions are obtained upon pure chemical compounds instead of complex mixtures. It is possible, therefore, to write equations which are entirely representative of what may occur instead of merely typical. The figures obtained are understood to be representative only of general tendencies but are of much value when interpreted in this light.

The figures in Table II represent equilibrium relations for a series of reactions, any or all of which may have occurred in the present experiments. A first point to be considered is the influence of variations in pressure. All the reactions occur with an increase in volume and therefore it is to be expected that the effect of pressure will be inimical. This consideration is, however, complicated by the necessity of taking account of another factor. The use of the Nernst formula assumes that the reactions have proceeded until equilibrium has been reached and it is doubtful if this is the case, especially for the reactions at lower temperatures.[1] According to the law of mass action, reaction velocity is proportional to the product of the concentrations of the reacting substances and concentration is, in the present case, directly proportional to pressure. It appears, therefore, that increase in pressure may be favorable up to a point where the reactions proceed with sufficient rapidity to attain to a state of equilibrium. Increase in pressure above this will undoubtedly tend to shift the equilibrium unfavorably for the reactions indicated from left to right in the equations.

Consideration of the effect of temperature is also complicated. The constants invariably increase with temperature and this should indicate that even greater degrees of heat would be favorable. It must be remembered, however, that no one reaction can be considered as happening alone. Each major reaction is coincident with a number of by-reactions and the

TABLE II—QUANTITATIVE STUDY OF EQUILIBRIA

| No. | Reactions | Heats of reaction | Volume changes | Formulas refer to partial pressures | Approximate $K_{650}$ | Approximate $K_{725}$ | Approximate $K_{800}$ |
|---|---|---|---|---|---|---|---|
| 1 | $4C_{10}H_{14} \rightleftarrows 5C_8H_{10} + 3H_2$ (Cymene ⟶ Xylene) | −18000 | 4 to 8 | $K = \frac{(C_8H_{10})^5 (H_2)^3}{(C_{10}H_{14})^4}$ | $6.8 \times 10^{32}$ | $4.7 \times 10^{32}$ | $4.7 \times 10^{32}$ |
| 2 | $7C_{10}H_{14} \rightleftarrows 10C_7H_8 + 9H_2$ (Cymene ⟶ Toluene) | −82000 | 7 to 19 | $K = \frac{(C_7H_8)^{10} (H_2)^9}{(C_{10}H_{14})^7}$ | $2.0 \times 10^{66}$ | $1.4 \times 10^{68}$ | $2.0 \times 10^{70}$ |
| 3 | $3C_{10}H_{14} \rightleftarrows 5C_6H_6 + 6H_2$ (Cymene ⟶ Benzene) | −68500 | 3 to 11 | $K = \frac{(C_6H_6)^5 (H_2)^6}{(C_{10}H_{14})^3}$ | $7.8 \times 10^{49}$ | $2.8 \times 10^{52}$ | $1.0 \times 10^{54}$ |
| 4 | $7C_8H_{10} \rightleftarrows 8C_7H_8 + 3H_2$ (Xylene ⟶ Toluene) | −90800 | 7 to 11 | $K = \frac{(C_7H_8)^8 (H_2)^3}{(C_8H_{10})^7}$ | 1.1 × 10 | $6.6 \times 10^{8}$ | $3.1 \times 10^{10}$ |
| 5 | $3C_8H_{10} \rightleftarrows 4C_6H_6 + 3H_2$ (Xylene ⟶ Benzene) | −65600 | 3 to 7 | $K = \frac{(C_6H_6)^4 (H_2)^3}{(C_8H_{10})^3}$ | $1.1 \times 10^{33}$ | $2.1 \times 10^{34}$ | $4.3 \times 10^{35}$ |
| 6 | $6C_7H_8 \rightleftarrows 7C_6H_6 + 3H_2$ (Toluene ⟶ Benzene) | −40700 | 6 to 10 | $K = \frac{(C_6H_6)^7 (H_2)^3}{(C_7H_8)^6}$ | $2.9 \times 10^{27}$ | $3.2 \times 10^{28}$ | $2.7 \times 10^{29}$ |

[1] ... *Jour.*, **29**, 1809, 2091.
[2] *Jour. Soc. Chem. Ind.*, **27** (1904), 403.
[3] *Jour. Chem. Soc.*, **101** (1912), 1483.
[4] Rittman, *Jour. ...*

[1] Rittman, THIS JOURNAL, **6** (1914), 1027; *Jour. Soc. Chem. Ind.*, **33** (1914), 626; Whitaker and Alexander THIS JOURNAL **7** (1915), 484

establishment of conditions which apparently are favorable for the main reaction may in actual fact hinder it on account of greater favoring of minor reactions; for example, benzene formation would seem to be favored by increasing temperature even beyond the 800° limit. It appears, however, that even at this mark the reaction has suffered on account of greater favoring of other products and the maximum yields of benzene occur in the 650° and 725° runs.

The chief value of the constants lies in the indication they give of the general tendencies of reactions. An examination of the values in Table II makes evident the fact that all the reactions should occur principally in the direction indicated from left to right in the equations. The magnitude of the reverse reactions would be proportional to the reciprocals of the constants and these in most cases are negligibly small.

## EXPERIMENTAL

The scheme of procedure followed in the present experiments was, with slight exceptions, identical with that described in the earlier communications.[1] The apparatus consisted of an electrically heated cracking furnace equipped at one end with an oil-feed cup and a vaporizing device, and at the other with a condenser, receivers for liquid reaction products, and a pressure-regulating device.

One modification in the making of the "run" is worthy of mention. In the earlier series of experiments pressures were built up in the cracking furnace by the decomposition of some of the oil used in the run. This necessitated the introduction of a source of error, which in the more recent experiments, it has been found possible to eliminate. Before the beginning of each pressure run the system was connected with a compressor and natural gas[2] pumped in until the gauge gave the proper reading. The compressor was then shut off by closing a valve and the run started.

For all the liquid hydrocarbons the original material was allowed to flow into the furnace at the rate of about 6 cc. per minute. In the cases when the solid hydrocarbons, naphthalene and anthracene, were used as starting-out material it was, of course, necessary to keep them in a molten condition during the run by applying heat to the feed cup. Even then considerable experimental difficulty was involved and no attempt was made to obtain results of more than qualitative accuracy.

The supplementary determinations were made upon quantities of recovered oil too small to permit separation of pure products. A single analytical distillation was made through an 8-in. Hempel column and cuts made at 100°, 125°, 150°, and 200°. The first cut was taken as representative of benzene, the second of toluene, the third of xylene, and the fourth of cymene. Above 200° the distillation was continued with a shorter fractionating column and cuts made at intervals of 50°. These distillates were chilled and examined for the separation of solid naphthalene and anthracene. On account of the smallness of the quantities obtained no attempt was made to obtain quantitative results for the solid products.

The total scheme of procedure may be summarized as follows:

### "RUN" OR MAJOR EXPERIMENT

1—Cracking of a quantity (generally 500–600 cc.) of hydrocarbon under regulated conditions of temperature and pressure.

2—Determination of quantities of liquid and solid reaction products.

### SUPPLEMENTARY DETERMINATIONS

1—Distillation of liquid reaction products through Hempel fractionating columns.

2—Determinations of specific gravities of total reaction products and of distillation cuts.

## EXPERIMENTAL MATERIAL

BENZENE was the purest material commercially obtainable. The sample used was particularly good as is shown by the data in Table III. TOLUENE and XYLENE were the "chemically pure" market products. CYMENE also was a commercial product.

TABLE III—ORIGINAL PRODUCTS USED IN EXPERIMENTS

| Product | Sp. gr. 15°/15° | Fractional Distillation | | | |
|---|---|---|---|---|---|
| Benzene | 0.879 | 98 per cent between 80 and 81° C. | | | |
| Toluene | 0.869 | Temp. 98 | 98–100 | 100–110 | 110–115° C. |
| | | % 1st drop | 0.2 | 92.0 | 4.0 |
| Xylene | 0.862 | Temp. 88 | 88–120 | 120–137° C. | |
| | | % 1st drop | 0.7 | 99.3 (flask dry) | |
| Cymene | 0.863 | Temp. 165° | 170–179° C. | | |
| | | % 1st drop | 90.0 | | |

## GENERAL RESULTS OF EXPERIMENTS

The entire collection of data obtained in the present series of experiments appears in Table IV. This table is, on account of its size and necessity arrangement, not particularly readable and special tables have been prepared to set forth the various indications obtained: it does, however, show the scope and magnitude of the work and indicates the nature of the measurements which have been made.

Results are recorded in terms of percentage by volume except in cases where either starting-out material or reaction product was a solid. In such instances mass relations are given.

It will be noted that for the four liquid hydrocarbons—cymene, xylene, toluene and benzene—the series of experiments are complete. Quantitative results for the distillations are given for cuts up to 200° and above that temperature the indications for naphthalene and anthracene are given by plus (+) and minus (—) signs. For the experiments where naphthalene and anthracene were starting-out material no distillates were obtained below 200° C. and all the results are therefore qualitative.

### ANALYSES OF QUANTITATIVE RESULTS (TABLE V)

(*a*) PERCENTAGE YIELD OF LIQUID REACTION PRODUCTS decreases with increase in temperature and in general with increase in pressure. This percentage represents the total of liquid products and soluble products which are soluble therein, excluding only carbon and gas. The figures given are in a way representative of the stability of the various compounds, their resistance to conversion into carbon

[1] Whitaker and Rittman, *Loc. cit.*; Rittman, *Loc. cit.*

[2] Natural gas was used because it is largely methane, which is one of the end products of all cracking reactions.

TABLE IV—GENERAL RESULT OF CRACKING EXPERIMENTS

| Temperatures (°C.) | 650 | 650 | 650 | 650 | 725 | 725 | 725 | 725 | 800 | 800 | 800 | 800 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CYMENE | Vac. | 1 At. | 12 At. | 18 At. | Vac. | 1 At. | 12 At. | 18 At. | Vac. | 1 At. | 12 At. | 18 At. |
| Volume used, cc. | 500 | 600 | 600 | 600 | 500 | 400 | 600 | 600 | 500 | 500 | 600 | 600 |
| Per cent vol. recovered | 83.0 | 62.0 | 53.3 | 40.8 | 52.0 | 40.0 | 27.5 | 25.0 | 49.0 | 17.6 | 15.8 | 0.0 |
| Per cent wt. carbon | 1.8 | 1.0 | 10.2 | 16.3 | 2.4 | 3.6 | 37.4 | 32.8 | 1.3 | 9.0 | 20.8 | 0.0 |
| Specific gravity | 0.895 | 0.921 | 0.924 | 0.916 | 0.927 | 0.982 | 0.945 | 0.934 | 0.951 | 0.995 | 0.926 | .. |
| First drop | 97° | 69° | 80° | 70° | 97° | .... | 75° | .... | 73° | .... | .... | .. |
| | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. |
| 0-100° | 0.2 | .... | 9.2 | 0.877 | 12.0 | 0.876 | 15.1 | 0.875 | 0.2 | .... | 3.7 | .... | 10.2 | 0.881 | 3.8 | 0.872 | 1.5 | .... | 1.6 | 0.872 | 3.8 | 0.865 | 0.0 | .. |
| 100-125° | 14.5 | 0.869 | 2.5 | 0.874 | 2.7 | 0.875 | 1.9 | 0.873 | 3.9 | 0.878 | 7.4 | 0.876 | 2.3 | 0.870 | 5.0 | 0.877 | 4.7 | 0.874 | 1.9 | 0.874 | 1.3 | 0.868 | 0.0 | .... |
| 125-150° | 17.8 | 0.872 | 5.9 | 0.876 | 4.0 | 0.874 | 4.9 | 0.867 | 8.9 | 0.880 | 5.2 | 0.885 | 2.1 | 0.870 | 2.8 | .... | 9.5 | 0.882 | 1.6 | 0.878 | 1.6 | .... | 0.0 | .... |
| 150-200° | 34.5 | 0.878 | 21.6 | 0.899 | 21.3 | 0.874 | 10.6 | 0.873 | 17.0 | 0.888 | 5.4 | 0.898 | 3.0 | 0.898 | 7.5 | 0.870 | 14.5 | 0.895 | 1.6 | .... | 5.7 | 0.880 | 0.0 | .... |
| Naphthalene | — | .... | — | .... | + | .... | + | .... | — | .... | + | .... | + | .... | — | .... | — | .... | — | .... | — | .... | — | .... |
| Anthracene | — | .... | — | .... | — | .... | + | .... | — | .... | — | .... | — | .... | — | .... | — | .... | — | .... | — | .... | — | .... |
| XYLENE | | | | | | | | | | | | | | | | | | | | | | | | |
| Volume used, cc | 500 | 500 | 600 | 600 | 500 | 500 | 600 | 600 | 500 | 590 | 600 | 425 |
| Per cent vol recovered | 95.0 | 69.0 | 66.0 | 64.3 | 72.0 | 60.0 | 54.2 | 46.6 | 66.0 | 27.1 | 31.7 | 11.5 |
| Per cent wt carbon | 0.9 | 1.5 | .... | 4.4 | 6.0 | — | 13.6 | 25.8 | 0.5 | 25.0 | 39.5 | 38.4 |
| Specific gravity | 0.879 | 0.905 | 0.914 | 0.899 | 0.888 | 0.906 | 0.911 | 0.900 | 0.912 | 0.923 | 0.904 | 0.945 |
| First drop | 77° | 80° | 60° | .... | 68° | 82° | 65° | 98° | 87° | 77° | 68° | .. |
| | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. |
| 0-100° | 0.3 | .... | 4.1 | 0.868 | 3.8 | 0.855 | 0.6 | .... | 0.0 | .... | 2.0 | .... | 3.2 | 0.857 | 0.0 | .... | 0.7 | .... | 8.3 | 0.878 | 9.1 | 0.866 | 5.4 | 0.875 |
| 100-125° | 2.6 | .... | 15.4 | 0.870 | 18.7 | 0.867 | 9.2 | 0.858 | 9.2 | 0.861 | 34.5 | 0.862 | 15.2 | 0.869 | 12.6 | 0.872 | 18.5 | 0.874 | 7.2 | 0.874 | 8.6 | 0.867 | 0.8 | 0.875 |
| 125-150° | 80.0 | 0.868 | 37.7 | 0.870 | 31.7 | 0.868 | 45.0 | 0.856 | 52.5 | 0.862 | 40.0 | 0.877 | 27.0 | 0.862 | 26.0 | 0.869 | 35.6 | 0.872 | 4.5 | 0.874 | 7.9 | 0.864 | 1.1 | 0.875 |
| 150-200° | 1.9 | .... | 2.2 | 0.911 | 0.7 | .... | 0.6 | .... | 2.4 | .... | 6.0 | 0.899 | 0.0 | .... | 1.6 | .... | 2.3 | .... | 0.9 | .... | .... | .... | 1.5 | 0.875 |
| Naphthalene | — | .... | — | .... | — | .... | + | .... | — | .... | + | .... | - | .... | + | .... | - | .... | — | .... | .... | .... | .... | .... |
| Anthracene | — | .... | — | .... | — | .... | — | .... | — | .... | + | .... | — | .... | — | .... | + | .... | — | .... | - | .... | .... | .... |
| TOLUENE | | | | | | | | | | | | | | | | | | | | | | | | |
| Volume used, cc | 500 | 600 | 480 | 600 | 500 | 600 | 600 | 475 | 500 | 600 | 600 | 600 |
| Per cent vol recovered | 98.0 | 98.3 | 94.8 | 60.8 | 85.0 | 64.2 | 48.3 | 18.0 | 66.0 | 32.5 | 34.2 | 11.7 |
| Per cent wt carbon | 0.0 | 1.0 | 4.7 | 5.9 | 1.4 | 1.3 | 20.1 | 34.0 | 1.8 | 40.0 | 24.3 | 23.4 |
| Specific gravity | 0.872 | 0.894 | 0.933 | 0.912 | .... | 0.924 | 0.918 | 0.929 | 0.903 | 0.931 | 0.925 | 0.927 |
| First drop | .... | 66° | 88° | 82° | 80° | 76° | .... | 73° | .... | .... | .... | .. |
| | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. |
| 0-100° | 0.0 | .... | 3.9 | .... | 21.8 | 0.872 | 18.2 | 0.877 | 2.1 | .... | 17.3 | 0.874 | 30.7 | 0.883 | 10.4 | 0.879 | 5.6 | .... | 17.6 | 0.880 | 16.4 | 0.866 | 3.0 | 0.874 |
| 100-125° | 91.6 | 0.871 | 85.0 | 0.875 | 55.0 | 0.868 | 31.0 | 0.874 | 70.5 | 0.870 | 34.0 | 0.873 | 7.5 | 0.870 | 2.7 | .... | 49.5 | 0.872 | 6.6 | 0.879 | 7.5 | 0.873 | 4.0 | 0.874 |
| 125-150° | 3.4 | .... | 0.2 | .... | 0.0 | .... | 0.0 | .... | 4.2 | .... | 0.0 | .... | 0.7 | .... | 0.0 | .... | 0.0 | .... | 0.0 | .... | 1.2 | .... | 1.6 | .... |
| 150-200° | .... | .... | 0.5 | .... | 0.0 | .... | 0.0 | .... | 0.2 | .... | 2.6 | .... | 1.2 | .... | 5.0 | .... | 0.1 | .... | 0.0 | .... | 0.0 | .... | 0.7 | .... |
| Naphthalene | + | .... | + | .... | — | .... | + | .... | + | .... | + | .... | — | .... | — | .... | + | .... | — | .... | + | .... | — | .... |
| Anthracene | — | .... | — | .... | — | .... | — | .... | — | .... | — | .... | + | .... | — | .... | + | .... | — | .... | + | .... | — | .... |
| BENZENE | | | | | | | | | | | | | | | | | | | | | | | | |
| Volume used, cc | 500 | 600 | 600 | 335 | 500 | 500 | 600 | 600 | 500 | 500 | 600 | 600 |
| Per cent vol. recovered | 90.0 | 86.6 | 87.5 | 73.1 | 94.0 | 90.0 | 58.3 | 53.3 | 87.0 | 62.0 | 22.5 | 18.3 |
| Per cent wt. carbon | 0.2 | 0.9 | 1.5 | 11.9 | 1.0 | 1.4 | 15.3 | 34.0 | 2.5 | 1.6 | 6.3 | 35.0 |
| Specific gravity | 0.896 | 0.898 | 0.941 | 0.921 | 0.904 | 0.945 | 0.946 | 0.923 | 0.906 | 0.959 | 0.922 | 0.928 |
| First drop | 64° | 69° | 69° | 76° | 76° | 65° | 70° | 71° | 77° | 76° | 68° | 64° |
| | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. | % Orig. | Sp. Gr. |
| 0-100° | 78.5 | 0.881 | 66.5 | 0.885 | 59.4 | 0.886 | 57.0 | 0.878 | 77.5 | 0.888 | 61.5 | 0.815 | 39.7 | 0.886 | 42.3 | 0.885 | 63.0 | 0.883 | 35.6 | 0.886 | 16.1 | 0.888 | 12.1 | 0.884 |
| 100-125° | 1.6 | 0.882 | 0.0 | .... | 0.1 | .... | 0.4 | .... | 1.4 | .... | 0.9 | .... | 0.0 | .... | 0.0 | .... | 0.9 | .... | 0.3 | .... | 0.0 | .... | 0.0 | .... |
| 125-150° | 0.8 | .... | 0.0 | .... | 0.0 | .... | 0.0 | .... | 1.4 | 0.864 | 0.7 | .... | 0.0 | .... | 0.0 | .... | 1.7 | .... | 0.5 | .... | 0.0 | .... | 0.0 | .... |
| 150-200° | 0.4 | .... | 1.2 | .... | 0.0 | .... | 0.0 | .... | 2.8 | 0.906 | 0.7 | .... | 0.0 | .... | 0.0 | .... | 6.9 | .... | 3.0 | .... | 0.0 | .... | 0.0 | .... |
| Naphthalene | + | .... | + | .... | + | .... | + | .... | + | .... | — | .... | + | .... | + | .... | + | .... | + | .... | + | .... | — | .... |
| Anthracene | + | .... | — | .... | — | .... | — | .... | — | .... | — | .... | + | .... | + | .... | — | .... | + | .... | + | .... | — | .... |
| NAPHTHALENE | | | | | | | | | | | | | | | | | | | | | | | | |
| Weight used, grams | 400 | 400 | 432 | .... | 400 | 414 | 384 | .... | 400 | 500 | 427 | .... |
| Per cent vol recovered | 76.0 | 65.7 | 30.0 | .... | 66.4 | 65.4 | .... | .... | 85.9 | 80.8 | 19.8 | .... |
| Per cent carbon | 0.0 | 3.3 | 21.0 | .... | 3.5 | 7.0 | 40.0 | .... | 9.5 | 13.6 | 5.0 | .... |
| First drop | 205° | 200° | 205° | .... | 200° | 210° | .... | .... | .... | .... | .... | .. |
| Naphthalene | + | + | + | .... | + | + | + | .... | + | + | + | .. |
| Anthracene | — | — | — | .... | + | + | + | .... | + | + | + | .. |
| ANTHRACENE | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .. |
| Weight used, grams | .... | 125 | .... | .... | 125 | .... | .... | .... | .... | .... | .... | .. |
| Per cent recovered | .... | 63.2 | .... | .... | 56.0 | .... | .... | .... | .... | .... | .... | .. |
| Per cent carbon | .... | 18.0 | .... | .... | 22.0 | .... | .... | .... | .... | .... | .... | .... |
| First drop | .... | 300° | .... | .... | ..... | .... | .... | .... | .... | .... | .... | .... |
| Naphthalene | .... | — | .... | .... | — | .... | .... | .... | .... | .... | .... | .... |
| Anthracene | .... | + | .... | .... | + | .... | .... | .... | .... | .... | .... | .... |

and gas being indicated by the amount of liquid product obtained. It appears that for the four liquid hydrocarbons, the order of decreasing stability is benzene, toluene, xylene and cymene. This is as would be expected on the grounds of the theory that with similar molecular form the more unwieldy units of matter are the more easily broken down.

(*b*) PERCENTAGE OF ORIGINAL HYDROCARBON RECOVERED is another index of the stability of the compounds cracked. It represents total resistance to transformation while the percentage yield of liquid products represents resistance to conversion into carbon and gas. It appears that the order of stability is the same as that indicated in (*a*) but that there are greater differences. The effects of temperature and pressure are analogous to those indicated in (*a*).

(*c*) BENZENE FORMATION—It appears from the figures in Table V*c* that benzene is formed in appreciable quantity from each of the three hydrocarbons, cymene, xylene, and toluene. The figures in Table IV indicate that neither benzene nor any of the other three monocyclic compounds are produced by the cracking of naphthalene or anthracene.

Section B of Table V*c* shows that optimum conditions for benzene formation are represented by the temperatures 650° and 725° and that pressure is favorable up to a certain limit which appears to be somewhere between 1 and 12 atmospheres. The runs at 18 atmospheres in general show decreases in the amount of benzene produced. This seems to indicate that somewhere between the pressures of 1 and 12 atmospheres a sufficient concentration is attained to permit the hydrocarbons to reach a state of equilibrium during their passage through the furnace and that the higher pressures are unfavorable for benzene production, as is indicated by the volume changes occurring in the reactions.

(*d*) TOLUENE FORMATION—Toluene may be formed from both xylene and cymene, most readily from the former. The amount which can be produced from benzene is negligible, that from naphthalene and anthracene nil. The effects of temperature and pressure seem rather irregular, very possibly on account of experimental error. The general tendency seems to be for maximum yields to occur with decreasing temperature as pressure increases. Thus in the xylene figures in Section B, Table V*d*, a maximum appears at 800° for vacuum runs, at 725° for runs at 1 atmosphere and at 650 for the runs at 12 atmospheres. Beyond this point the curve seems to swing the other way. A like tendency will be noted among cymene figures if the obviously wrong bracketed value is omitted from consideration.

(*e*) XYLENE FORMATION—The figures in Table V*e* show that while xylene may be formed in moderate quantity from cymene, the amounts produced from toluene and benzene are exceedingly small. The formation of xylene seems to be favored by low temperature and low pressure.

(*f*) CYMENE FORMATION—Cymene is formed in negligible quantity from xylene, toluene, and benzene (Table V*f*), and not at all from naphthalene and anthracene. This compound appears to be particularly unstable under conditions included in the present experiments, as is evidenced by the fact that only a small amount (13.0 per cent on the average) remains unchanged when this hydrocarbon is employed as starting-out material.

TABLE V—ANALYSIS OF QUANTITATIVE RESULTS

| | | (*a*) YIELD (%) OF LIQUID REACTION PRODUCTS | | | | (*b*) RECOVERY (%) OF ORIGINAL HYDROCARBON | | | | PERCENTAGE FORMATION OF LIQUID AROMATIC HYDROCARBONS | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | (*c*) BENZENE FORMATION | | | | (*d*) TOLUENE FORMATION | | | | (*e*) XYLENE FORMATION | | | | (*f*) CYMENE FORMATION | | | |
| SECTION A: | | | | | | | | | | | | | | | | | | | | | | | |
| Temp. °C. | Press. Atm. | Cymene | Xylene | Toluene | Benzene | Cymene | Xylene | Toluene | Benzene | Cymene | Xylene | Toluene | Benzene | Cymene | Xylene | Toluene | Benzene | Cymene | Xylene | Toluene | Benzene | Cymene | Xylene | Toluene | Benzene |
| 650 | Vac. | 83.0 | 95.0 | 98.0 | 90.0 | 34.5 | 80.0 | 91.6 | 78.5 | 0.2 | 0.3 | 0.0 | 78.5 | [14.5] | 2.6 | 91.6 | 1.6 | 17.8 | 80.0 | 3.4 | 0.8 | 34.5 | 1.9 | 0.0 | 0.4 |
| | 1 | 62.0 | 69.0 | 98.3 | 86.6 | 21.6 | 37.7 | 85.0 | 66.5 | 9.2 | 4.1 | 3.9 | 66.5 | 2.5 | 15.4 | 85.0 | 0.0 | 5.9 | 37.7 | 0.0 | 0.0 | 21.6 | 2.2 | 0.5 | 1.0 |
| | 12 | 53.3 | 66.0 | 94.8 | 87.5 | 21.3 | 31.7 | 55.0 | 59.4 | 12.0 | 3.8 | 21.8 | 59.4 | 2.7 | 18.7 | 55.0 | 0.1 | 4.0 | 31.7 | 0.0 | 0.0 | 21.3 | 0.7 | 0.0 | 0.0 |
| | 18 | 40.8 | 64.3 | 60.8 | 73.1 | 10.6 | 45.0 | 31.0 | 57.0 | 15.1 | 0.6 | 18.3 | 57.0 | 1.9 | 9.2 | 31.0 | 0.5 | 4.9 | 45.0 | 0.0 | 0.0 | 10.6 | 0.6 | 0.0 | 0.0 |
| 725 | Vac. | 52.0 | 72.0 | 85.0 | 94.0 | 17.0 | 52.5 | 70.5 | 77.5 | 0.2 | 0.0 | 2.1 | 77.5 | 3.9 | 9.2 | 70.5 | 1.4 | 8.9 | 52.5 | 4.2 | 1.4 | 17.0 | 2.4 | 0.2 | 2.8 |
| | 1 | 40.0 | 60.0 | 64.2 | 90.0 | 5.4 | 40.0 | 34.0 | 61.5 | 3.7 | 2.0 | 17.3 | 61.5 | 7.4 | 34.5 | 34.0 | 0.9 | 5.2 | 40.0 | 0.0 | 0.7 | 5.4 | 6.0 | 1.6 | 0.7 |
| | 12 | 27.5 | 54.2 | 48.3 | 58.3 | 3.0 | 27.0 | 7.5 | 39.7 | 10.2 | 3.2 | 30.7 | 39.7 | 2.3 | 15.2 | 7.5 | 0.0 | 2.1 | 27.0 | 0.7 | 0.0 | 3.0 | 0.0 | 1.2 | 0.0 |
| | 18 | 25.0 | 46.6 | 18.0 | 53.3 | 7.5 | 26.0 | 2.7 | 42.3 | 3.8 | 0.0 | 10.4 | 42.3 | 5.0 | 12.6 | 2.7 | 0.0 | 2.8 | 26.0 | 0.0 | 0.0 | 7.5 | 0.0 | 0.9 | 0.0 |
| 800 | Vac. | 49.0 | 66.0 | 66.0 | 87.0 | 14.5 | 35.6 | 49.5 | 63.0 | 1.5 | 0.7 | 5.6 | 63.0 | 4.7 | 18.5 | 49.5 | 1.0 | 9.5 | 35.6 | 0.0 | 1.7 | 14.5 | 2.3 | 0.1 | 6.9 |
| | 1 | 17.6 | 27.1 | 32.5 | 62.0 | 1.6 | 4.5 | 6.6 | 35.6 | 1.6 | 8.3 | 17.6 | 35.6 | 1.9 | 7.2 | 6.6 | 0.5 | 1.6 | 4.5 | 0.0 | 0.5 | 1.6 | 0.9 | 0.0 | 3.0 |
| | 12 | 15.8 | 31.7 | 34.2 | 22.5 | 5.7 | 7.9 | 7.5 | 16.1 | 3.8 | 9.1 | 16.4 | 16.1 | 1.3 | 8.6 | 7.5 | 0.0 | 1.6 | 7.9 | 1.2 | 0.0 | 5.7 | 0.0 | 0.0 | 0.0 |
| | 18 | 0.0 | 11.5 | 11.7 | 18.3 | 0.0 | 1.1 | 4.0 | 12.1 | 0.0 | 5.4 | 3.0 | 12.1 | 0.0 | 0.8 | 4.0 | 0.0 | 0.0 | 1.1 | 1.6 | 0.0 | 0.0 | 1.5 | 6.7 | 0.0 |
| Average | | 38.8 | 54.2 | 59.3 | 65.5 | 11.9 | 30.6 | 37.1 | 50.7 | 5.1 | 3.1 | 12.3 | 50.7 | 4.0 | 11.4 | 37.1 | 0.5 | 5.4 | 30.6 | 0.9 | 0.4 | 11.9 | 1.2 | 0.9 | 1.2 |

| SECTION B | | | 1 | 12 | 18 | | 1 | 12 | 18 | | 1 | 12 | 18 | | 1 | 12 | 18 | | 1 | 12 | 18 | | 1 | 12 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hydrocarbon | Temp. °C | Vac. | Atm. | Atm. | Atm. | Vac. | Atm. | Atm. | Atm. | Vac. | Atm. | Atm. | Atm. | Vac. | Atm. | Atm. | Atm. | Vac. | Atm. | Atm. | Atm. | Vac. | Atm. | Atm. | Atm. |
| Cymene | 650 | 83.0 | 62.0 | 53.3 | 40.8 | 34.5 | 21.6 | 21.3 | 10.6 | 0.2 | 9.2 | 12.0 | 15.1 | [14.5] | 2.5 | 2.7 | 1.9 | 17.8 | 5.9 | 4.0 | 4.9 | 34.5 | 21.6 | 21.3 | 10.6 |
| | 725 | 52.0 | 40.0 | 27.5 | 25.0 | 17.0 | 5.4 | 3.0 | 7.5 | 0.2 | 3.7 | 10.2 | 3.8 | 3.9 | 7.4 | 2.3 | 5.0 | 8.9 | 5.2 | 2.1 | 2.8 | 17.0 | 5.4 | 3.0 | 7.5 |
| | 800 | 49.0 | 17.6 | 15.8 | 0.0 | 14.5 | 1.6 | 5.7 | 0.0 | 1.5 | 1.6 | 3.8 | 0.0 | 4.7 | 1.9 | 1.3 | 0.0 | 9.5 | 1.6 | 1.6 | 0.0 | 14.5 | 1.6 | 5.7 | 0.0 |
| Xylene | 650 | 95.0 | 69.0 | 66.0 | 64.3 | 80.0 | 37.7 | 31.7 | 45.0 | 0.3 | 4.1 | 3.8 | 0.6 | 2.6 | 15.4 | 18.7 | 9.2 | 80.0 | 37.7 | 31.7 | 45.0 | 1.9 | 2.2 | 0.7 | 0.6 |
| | 725 | 72.0 | 60.0 | 54.2 | 46.6 | 52.5 | 40.0 | 27.0 | 26.0 | 0.0 | 2.0 | 3.2 | 0.0 | 9.2 | 34.5 | 15.2 | 12.6 | 52.5 | 40.0 | 27.0 | 26.0 | 2.4 | 6.0 | 0.0 | 0.0 |
| | 800 | 66.0 | 27.1 | 31.7 | 11.5 | 35.6 | 4.5 | 7.9 | 1.1 | 0.7 | 8.3 | 9.1 | 5.4 | 18.5 | 7.2 | 8.6 | 0.8 | 35.6 | 4.5 | 7.9 | 1.1 | 2.3 | 0.9 | 0.0 | 1.5 |
| Toluene | 650 | 98.0 | 98.3 | 94.8 | 60.8 | 91.6 | 85.0 | 55.0 | 31.0 | 0.0 | 3.9 | 21.8 | 18.3 | 91.6 | 85.0 | 55.0 | 31.0 | 3.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 | 0.0 | 0.0 |
| | 725 | 85.0 | 64.2 | 48.3 | 18.0 | 70.5 | 34.0 | 7.5 | 2.7 | 2.1 | 17.3 | 30.7 | 10.4 | 70.5 | 34.0 | 7.5 | 2.7 | 4.2 | 0.0 | 0.7 | 0.0 | 0.2 | 1.6 | 1.2 | 0.9 |
| | 800 | 66.0 | 32.5 | 34.2 | 11.7 | 49.5 | 6.6 | 7.5 | 4.0 | 5.6 | 17.6 | 16.4 | 3.0 | 49.5 | 6.6 | 7.5 | 4.0 | 0.0 | 3.0 | 1.2 | 1.6 | 0.1 | 0.0 | 0.0 | 6.7 |
| Benzene | 650 | 90.0 | 86.6 | 87.5 | 73.1 | 78.5 | 66.5 | 59.4 | 57.0 | 78.5 | 66.5 | 59.4 | 57.0 | 1.6 | 0.0 | 0.1 | 0.5 | 0.8 | 0.0 | 0.0 | 0.0 | 0.4 | 1.0 | 0.0 | 0.0 |
| | 725 | 94.6 | 90.0 | 58.3 | 53.3 | 77.5 | 61.5 | 39.7 | 42.3 | 77.5 | 61.5 | 39.7 | 42.3 | 1.4 | 0.9 | 0.0 | 0.0 | 1.4 | 0.7 | 0.0 | 0.0 | 2.8 | 0.7 | 0.0 | 0.0 |
| | 800 | 87.0 | 62.0 | 22.5 | 18.3 | 63.0 | 35.6 | 16.1 | 12.1 | 63.0 | 35.6 | 16.1 | 12.1 | 1.0 | 0.5 | 0.0 | 0.0 | 1.7 | 0.5 | 0.0 | 0.0 | 6.9 | 3.0 | 0.0 | 0.0 |

### ANALYSIS OF QUALITATIVE RESULTS (TABLE VI)

NAPHTHALENE FORMATION—The qualitative indications of Table VI point out the fact that naphthalene is generally one of the products of the cracking of the monocyclic compounds: cymene, xylene, toluene and benzene. This is in part contrary to the observation of Haber[1] who states that while diphenyl may be

[1] *Loc. cit.*

produced by the thermal decomposition of benzene, naphthalene is not so formed. Diphenyl was undoubtedly produced in the present experiments, although no attempt was made to isolate or identify

TABLE VI—ANALYSIS OF QUALITATIVE RESULTS

| Temp. C. | Press. Atm. | Naphthalene Formation: Cymene | Xylene | Toluene | Benzene | Anthracene Formation: Cymene | Xylene | Toluene | Benzene | Naphthalene |
|---|---|---|---|---|---|---|---|---|---|---|
| 650 | Vac. | + | — | + | + | — | — | — | + | — |
| | 1 | — | — | + | + | — | — | — | — | — |
| | 12 | + | — | — | + | — | — | — | — | — |
| | 18 | + | + | + | + | — | — | — | — | — |
| 725 | Vac. | — | — | + | — | — | — | — | — | + |
| | 1 | + | + | + | — | — | — | — | — | + |
| | 12 | + | — | + | + | — | — | + | + | — |
| | 18 | — | + | — | + | — | — | — | — | — |
| 800 | Vac. | — | — | + | + | — | — | — | — | + |
| | 1 | — | — | — | + | — | — | — | — | + |
| | 12 | — | + | + | + | — | — | + | — | + |
| | 18 | — | — | — | + | — | — | — | — | — |

it. Direct evidence was obtained of the formation of naphthalene and in some cases, notably in the benzene series, it appeared in considerable quantity in the cooled distillates.

ANTHRACENE FORMATION—The indications of anthracene formation are not particularly satisfactory except that they establish the fact that anthracene may be formed by the heating of the other hydrocarbons. Anthracene is formed with some readiness by the cracking of naphthalene and it occasionally appears in the higher distillation cuts from the runs with liquid hydrocarbons.

## SUMMARY

It will be noted from the results of the present experiments that from cymene it is possible to produce by "cracking" all the other hydrocarbons of the series, such as xylene, toluene, benzene, naphthalene and anthracene. From xylene results toluene, benzene, naphthalene, and anthracene but no cymene. Toluene yields benzene, naphthalene, and anthracene, but no cymene and no xylene. Benzene goes to naphthalene and anthracene but not to any of its higher homologs. From naphthalene, anthracene is readily obtainable but none of the monocyclic hydrocarbons, benzene, toluene, xylene and cymene, are produced. Anthracene yields no naphthalene but goes to tarry matter, carbon and gas. These relations can be rendered clearer by the following scheme:

$C_6H_{12} \longrightarrow C_6H_6\ C\ H_2\ C_7H_8\ C_8H_{10}\ C_{10}H_8$

CYMENE ⟶ Xylene, Toluene, Benzene, Naphthalene, Anthracene
XYLENE ⟶ Toluene, Benzene, Naphthalene, Anthracene (No *Cymene*)
TOLUENE ⟶ Benzene, Naphthalene, Anthracene (No *Cymene, Xylene*)
BENZENE ⟶ Naphthalene, Anthracene (No *Cymene, Xylene, Toluene*)
NAPHTHALENE ⟶ Anthracene (No *Cymene, Xylene, Toluene, Benzene*)
ANTHRACENE ⟶ Tarry Matter, Carbon and Gas (No *Naphthalene, etc*).

Other compounds such as diphenyl, methyl naphthalenes and anthracenes, phenanthrene, etc., are undoubtedly formed but in the absence of identification they have been omitted from mention in the present connection.

On the basis of the evidence at hand it seems justifiable to state that the course of the cracking reaction in the aromatic series may be indicated as follows and that reverse action occurs in practically negligible amount: Higher benzene homologs ⟶ lower benzene homolog ⟶ benzene ⟶ (diphenyl) ⟶ naphthalene ⟶ anthracene ⟶ carbon and gas.

CHEMICAL SECTION OF THE PETROLEUM DIVISION
U. S. BUREAU OF MINES

## PRACTICAL METHODS FOR THE DETERMINATION OF RADIUM.[1] II—THE EMANATION METHOD

By S. C. Lind

Received August 31, 1915

In a recent communication[2] a description was given of an "interchangeable electroscope" and its use with particular reference to the quantitative determination of radium by the emanation method. In the present paper some methods are given for the chemical treatment and other manipulations involved in preparing emanation for the electroscopic measurements already described.

One should recognize primarily that there is no universal method at present for the determination of radium, even when confined to the emanation method. Each radioactive product requires study and the adaptation of a method suited to its own peculiar chemical and physical characteristics. Nevertheless, it is sought in the following to discuss some of the broader principles to be followed and then to unify and simplify procedures as far as is consistent with accuracy.

The methods to be presented are suited for use in the case of ores and the various products that arise in the production of radium on a plant scale. Their applicability has been tested by a large number of determinations carried out during more than a year of actual operation. Other analysts will undoubtedly meet with products for which still different methods may appear better suited, and in practice modifications and improvements will suggest themselves. But in the absence of published descriptions of methods of radium analysis for plant control, various procedures will be described with some minuteness in the following. It should be borne in mind, however, that before the final adoption of any method for a given product, it will always be well to try several others, selecting the one which appears by comparison to give satisfactory results with least expenditure of effort.

### GENERAL DISCUSSION OF PROCEDURES

The underlying principle for the determination of radium by the emanation method consists in separating radium emanation (as gas) from its parent radium in order to measure its quantity in a gas-tight electroscope previously standardized with a known quantity of radium emanation. Analyzed pitchblende or standard radium solutions may be employed to furnish known quantities of emanation for standardization purposes.

The three following procedures may be employed in general:

I—Liberate and measure electroscopically the emanation from a substance in which equilibrium exists between radium and radium emanation. This condition of equilibrium will, as a rule, not be fulfilled except in substances that have been enclosed for a month or more in a gas-tight container. When this condition is not fulfilled, more or less emanation diffuses away and is not subject to determination directly. In exceptional cases radium might be con-

[1] Published with permission of the Director of the Bureau of Mines.
[2] THIS JOURNAL, 7 (1915), 406.

tained in a solid of such compact structure that no spontaneous loss of emanation could take place. But even from pitchblende the loss of emanation (called *emanating power* and expressed in terms of per cent of the total emanation) amounts to a few per cent.

II—Liberate and measure the amount of emanation retained in the solid substance and apply as additive correction the *emanating power*, which must be determined separately by measuring the emanation diffusing from the radioactive substance in a closed vessel.

Both procedures I and II have already been described by the author in detail.[1] In practice they involve long delays, and while suited to scientific investigation, are not adaptable to the purposes of plant control where rapidly obtainable results are essential. Whenever possible it is preferable to use the following shorter procedure:

III—By means of suitable operations (see later) remove emanation completely from the substance to be analyzed for radium, close the de-emanated substance in a gas-tight vessel and allow emanation to accumulate for a convenient period (one to four days). After this accumulation the emanation is collected and measured. A time correction must be applied to ascertain the maximum amount that would be obtained after the attainment of equilibrium with the radium content. As is well known, the regeneration of radium emanation takes place according to the logarithmic law: $E_t = 1 - e^{-\lambda t}$, where $E_t$ is the percentage regeneration at any time $t$, $e$ is the base of the Naperian logarithms, and $\lambda$ is the time constant for radium emanation ($= 0.0075$ hr.$^{-1}$). The solution of the function $e^{-\lambda t}$ for intervals of time from 1 hour to 30 days will be found in the Kolowrat Table I.[2]

For liberation of emanation (de-emanation), a radioactive substance may be either in a state of solution or fusion. Some substances like carnotite can be de-emanated merely by heating to a high temperature without fusion, but are so changed in physical property that a second ignition does not remove all the emanation. It is therefore evident that direct ignition can be used only in case of a month's accumulation method.

The removal of emanation from solution may be accomplished by aspiration or preferably by boiling. Only the latter has been used and will be described in the present paper.

The removal of emanation from a fusion is brought about by passing air or some other gas over the fused mass. When possible, it is better to bubble air through the melt or to produce in it an evolution of gas to insure the complete removal of emanation. Yet another procedure that has been found very useful in the case of carbonate fusions, in the absence of silica, consists in dissolving the cold fusion in 1–1 $HNO_3$ with evolution of $CO_2$ followed by boiling. The further elaboration of the procedures indicated above will be found in the subsequent sections.

[1] Lind and Whittemore, *J. Am. Chem. Soc.*, **36**, 2072, also U. S. Bureau of Mines, *Tech. Paper* **88**.

[2] Léon Kolowrat, *Le Radium*, **6**, 195–6, also Mme. Curie, *Traité de Radioactivité*, **1**, 419–20, also *Chem. Kalender*, **2** (1914), 361–2.

PROCEDURE FOR RADIUM IN SOLUTION OR IN A SOLUBLE FORM

The direct determination of radium in solution can be readily carried out in most cases, if certain precautions are carefully observed. These precautions are necessitated by the oft-repeated observation that radium solutions show a tendency to lose radium from solution on standing, which is manifested by the decrease in the successive quantities of emanation which can be liberated from the solution. This fact has resulted in the almost complete abandonment of the practice of preserving radium solutions for long periods of time for standardization purposes; and also in analytical work, this method will result in very erroneous conclusions unless special care is taken.

This loss of radium from solution is to be attributed to the precipitation or adsorption of radium from solution in a form that will not readily give up its emanation. On account of the very small quantities of radium employed in analysis, a loss of a very small absolute quantity represents a large relative loss. The presence of precipitates or suspensions in solution should in general be avoided, although this source of error has been frequently overestimated. According to the latest ideas of adsorption[1] of the radioelements only those adsorbents are to be guarded against, the negative radical of which would form with the radioelement in question a compound insoluble in the given solution. Accordingly the loss of radium by the action of small quantities of sulfate originating in the glass of the container or in the reagents should be carefully avoided. This may be done by the addition of a considerable excess of "*protective barium*" and the maintenance of a fairly high concentration of nitric acid.

The *protective* action of excess of barium in radium solutions depends on the chemical similarity of the two elements, due to which, any precipitant such as sulfate that would remove radium will be removed by the excess of barium, or rather radium and barium will be precipitated in the same proportion in which they occur in solution, and hence the greater the excess of barium the more insignificant becomes the loss of radium. The action of nitric acid consists in increasing the solubility of radium sulfate and also in preventing the formation of any basic salts of radium which are formed by the action of the $\alpha$ radiation and which would be precipitated in neutral solution. The solubility of barium nitrate in concentrated nitric acid is not very great, so that care must be taken that the two shall not exceed the solubility product of barium nitrate in boiling solution.

The two important factors in dealing with radium solutions analytically consist then in maintaining excess of barium and a rather high concentration of nitric acid. All solutions will fall into one of the three following classes, and the reasons for the treat-

[1] F. Paneth, *Physik. Zeit.*, **15** (1914), 924–9; K. Horowitz and F. Paneth, *Z. physik. Chem.*, **89** (1915), 513–28.

ment prescribed for each will be clear from the foregoing discussion:

1 SOLUTIONS CONTAINING BARIUM IN LARGE EXCESS OF THE RADIUM

Take a suitable portion of the solution (to contain about $1 \times 10^{-8}$ g. of radium) and add it to 1:1 $HNO_3$ in a small Jena flask. Add a few glass beads and boil for 5 to 10 minutes to remove all emanation. Allow to cool slightly before closing tightly with a one-hole stopper provided with a glass tube drawn out to a capillary at the upper end. Seal off the capillary while some steam is still in the flask in order to produce a partial vacuum, which should be retained until the flask is again opened, thus affording a proof that no outward leak of gas has taken place. Note the exact time and date of closing the flask, and hold for accumulation of emanation.

2 SOLUTIONS CONTAINING LITTLE OR NO BARIUM

Add a suitable portion of the solution to 1:1 $HNO_3$ saturated with barium nitrate and proceed as in (1).

3—SOLUTIONS CONTAINING NO BARIUM BUT AN EXCESS OF A BARIUM PRECIPITANT SUCH AS SULFATE OR CARBONATE

Solutions of this character, which are usually filtrates from a radium-barium precipitation, require especially careful treatment to avoid very erroneous results, either high or low. If such solutions were boiled off and sealed directly, the results might be low as much as tenfold, owing to a decreasing emanating power, continuing as long as they remained closed. This behavior has suggested that the precipitation of radium at very low concentrations, or at any rate its removal, whatever the process, is a progressive time reaction. This same circumstance may, on the other hand, lead to high results through incorrect sampling, even in the use of a correct chemical procedure, when, for example, too much of the fine (frequently invisible) precipitate may have been included in a given volume of liquid. This might easily occur in siphoning the liquid from above a sulfate precipitate if the sample were taken too near the end of the operation. It is preferable to take several samples at intervals and make a composite.

PROCEDURE FOR LIQUIDS OF THE THIRD CLASS—Add a small sample of suitable volume to a solution containing an excess of barium and filter off the precipitate after allowing to stand over night. The filtrate containing excess of barium is made acid to the saturation point with nitric acid and treated as in (1). The precipitate, if $BaSO_4$, is fused with 4 to 5 times its weight of a 1:1 molar $Na_2CO_3$–$K_2CO_3$ mixture, and treated as described later for fusions. If the precipitate is $BaCO_3$, it is dissolved in $HNO_3$ containing enough $H_2SO_4$ to precipitate an amount of $BaSO_4$ convenient for fusion, which is filtered off, dried and fused. The filtrate is combined with the original and treated as in (1). All the radium is then contained either in the filtrate with excess of protective barium or in the fused precipitate, both of which fractions should be handled, both before and after the accumulation of radium, as nearly simultaneously as possible (within 15 minutes) in order that both lots of emanation can be introduced into the same electroscope.

FUSION METHODS

If radium is contained in a substance not soluble n aqueous or acid solution, such as a radium-barium sulfate, a fusion method is resorted to, which may also prove more convenient even for soluble substances. Fuse a suitable quantity of the material in a small platinum or porcelain boat with a carbonate fusion mixture noting the exact time of cooling. Close this boat at once in a glass tube of the type shown in Fig. I. The ends of the tube are drawn down so as to accommodate rubber tubing, and then to capillary tips to be broken inside the rubber on opening.

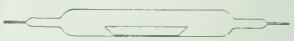


FIG. I

Emanation is allowed to collect for one or more days. Connect the glass tube at one end by means of rubber tubing to a glass stop-cock and at the other to the partially evacuated emanation chamber of the interchangeable electroscope. Break the glass tips inside the rubber connections, and exhaust the air from the glass tube into the electroscope, refilling the glass tube several times by means of the stop-cock, but being careful to leave enough vacuum in the electroscope chamber to accommodate the gas to be introduced later from the further treatment of the fusion. Disconnect the glass tube, break it, remove the boat and contents, wrap in a filter paper, and place in the neck of a Jena flask (as shown in Fig. II) which is half filled with 1:1 $HNO_3$. After connecting the flask with the gas-burette (as shown in Fig. III), a little of the acid is brought into contact with the carbonate fusion thus setting up an evolution of $CO_2$. The stop-cock leading to the gas burette is immediately opened and the boat and contents are thoroughly wet with acid and then shaken down into the body of the acid.

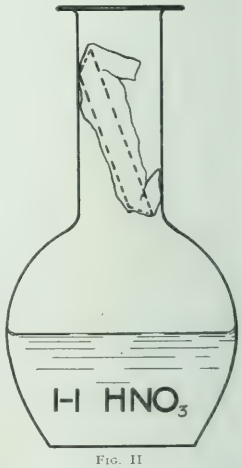



FIG. II

In the case of large fusions the evolution of $CO_2$ becomes very rapid and special precautions must be taken. But in the case of small fusions not exceeding 1 to 2 grams, the boat may be brought down at once into the acid, which is boiled as soon as the gas evolution begins to slacken. All of the $CO_2$ is of course absorbed by the NaOH solution in the burette. The boiling off of the emanation from this point on is identical with that of solutions to be described later.

For small fusions of substances containing radium in the order of one part per million, such as the usual

crude $Ba(Ra)SO_4$ and high-grade pitchblende, of which one would fuse a sample of 20 to 40 mg., it has been found convenient to employ small boats folded from a piece of platinum foil $1^1/_2$ in. in length and $^3/_4$ in. broad, which makes a boat about 1 in. long and $^1/_4$ in. in cross section. The foil used is $^1/_{1000}$ in. thick and has quite a long life provided the substance fused does not contain lead. For substances much poorer in radium, porcelain boats have been used, and flasks as large as a liter are required to dissolve the fusion; a gas burette with a bulb enlargement at the top is used to contain a sufficient quantity of NaOH solution. In this case the fusion should not be brought down into the liquid until a considerable part of the evolution has been conducted by manipulation of the flask.

DIRECT FUSION METHOD—If preferred one can employ fusion both before and after collection of emanation, instead of dissolving the fusion in acid as just described. As soon as the initial fusion has cooled, it is removed from the boat by unfolding the platinum foil (for which purpose the thin foil is most convenient) and put into a Jena glass tube of the form already described (Fig. I) where it is held in place by glass-wool plugs. The glass-wool also has the advantage of reacting with the carbonate during the second fusion to produce a vigorous evolution of $CO_2$ which aids in the complete removal of emanation.

If the radioactive substance is free from thorium, air may be drawn directly over the melt into the electroscope. A solution of NaOH is interposed before the electroscope to prevent the introduction of any $CO_2$. In this connection it may be mentioned that no gas except air should ever be introduced into the electroscope together with emanation, because the specific ionization of the various gases varies very much from that of air, roughly in proportion to their densities. It is also well to place a sulfuric acid drying bulb before the electroscope and another at the entrance to the train to control the flow of gas as well as for drying purposes.

To produce the second fusion, the hard glass tube after being properly connected with asbestos protectors for the rubber tubing, is strongly heated with a Méker burner while air is being drawn through to the electroscope. The heating is continued until the glass finally collapses completely, which should not be allowed to take place, however, until a large quantity of air has been passed and the vacuum is nearly refilled. It may also be advantageous to allow the tube to bend into a U shape or to constrict itself so that air actually bubbles through the melt.

Both modifications of the fusion method are very unfavorably affected by the presence of a high percentage of silica, which increases the viscosity of the melt thus rendering the removal of emanation by direct fusion difficult, and also makes complete solution in the acid method impossible by the separation of silicic acid gel on the surface preventing further attack of the acid and producing adsorption of radium and radium emanation. This point is more fully discussed later under the method for carnotite and tailings.

METHOD AND APPARATUS FOR BOILING OFF AND TRANSFERRING EMANATION

Set up apparatus as shown in Fig. III. Wire the rubber connections at *A* and *B*. Put into the leveling bulb *C* a stick of NaOH 2 to 3 inches long (use more in case of large quantities of $CO_2$ to be absorbed). Make sure that stop-cock *D* is closed and *E* open. Pour boiling water into the leveling bulb which rapidly dissolves the NaOH with evolution of much heat. If the boiling becomes too vigorous place a one-hole stopper in the mouth of the leveling bulb to prevent liquid from being thrown out. After complete solution raise the level until the gas burette is filled to the upper stop-cock which is at once closed and the leveling bulb lowered to its original position. If the amount

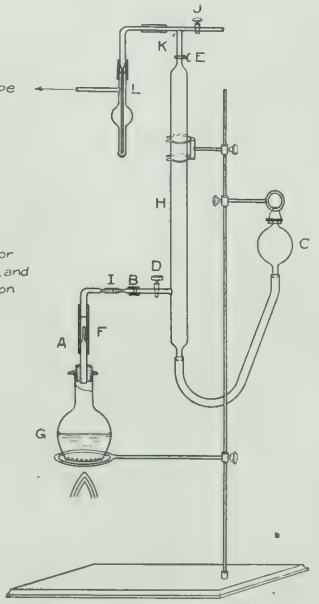



FIG. III

Showing apparatus for boiling off, collecting, and transferring emanation into electroscope

of air to be introduced is small, some air may be left initially in the burette.

Break the glass tip *F* inside the rubber tubing[1] and slowly open *D* to ascertain if there is vacuum remaining in the flask *G*. If so, close *D* again and begin to heat *G* over a wire gauze with a Bunsen burner. Test the vacuum every few seconds and as soon as the pressure is outward, open *D* and begin to boil vigorously. Boiling is continued 5–10 minutes until live steam has raised the temperature of all the liquid in the gas burette to boiling.

After the boiling off is complete, remove the flame and as soon as the liquid begins to draw back, close *D*, and remove the flask entirely. If desired, the flask

[1] The glass tip *F* after being broken off has shown a great tendency to be carried upward by the current of steam, and in some cases has lodged in the stop-cock *D* causing serious explosions. This may be prevented either by using a stop-cock of wide bore or by placing at *I* a roll of thin platinum foil, which is held in place by constricting the glass on both sides, and prevents the passage of any solid material.

may be closed again for a second accumulation of emanation, but usually if duplicates are desired, two or more flasks are closed originally.

Evacuate the electroscope chamber to a suitable degree either with a hand pump or with an aspirator. Connect a $H_2SO_4$ drying bulb *L* to the evacuated chamber and to the gas burette, as shown in Fig. III. Be sure that stop-cock *J* is closed. Open the stop-cock of the electroscope for a moment to produce vacuum in the drying bulb, reclose it, slowly open *E* to full width, and then again gradually open the stop-cock of the electroscope so as to allow gas to pass through the drying bulb at a fairly rapid rate.

When the liquid in the gas burette has risen exactly to the point *K*, close *E*, and open *J* to allow dry dust-free air taken from outside the laboratory to sweep out the connections for a short time. Close the stop-cock to the electroscope, open *E*, allow the liquid to fall 4 to 5 inches below the shoulder of the burette. Close *E* and *J* and pour out all the excess liquid from the leveling bulb *C*. Open again to the electroscope and allow the inflowing air to bubble from the bottom through the full length of the liquid in the gas burette to insure complete removal of whatever emanation that may have dissolved in the NaOH solution. This precaution is perhaps unnecessary, since the hot solution of NaOH certainly does not dissolve much emanation during the limited exposure, but it is a precaution in the direction of accuracy which can be observed without additional effort. Air is thus passed into the electroscope chamber until external pressure is restored. If desired, one 3-way stopcock may be substituted for *E* and *J*.

The same procedure is followed in boiling off and in handling the solutions derived from dissolving any fusion or other solid material which one may have occasion to dissolve directly. For example, ground carnotite or pitchblende ores may be wrapped in filter paper and handled in the same way as shown for a fusion in Fig. II, applying, of course, the correction for emanating power already mentioned. Or the ore may be sealed for a month in a thin glass bulb which is opened by crushing against the bottom of the flask by tapping on the glass stem projecting above through a second hole in the rubber stopper closing the flask.[1]

To economize time two of the boiling and transferring operations can be carried on simultaneously by one operator.

### CHOICE OF METHOD

In the following, some indications are given as to the applicability of the various methods just discussed to different products that frequently present themselves for radium analysis.

PITCHBLENDE—High-grade pitchblende is low in silica[2] and readily soluble in boiling 1:1 $HNO_3$. Therefore solution as well as fusion methods are available. Low-grade pitchblende with high silica content is subject to the same difficulties of analytical treatment as carnotite (which see). Since the Ra/U ratio is constant and normal ($3.33 \times 10^{-7}$) in various pitchblendes,[1] it may be used in calculating the radium from the uranium content. This statement also applies to carnotite in large and well sampled lots.[2]

CARNOTITE, the principal American radium-bearing ore, is primarily a sandstone impregnated more or less with uranium vanadate. The latter is readily soluble, together with the radium, in excess of boiling 1:1 $HNO_3$. One of the best methods for its radioactive analysis is solution from a sealed glass tube after a month's accumulation, or ignition in a hard glass tube sealed under the same conditions. Direct solution in hot 1:1 $HNO_3$ saturated with $Ba(NO_3)_2$ followed by accumulation in a closed flask for a few days without filtering also gives approximately correct results but is not to be so highly recommended as the two longer methods just mentioned. On account of the high silica content of carnotite the carbonate fusion melt is very viscous at temperatures suitable for the use of Jena glass, hence it is difficult for the radium emanation to be liberated. Higher temperature[3] or the direct bubbling of air through the melt help to obviate this difficulty, but experience in this laboratory has been in general unfavorable to the use of fusion methods for carnotite. Dropping the fusion into acid fails completely for reasons already stated.

CARNOTITE RESIDUES OR TAILINGS—All the difficulties arising in the analytical treatment of carnotite are many times multiplied in its extracted residues, with the additional difficulty that, since the radium has already resisted solution it is not permissible to apply solution methods. Fusion methods may be applied only after the removal of all the silica with HF from at least a 10-gram sample. Usually the solid $\alpha$-ray method[4] has been sufficiently accurate for the residues, which are so low in radium that a large relative error produces but a small absolute error in estimating the percentage of radium extraction.

ACID FILTRATES FROM ORE EXTRACTION Liquors of this character can be boiled and sealed directly after the addition of a little barium as prescribed. Carnotite ore contains a considerable amount of barium so that little more need be added. This is not the case for pitchblende, which contains little barium.

BARIUM (RADIUM) SULFATES AND SULFIDES are fused with carbonate mixture in platinum or porcelain boats (described under Fusion Method), sealed in glass tubes for the accumulation of emanation, and are either dissolved in acid or fused again to effect de-emanation.

FILTRATES WITH EXCESS OF SULFATE OR CARBONATE must be treated with observance of all the precautions prescribed for liquids of this character.

BARIUM (RADIUM) CHLORIDE (OR BROMIDE) LIQUORS OR CRYSTALS may be treated after suitable dilution according to Method 1 for liquids. For solutions of fairly high-grade radium salts the necessary degree of dilution becomes very considerable, as much as 1 to 1,000,000 or more, in some cases. This dilution

[1] See Lind and Whittemore, *J. Am. Chem. Soc.*, **36**, 2072; also U. S. Bureau of Mines, *Tech. Paper* **88**, 13.

[2] A. Becker and P. Jannasch, *Jahrb. d. Radioakt. u. Electronik*, **12** (1915), 14.

[1] B. Heimann and W. Marckwald, *Jahrb. d. Radioakt. u. Electronik*, **10** (1913), 299–323.

[2] Lind and Whittemore, *Loc. cit.*

[3] H. Schlundt, *Trans. Amer. Electrochem. Soc.*, **26** (1914), 170.

[4] R. B. Moore and K. L. Kithil, U. S. Bureau of Mines, *Bull.* **70**, 64-5.

is carried out with pipettes and measuring flasks according to the usual procedures of volumetric analysis and with due regard for the principle of *protective barium and acid* throughout. An unusual amount of care must be taken in rinsing the vessels in which such large steps of dilution are carried out. It is advisable to have a large number of pipettes and flasks and never to use the same ones through too great a range of concentration.

GENERAL—The special methods employed for the analysis of substances extremely low in radium content, such as rocks, soils, and natural waters, are beyond the scope of the present paper, except in so far as all solutions and waters are subject to treatment by the boiling off method herein described for liquids.

It is believed that the application of the principles that have been discussed in the foregoing should suggest a mode of procedure for any other substances that may present themselves for radioactive analysis in connection with plant control in the production of radium. But it is well to bear in mind that a new method or an old method applied to a new product should always be checked in as many ways as possible before deciding on its suitability.

U. S. BUREAU OF MINES, DENVER, COLORADO

## GASOLINE FROM HEAVIER PETROLEUM OILS

By CARLETON ELLIS AND A. A. WELLS

Received October 11, 1915

The object of the investigation, some of the results of which are briefly described below, was to determine the commercial feasibility of certain methods of production of gasoline and the applicability of the product as a fuel for motor vehicles and for extraction purposes.

In the early days of petroleum refining, gasoline was practically a waste product and the object of every refiner was to make the gasoline cut as low as possible and the burning oil, or kerosene cut, as large as possible, as at that time the latter was the more valuable product. Thus it is that until very recently, kerosene of 45° B. (or even lighter) was considered the proper gravity in good refining practice, while under modern methods, this burning oil fraction is again distilled, yielding an additional quantity of gasoline and affording a finished burning oil of 42° B.

It was in the early days of oil refining that the property of cracking was discovered. In the city of Newark in 1861–62, a still man had taken the gravity of his distillate and had fixed his fire as usual while he went to lunch. He was detained for several hours and when he returned and had again taken the gravity he was surprised to find, instead of the heavy oil which he had expected was passing into his burning oil cut, that the runnings were lighter than when he left the still. On repeating the conditions he found that by banking his fires after a certain gravity had been reached, he could greatly increase his burning oil fraction.

From time to time, stills have been constructed which had for their object the cracking of the heavier oils into the lighter burning oils. In general, the mode of operation was to allow the oil vapors to condense on the relatively cool top of the still, from which point the condensed oil would drop into the highly heated oil at the bottom of the still and be cracked by this superheating. Later the coke still was developed. This still was charged, not with crude oil but with the heavier distillates. The condenser was constructed with traps which returned the heavy portions to the still for further cracking. The operation was continued until the residue in the still was reduced to coke. The method has practically been abolished at the present time on account of the high cost of maintenance. The bottoms of the coke stills became red hot during the operation and quickly burned out. It has been stated that such stills were run even when they leaked so badly that after charging, streams of blazing oil could be seen running out of openings in the still bottoms. The openings soon filled with coke and the leaks were thus stopped, until the coke was removed from the still at the end of the run.

It is well recognized among practical oil refiners that petroleum cannot be refined, even with the modern still, without the occurrence of a certain amount of cracking. As the quality of the lubricating oils is often impaired by cracking reactions the modern still man must know how to keep his fires in order to prevent such changes as much as possible. For this reason there are times during the operation when the fire must be increased to its fullest capacity, while at other stages it must be banked to obtain the best results. The method of firing depends to a great extent on the grade of oil in the still.

The principal methods of cracking petroleum oil are embraced in Table I.

TABLE I

| | | |
|---|---|---|
| I—Still cracking | A—Normal pressure | |
| | B—High pressure | |
| II Tube cracking | A—Normal pressure | 1—Treatment of vapors |
| | B—High pressure | 2—Treatment in the liquid state |
| III—Heating with reagents, such as aluminum chloride | | |
| IV—Contact with molten metal | | |

Some of the objections urged to each of these methods are:

STILL CRACKING UNDER NORMAL PRESSURE—The cost of maintenance is very high on account of the excessive heat on the still bottoms. The life of a cracking still is very short and cost of renewal is high. This method has practically been abandoned by modern refiners although its use was quite extensive at one time.

STILL CRACKING UNDER HIGH PRESSURE—The same heating difficulties apply as above and added to this is the fact that the size of the still is limited. Very large stills would not stand the pressure. The life of the still is short, for as soon as a seam starts to open, there is danger of an explosion.

TUBE CRACKING—The two objections are the local superheating of the tubes and the formation of carbon on the tube walls which clogs the tube and tends by carbonization to weaken the metal. This is true especially at the points of local superheating.

HEATING WITH REAGENTS: ALUMINUM CHLORIDE—

The high cost of reclaiming the reagents apparently is a serious drawback.

CONTACT WITH MOLTEN METAL—The efficient mixture, in a cheap manner, of the oil with the molten material in order to utilize to good advantage the heat required.

A considerable number of these cracking methods have been examined by us and it is the purpose of this paper to discuss some of the results obtained by cracking operations with tubular apparatus.

## EXPERIMENTAL

DESCRIPTION OF THE APPARATUS USED—During the course of the investigation four different pieces of tubular cracking apparatus were employed.

I—For preliminary experiments a single tube was used which was connected to an ordinary laboratory condenser. The tube was approximately 4 ft. long and 1 in. in diameter heated by a battery of Bunsen burners which ran the full length of the tube and were spaced about 2 in. apart. The condenser was approximately 6 ft. long and consisted of a glass tube and jacket cooled by running water. The yields from this apparatus were satisfactory, especially if the oil was passed through very slowly. Yields as high as 30 per cent were obtained of material boiling below 150° C. The vapor losses were quite heavy, owing to the fact that there was not enough condenser surface.

II—A larger apparatus was then constructed which consisted of a series of sections of 1 in. pipe so constructed that the ends of each section could be readily opened for examination and for the removal of any carbonaceous deposit. The condenser for this apparatus was a copper coil containing about 15 ft. of $^1/_2$ in. copper pipe. With this condenser, ice could be used to facilitate the condensation of the lighter products. The outlet of the condenser carried a tee connection so that the gases could be collected or passed through a bath of oil to scrub out the lighter fractions which were not condensed.

III—Another apparatus was constructed using approximately the same length of pipe as in the previous apparatus but in place of 1 in. pipe, a pipe of 2 in. diameter was substituted. The condenser for this apparatus was constructed of approximately 30 ft. of 1 in. iron pipe, water-cooled. The water used was chilled with ice whenever the tap water was too warm to give the desired condensation.

IV—The next apparatus was built on a somewhat larger scale. This consisted of ten 10 ft. lengths of 3 in. pipe connected to form a zigzag 100 ft. in length. Ammonia fittings were used for connections so as to give free access to the tube at all times for the purpose of examination and for the insertion of various catalytic agents. The feed of oil in this apparatus was controlled by connecting the top of the closed oil tank with the apparatus itself. In this way there was always an equilibrium of pressure between the tank and the apparatus. A sight feed was inserted in the oil feed pipe to show the rate of flow. The condenser for this apparatus was much larger than the condensers used in previous cases. An air condenser was used which consisted of about 40 ft. of 2 in. pipe. The vapors from the decomposing apparatus were passed in at the bottom and out at the top into a water condenser. Drain pipes were placed at the lowest points in the three sections of the air condenser so that the heavier portions of the oil could be drawn off to be re-run in the apparatus without distillation. The water condenser consisted of about 30 ft. of 2 in. pipe and 10 ft. of 1 in. pipe. The condensed material was drawn off from the bottom of a trap which was placed at the end of the condenser while the gases escaped from the top of the trap. The gas line from the condenser was connected with a gas compresser so that the waste gases could be compressed, and considerable material which was not condensed in the water condenser was collected in a receptacle beyond the compresser. The top of the receptacle which received the compressed gases was connected to the top of the oil feed so that the decomposing apparatus could be run under considerable pressure. A water feed pipe was connected to the apparatus for the introduction of water and its admixture with oil. This water line was also equipped with a by-pass into a coil which extended around the top of the furnace, so that instead of using water mixed with oil, superheated steam could be used. The pipe coil acted as a flash boiler and superheater.

## SEMI-COMMERCIAL APPARATUS

A semi-commercial apparatus was next constructed. This was of a size large enough so that about 1000 gallons of oil could be run through the apparatus in a day. This apparatus consisted of three parts, *viz.*, a 1000 gallon capacity still, especially constructed to carry pressure, a decomposer, and a condenser with three receiving tanks.

THE STILL—The still was constructed in the usual manner, with the exception that it had no dome. It was heated by a single gas burner and by means of a baffle running laterally in the fire chamber, the heating gases passed along the bottom to the rear, thence along the top to the front again, where the outlet to the stack was placed. The still was entirely enclosed in brick, so that no vapors were condensed in the still chamber. A 6-in. vapor line leading from the still to the decomposer was equipped with a by-pass leading directly to the condenser, so that the decomposer could be cut in or out at will. This was useful when crude oil was charged in the still.

THE DECOMPOSER—The decomposer consisted of six coils or sections of 3-in. iron pipe, each section being approximately 75 ft. in length, of welded stock, and flanged at each end for connection with 10 in. headers or manifolds. The coils were surrounded by a furnace setting of bricks and were supported in position in the furnace by three 1-in. iron pipe supports. Water was kept flowing through these in order that they might not become heated enough to bend under the load. The gaskets used in the flanges were prepared from asbestos soaked in slaked lime.

The furnace proper was supported on two brick piers 8 ft. long and 13 in. thick, and $8^1/_2$ ft. high.

On these piers was a re-enforced concrete slab, having four 7-in. I beams running lengthwise of the furnace. The furnace walls were composed of 9 in. of red brick laid in cement mortar, lined with 4 in. of fire brick laid in fire clay. The roof was built of one thickness of fire brick laid on edge, supported by tee bars, and two thicknesses of red brick, with a thin layer of concrete on top to keep out the moisture. At one end was a small stack 2 ft. high, which supported a damper and a 12 in. galvanized stack 9 ft. high. The furnace was heated by two gas burners made of 2-in. iron pipe slotted to admit air, the latter being controlled by means of a long screw thread, and a 2-in. coupling. The 2-in. pipe was reduced to 1 in. as a gas inlet. These burners were fed by a 2-in. main which carried from 7 to 12 lbs. gas pressure of natural gas. The flame from the burners impinged on a fire brick checker wall which broke up the flame. There were four 6-in. circular air inlets at the bottom of the furnace, through two of which the burners entered. The other two had caps, by means of which the entrance of air could be regulated. The stack and burners were located at the same end of the furnace so that the heat traveled the length of the furnace twice before coming to the stack. The furnace walls were supported by buckstays of 2-in. angle iron at each corner. The rods holding these stays passed through the walls the entire length of the furnace.

THE CONDENSERS—The condensers consisted of two pans connected by a header, each pan containing approximately 500 feet of 2-in. pipe, these in turn connecting to headers at each end of the coils, and entering the look box in a common 2-in. pipe. A gate valve was placed between the condensers and the look box to enable the vapors to be condensed under pressure. From the look box, a 2-in. pipe led to three receiving tanks, which were arranged with valves, so that any one could be used at will.

### OILS USED IN THE EXPERIMENTS

Four different grades of oil were used in the experiments, (1) Illinois crude, gravity 33° B.; (2) test distillate, gravity 42.5° B. (all naphtha had been taken from this oil); (3) gas oil, gravity 34° B.; (4) fuel oil, gravity 21 to 22° B.

### OPERATION

The method of operation of the apparatus was practically the same in each case. The furnace was heated until the desired temperature was reached. This point was determined by means of a portable pyrometer which was connected to four thermocouples by means of a four-way switch enabling the determination of the temperatures of four parts of the furnace. One of the thermocouples was inserted in the end of the last tube of the decomposer and gave the temperature of the vapors just before they left the furnace; the other three were inserted in the furnace proper.

When the desired temperature was reached the oil, or oil and steam, or oil and water, were introduced into the heated tubes. The first portion to pass through the furnace was discarded in the determination of yields because it was found that the decomposition was not uniform until the furnace had been run for some time and a uniform heat equilibrium obtained. After operation for about half an hour the distillate usually was found to be quite uniform and samples were then taken. The oil feed tank was equipped with a graduated glass gauge, by means of which the amount of oil passed into the furnace in a given length of time was shown. The volume of the original oil used and the resulting distillate were measured at the same intervals. From the difference of these two readings the loss was determined. The distillate from the decomposer was fractionated and yields are reported on the basis of this fractional distillation.

The residues from fractional distillation were in every case heavier than the original oil. From kerosene having an original gravity of 42° B., the residues in one case had a gravity as low as 34° B. on being passed through the apparatus once.

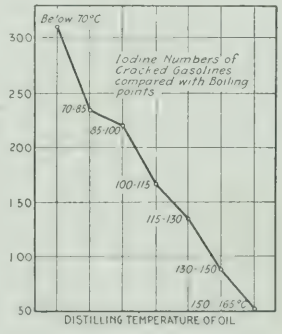
### YIELDS

With the third apparatus described, at temperatures ranging from 450–600° C., yields of gasoline varied from 18 to 28 per cent. when starting with kerosene and passing through the apparatus once. After distilling off the lighter materials the residues were again passed through the apparatus. Yields up to as high as 26 per cent were obtained.

By running a sample of kerosene, distilling to 150° C. and then re-running the residues from distillation and oil scrubbing the gases which were given off, yields of 40–45 per cent were readily obtained.

The losses as gas were very constant at 16–18 per cent. These results are typical of all the forms of apparatus used.

The light products from the decomposition of petroleum were practically the same in each apparatus used. They were invariably heavier than gasoline of the same boiling point obtained from fractional distillation of crude petroleum.




IODINE VALUE—The light products obtained were unsaturated as shown by iodine value. The iodine absorption rises in a fairly regular curve as the boiling point decreases. The fraction between 150 and 165° had an iodine number of approximately 50, while the fraction obtained below 70° C., was 310. The accompanying curve is plotted from a number of observations, the results being the average of determinations made on several different samples.

INDEX OF REFRACTION—The light products also showed a marked change in the index of refraction from that of natural gasoline. Table II indicates

the results of a series of determinations of the refractive index of various samples.

TABLE II—REFRACTIVE INDICES OF GASOLINES OBTAINED BY CRACKING

| | Description of Sample | Refr. ind. |
|---|---|---|
| (*a*) | Boiling below 70° C. | 1.4585 |
| (*b*) | Boiling from 70–85° C. | 1.4460 |
| (*c*) | Boiling from 85–100° C. | 1.4435 |
| (*d*) | Boiling from 100–115° C. | 1.4480 |
| (*e*) | Boiling from 115–130° C. | 1.4478 |
| (*f*) | Boiling from 130–150° C. | 1.4440 |
| (*g*) | Boiling above 150° C. | 1.4450 |
| (*h*) | Boiling below 150° C., run with pressure | 1.4550 |
| (*i*) | Boiling below 150° C., no pressure | 1.4429 |
| (*j*) | Same as (*i*), hydrogenated | 1.4416 |
| (*k*) | Boiling below 150° C., treated with $H_2SO_4$ and NaOH | 1.4257 |
| (*l*) | Natural gasoline | 1.4142 |

### POLYMERIZATION

On standing for a long time it was noted that the color of the light distillate became darker. The odor also changed somewhat.

A sample of the distillate which had been standing for several weeks was subjected to redistillation. The operation proceeded smoothly until a temperature of about 160° C. was reached, when suddenly the residue in the flask began to froth violently and run over into the condenser. This action lasted only a minute or so and then subsided, leaving a dark brown viscous residue which was quite different from the original material.

Some of the light fractions which had been standing for a few weeks were subjected to fractional distillation *in vacuo*. At about 110° C. and a vacuum of 6–10 mm. mercury, the thermometer suddenly rose to 160° C., and some of the same dark brown viscous material passed into the condenser. On careful distillation a heavy residue of polymerized material was obtained which was dark orange in color and very viscous and tacky. Various tests were performed on this heavy material to determine some of its properties. Its reactivity with sulfur is of interest. A portion of the polymer was heated with sulfur and the mass suddenly reacted violently, forming a viscous oily mass quite different in its physical properties from the original substance. Sulfur chloride also reacts readily. When sulfur chloride was thoroughly mixed with the material the reaction became very violent and the same decomposition occurred as in the previous case. A quantity of the polymer mixed with about 2 per cent sulfur was heated in a sealed tube. Heat was applied very gently and as soon as it was seen that reaction had started, the tube was removed from the flame. The reaction continued and finally the tube exploded with marked violence. Another portion of the heavy material was heated very carefully in an air bath to determine the temperature at which decomposition occurred. In several experiments when the temperature had been raised to about 110° C. it was noted that some slight decomposition had taken place and at about 125° C. apparently the same decomposition occurred as had taken place when the material was heated with sulfur. This heavy material also absorbed iodine, although not to so marked an extent as the original light distillate. The iodine number of the polymer was 35.6 and after heating to the decomposition point of 125° C. the iodine number was 61.3. It is peculiar that after decomposition, the iodine number was higher instead of lower as might be expected.

### HYDROGENATION

Inasmuch as these light distillates absorbed iodine so readily, samples were treated with hydrogen to partial saturation. In most cases no attempt was made to reduce the iodine number to zero. On treatment with hydrogen it was noted that the odor was materially bettered and the color changed from light straw-yellow to a water-white. The refractive index also changed and on long standing none of the thick viscous polymer was obtained as in the case of the distillate which had not been treated with hydrogen.

### GASES

The cracking process is accompanied at all times by the formation of fixed gases. The amount will vary according to the process used for cracking. By the treatment described the losses due to gas and entrained vapors are from 16–18 per cent. Analysis of samples of this gas show, as would be expected, that it is not of the same composition under various conditions.

In general, it may be said that the olefin content is high, often approaching 40 per cent, and that the content of carbon dioxide, carbon monoxide, oxygen and hydrogen are very small.

The gas takes up chlorine gas very readily, forming a liquid which in one case boiled between 90–200° C. At about 200° C. this material was decomposed and hydrochloric acid gas was given off. The gravity of the chlorinated product was 1.176.

### EFFECT OF WATER OR STEAM

So far as our experience goes there is no distinction between water and steam in their effect on the cracking process, although others have thought that different results are obtained when steam is used in place of water in tubular cracking apparatus.

The experiments along this line all seem to point to the same general conclusion. An example will show the effect of water in a general way: in one experiment, the water content was determined, then increased and diminished. The fires were kept the same throughout and the same flow of oil maintained as nearly as possible throughout the run. The products were collected, the water separated from the oil and a distillation made from which the yields were computed.

| | | | | | |
|---|---|---|---|---|---|
| Per cent oil | 80 | 50 | 45 | 70 | 80 |
| Per cent water | 20 | 50 | 55 | 30 | 20 |
| Per cent gasoline yield | 19 | 15 | 14 | 18.5 | 18 |

### CARBURETOR EXPERIMENTS

A carburetor was constructed entirely of glass so that the action of air on the light distillate could be examined. Some of the light distillate was carbureted. The material volatilized very readily but an examination of the interior of the carburetor disclosed a quantity of a gummy residue adhering to the sides of the air chamber. Samples treated with moderate amounts of strong sulfuric acid and then washed free from acid were carbureted and the inside

of the air chamber examined. An appreciable amount of gummy material was found adhering to the sides of the vessel.

A sample which was treated with sulfuric acid in larger amounts, then with caustic soda solution and afterwards distilled to 110° C. did not leave an appreciable amount of gummy residue in the carburetor.

Light distillate, which had been treated with hydrogen until it was water-white, was carbureted. No gummy material deposited in the air chamber. The effect of the hydrogenation process on gasoline of this character is decidedly beneficial and even partial hydrogenation suffices to stabilize the product to a surprising degree.

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## THE RESINS IN HOPS FROM VARIOUS GEOGRAPHIC LOCALITIES

By G. A. RUSSELL[1]

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The soft resins found in hops have been a subject of special interest to investigators for a number of years. Since the soft resins are generally credited with the greatest commercial value, a determination of the percentage of these resins has usually been the principal aim of the investigator. For the accurate determination of the percentage of these resins, various methods have been devised. From the results obtained by the writer, it is thought that the variations in the hops themselves account in great part for the variations in the results obtained by other investigators. Apparently, the technique of the method employed does not influence the results to the degree generally supposed.

In a recent publication, Winge and Jensen[2] have shown that the hard resin also has some apparent commercial value, and these authors maintain that the hard resin can no longer be disregarded as an important factor in hop analysis. Its presence, if in any quantity, may exert considerable influence on the commercial value of the hops. In addition, if determined separately, the percentage of hard resin present in a given sample may afford some index to the age of the hops.

Inasmuch as the various methods employed by previous investigators are familiar to all interested in this subject, the following brief list of the more important investigators is deemed sufficient.

Hayduck,[3] in 1888, pointed out a line of investigations that has been more or less adhered to ever since. Hantke,[4] Lintner,[5] Siller,[6] Briant and Meacham,[7] Seyffert and Autropoff,[8] Remy,[9] and Tartar and Bradley[10] have presented various methods or modifications of previous methods.

[1] Published by permission of the Secretary of Agriculture.

[2] O. Winge and J. H. P. Jensen, "A method for quantitative determination of resins in hops," *Comptes rendus des travaux du Laboratoire de Carlsberg*, 11me volume, 2me Livraison, 1914.

[3] *Wochenschrift fur Brauerei*, No. 3, p. 537 (1888).

[4] *Transactions of American Brewers' Institute*, No. 2, p. 234 (1903).

[5] *Chem. Zeit.*, No. 32, p. 1068 (1908).

[6] *Zeitschrift fur Untersuchung der Nahrungs und Genussmittel*, No. 18, p. 241 (1909).

[7] *Journal of the Federated Institute of Brewing*, No. 3, p. 233.

[8] *Zeitschrift fur die gesamte Brauwesen*, Nos. 4, 5, and 6, 1892.

[9] *Wochenschrift für Brauerei*, No. 15, p. 530 (1898).

[10] THIS JOURNAL, 4 (1912), p. 200.

In the course of a series of investigations carried on in connection with drug-plant investigations, a number of determinations were made on hops from various geographical sources. The methods employed were based on the principle that petrolic ether removes all of the soft resins and none of the hard, while ether removes the hard resin after the soft resins have been removed. Thus one sample of hops is used for both determinations.

### METHODS OF ANALYSES

SOFT RESINS—A 1500-gram sample of hops was ground, packed in a percolator, and macerated with petrolic ether (b. p. 35°–60° C.) for 48 hours. The petrolic ether was then percolated off, a fresh supply added, and the hops allowed to macerate again for 24 hours. The petrolic ether was again percolated off, the marc washed with fresh petrolic ether, the percolates united, and the major portion of the petrolic ether recovered on a water bath. The remainder of the solvent was allowed to evaporate spontaneously, and the weight of extract considered as percentage of soft resins. The wax which came out in this solvent was not removed except for purposes of comparison, and then only on a small weighed portion of the mixture of soft resins and wax.

The point at which to weigh the soft resins was found by experiment. Drying *in vacuo* to constant weight did not permit a true estimate of the soft resins present, inasmuch as these products continually lost weight. By allowing the last trace of the solvent to evaporate spontaneously and weighing as soon as this solvent was removed, it was found that accurate and comparable results could be obtained.

HARD RESIN—Only 100 grams of hops freed from soft resins were extracted: the extraction was carried out in a large Soxhlet apparatus, and continued until the sample was exhausted, which usually took about six hours. The solvent was then partially recovered, the remaining solution placed in a tared flask and practically all the remaining solvent recovered. The last trace was removed by drying for 30 minutes in an electrically heated oven. In the calculation, the weight of soft resins was returned and the yield of hard resin calculated with reference to the original dry hops.

WAX—A weighed portion of the petrolic ether extract of soft resins and wax was warmed and 5 cc. of petrolic ether added. To this solution was added about 50 cc. of methyl alcohol. The wax separated out in large, flocculent particles easily filtered off onto a weighed filter, where it was thoroughly washed with methyl alcohol. The filter and wax were then dried at 70° C., cooled in a desiccator over calcium chloride and weighed.

MOISTURE—A 60-gram sample of hops was dried in an oven at about 90° C. for 5 hours. This method gave results that checked very closely with the average of several 10-gram samples dried over sulfuric acid.

ASH—Two samples of hops were ashed in open crucibles, over a Bunsen burner. The average of these two determinations was returned as the ash content.

It has always seemed to the writer that in determining the amounts of soft and hard resins in hops it would

be advisable to use a larger sample than the usual 10-gram sample employed, as the error would naturally be less and the selection of a more representative sample possible. In order to substantiate this supposition a series of determinations was made on 10-gram samples, and the results compared with those obtained from extracting a large representative sample. The results obtained justified the use of the larger sample (Tables I and II). The 10-gram samples were selected from a quantity of hops weighing 15 kg. To make the extractions the samples were first ground in a mortar with sea sand and packed in a small Soxhlet extraction apparatus. Petrolic ether (b. p. 35°–60° C.) was used as a solvent for the soft resins and ether as a solvent for the hard resin, the same sample answering for both determinations.

The results expressed in Tables I and II show a wide range in the amount of soft and hard resins present in the samples picked at random, and also in the selected samples. In Table I, the lowest yield of soft

TABLE I.—PERCENTAGE ANALYSES OF SAMPLES SELECTED AT RANDOM

| Sample | Moisture | Weight of dry hops extracted = 10.00 grams Soft resins | Hard resins | Total resins | Wax |
|---|---|---|---|---|---|
| 1*a* | 6.09 | 20.38 | 2.80 | 23.18 | 0.553 |
| 2*a* | 6.45 | 21.67 | 3.20 | 24.87 | 0.473 |
| 3*a* | 4.50 | 22.08 | 2.33 | 24.41 | 0.484 |
| 5*a* | 9.20 | 20.06 | 2.60 | 22.66 | 0.489 |
| 6*a* | 4.21 | 20.06 | 2.27 | 22.33 | 0.514 |
| 7*a* | 8.95 | 16.08 | 2.94 | 19.02 | 0.498 |
| 1*b* | 4.77 | 20.89 | 2.85 | 23.74 | 0.509 |
| 2*b* | 4.70 | 18.89 | 3.45 | 22.34 | 0.429 |
| 3*b* | 7.08 | 17.64 | 3.60 | 21.24 | 0.432 |
| 5*b* | 6.41 | 18.39 | 3.55 | 21.94 | 0.457 |
| 6*b* | 3.80 | 18.83 | 3.70 | 22.53 | 0.526 |
| 7*b* | 4.87 | 19.01 | 4.65 | 23.66 | 0.536 |
| Average, | 5.91 | 19.49 | 3.16 | 22.66 | 0.491 |

resins is 3.41 per cent below the average, and the highest 2.59 per cent above the average. Expressed in terms of percentage, considering the average yield as 100 per cent, the lowest yield is 17.44 per cent lower than the average, and the highest 13.28 per cent above the average. This great variation in yield of soft resins indicates how great an error may be made in valuing a bale of hops if the determination is based on only one 10-gram sample. Furthermore, if the 10-gram sample consists of only perfect cones, an even greater error is introduced into the valuation of a quantity of hops. In Table II, it is noted that the

TABLE II—PERCENTAGE ANALYSES OF SAMPLES SELECTED FROM PERFECT CONES

| Sample | Moisture | Weight of dry hops extracted = 10.00 grams Soft resins | Hard resins | Total resins | Wax |
|---|---|---|---|---|---|
| 1*c* | 6.57 | 25.54 | 3.64 | 29.18 | 0.531 |
| 2*c* | 6.57 | 22.84 | 3.05 | 25.89 | 0.451 |
| 3*c* | 6.57 | 25.67 | 4.22 | 29.89 | 0.458 |
| 5*c* | 5.00 | 25.87 | 3.05 | 28.92 | 0.507 |
| 6*c* | 5.00 | | 2.85 | | |
| 7*c* | 5.00 | 22.19 | 2.90 | 25.09 | 0.525 |
| 2*d* | 3.33 | 22.45 | 3.00 | 25.45 | 0.344 |
| 5*d* | 3.62 | 23.48 | 2.80 | 26.28 | 0.412 |
| 7*d* | 4.29 | 23.48 | 3.45 | 26.93 | 0.365 |
| Average, | 5.10 | 23.94 | 3.21 | 27.20 | 0.449 |

range in yield of soft resins extends from 1.75 per cent below to 1.93 per cent above the average. If, however, the average yield is considered as 100 per cent, this variation gives 7.30 per cent below and 8.06 per cent above the average. Considered with reference to the variation shown in Table I, the variation in Table II is not so pronounced. If, however, the averages are compared with the results given in Table III, it becomes apparent that the average from selected cones runs entirely too high, whereas the average from samples selected at random is practically the same as the result obtained in extracting one 1500-gram sample.

TABLE III—COMPARISON OF THE AVERAGE PERCENTAGES FROM TABLES I AND II WITH PERCENTAGES OBTAINED ON EXTRACTING A 1500-GRAM SAMPLE

| Averages from | Moisture | Grams of dry hops extracted | Soft resins | Hard resins | Total resins | Wax |
|---|---|---|---|---|---|---|
| Table I | 5.91 | 10.00 | 19.49 | 3.16 | 22.66 | 0.491 |
| Table II | 5.10 | 10.00 | 23.94 | 3.21 | 27.20 | 0.449 |
| Large sample | 5.43 | 1418.55 | 19.38 | 3.66 | 23.04 | 0.473 |

From the data presented in Table III, it at once becomes evident that the averages from the several samples picked at random coincide very closely with the results obtained in extracting one large representative sample of approximately 1500 grams, dry weight. The supposition is then true that one 10-gram sample of hops picked either as representative or from selected cones, gives an erroneous measure of the soft resins in a large quantity of hops.

### ANALYSES OF LARGE SAMPLES

Taking therefore, for a series of years, a 1500-gram sample for extraction, the data in Table IV have been obtained regarding the percentage of soft resins present in hops from various geographical localities.

The yield of soft resins in the hops from the various geographic sources was found to vary widely from year to year. Those from Saaz No. 1, Cosumne No. 2, Perkins No. 1, Washington and New York, run fairly uniform throughout the four years. Of these the hops from New York State present the nearest uniform yield. In considering the yield of soft resins year by year, it is found that in the greater number of samples, the percentage was somewhat higher in 1912 than in the other years. This difference is due in part to the fact that in that year less time elapsed between the time of harvest and the time the extractions were made than in any other year. This is especially true of the samples from the western United States, for these hops were extracted four to five weeks nearer picking time than they were in the other years. As far as can be learned of the history of the foreign samples, the difference between the time of extraction and the time of harvest varied each year. This accounts in part for the variation in the soft resin content. The New York samples were all extracted at approximately the same time after harvest.

Since the commercial value of hops is in a measure dependent on the soft resin content, the fluctuation in these products is worthy of note. Climatic conditions, no doubt, influence the yield of soft resins from year to year. This, as well as other factors, chief of which is length of storage, exerts an influence on hops which tends to decrease the amount of soft resins. If, therefore, a systematic and rational basis for determining the commercial value of hops is to be employed, it seems probable that each bale of hops must be examined as it is used and a value placed thereon, comparable to some established standard.

Vieweg has pointed out[1] that the mineral constituents of hops have also some probable value in a commercial way. However, aside from any commercial value the mineral constituents may have, the ash

[1] *Pure Products*, **3** (1907), 332.

TABLE IV -RESINS AND ASH IN HOPS FROM VARIOUS LOCALITIES

| Source of Hops | Per Cent Soft Resins | | | | Per Cent Hard Resins | | | | Per Cent Total Resins | | | | Per Cent Ash in Hops | | | | Average ash |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1910 | 1911 | 1912 | 1913 | 1910 | 1911 | 1912 | 1913 | 1910 | 1911 | 1912 | 1913 | 1910 | 1911 | 1912 | 1913 | |
| FOREIGN: | | | | | | | | | | | | | | | | | |
| Auscher | 15.44 | 17.28 | 16.90 | 11.04 | .... | .... | 6.35 | 6.30 | .. | .. | 23.25 | 17.34 | 7.13 | 9.00 | 8.15 | 7.60 | 7 97 |
| Austrian | 10.56 | 15.65 | 20.04 | 15.68 | .. | .. | 5.31 | 4.74 | .. | .. | 25.35 | 20.42 | 7 60 | 8.03 | 7.90 | 8.70 | 8 10 |
| Dauber | 10.93 | 13.89 | 15.77 | 14.17 | .. | .... | 4.92 | 4.60 | .. | .. | 20.69 | 18.77 | 9.60 | 9.36 | 8.05 | 9.60 | 9 15 |
| Saaz No. 1 | 18.51 | 16.04 | 17.62 | .... | .. | .. | 5.95 | .... | .. | .. | 23.57 | .. | 8.00 | 8.64 | 7.45 | 9.50 | 8 39 |
| Saaz No. 2 | 12.24 | 12.91 | 18.36 | 18.06 | .... | .. | 7.76 | 3.00 | ..... | .. | 26.12 | 21.06 | 9.10 | 8.66 | 7 70 | 7.45 | 8 24 |
| CALIFORNIA: | | | | | | | | | | | | | | | | | |
| Brewer | 9.75 | 13.85 | 16.90 | 13.64 | .... | .... | 8.31 | 4.00 | .. | .. | 25.21 | 17.64 | 12 60 | 14.58 | 13 70 | 13.90 | 13.69 |
| Cosumne No. 1 | 14.40 | 11.31 | 19.74 | 12.74 | .. | .. | 6.67 | 5.01 | .. | .. | 26.41 | 17.75 | 13 60 | 14.72 | .... | 14.05 | 14.12 |
| Cosumne No. 2 | 12.17 | 11.60 | 13.79 | 14.62 | .. | .. | 6.36 | 3.84 | .. | .. | 20.15 | 18.46 | 12.00 | 15.08 | 13.80 | 12.80 | 13.42 |
| Del Paso | .... | .... | 16.19 | 14.67 | .. | .. | 7.90 | 3.45 | . | .. | 24.09 | 18.12 | .. | .... | 15.17 | 13.90 | .. |
| Perkins No. 1 | 12.40 | 12.32 | 13.87 | 14.10 | .. | 5.26 | 6.58 | 4.46 | .. | 17 58 | 20.45 | 18.56 | 12.60 | 15.04 | 14.65 | 14.10 | 14.09 |
| Perkins No. 2 | ..... | 11.17 | .... | .... | .. | 6.43 | .... | .... | .. | 17.60 | ..... | .... | .. | 16.76 | ..... | ..... | .... |
| Ukiah | 11.50 | 17.16 | 19.38 | 15 78 | .. | .. | 3.66 | 3.00 | .. | .. | 23.04 | 18.78 | 9.30 | 8.44 | 8 78 | 7.80 | 8 55 |
| Wheatland No. 6 | 14.70 | 10.58 | 15.97 | 15.43 | .... | .... | 3.74 | 4.50 | .. | .. | 19.71 | 19.93 | 10.60 | 10.83 | 11.45 | 10.65 | 10.86 |
| Wheatland No. 23 | 11.89 | 13.62 | 16.56 | 15.23 | .... | .... | 5.44 | 4.17 | .. | .. | 22.00 | 19.40 | 10 40 | 11.95 | 11.70 | 12.50 | 11.64 |
| OREGON | 13.67 | 17.53 | 19.17 | 15.91 | .... | .... | 3.81 | 5.51 | .... | .... | 22 98 | 21.42 | 8.80 | 7.88 | 9.35 | 9.58 | 8 90 |
| WASHINGTON | 17.14 | 15.65 | 18.51 | 17 35 | .... | .. | 3.26 | 3.10 | .. | ..... | 21.77 | 20.45 | 6.80 | 10.50 | 7.95 | 7 20 | 8.61 |
| NEW YORK | 13.63 | 13.87 | 13.64 | 10.70 | .... | .. | 5.96 | 5.63 | . | ..... | 19 60 | 16.33 | 8 00 | 8.04 | 9.25 | 8.60 | 8.47 |

should be determined in order to ascertain the amount of extraneous matter that probably sticks to the hop cones in localities where the wind blows steadily from one direction and where the soil is of a light sandy or dusty nature. It is interesting also to note the variation in the percentage of ash in hops from various localities. As this variation exists from year to year it might possibly be employed as a partial means of identification in hops of doubtful origin. The percentage of ash in hops from various localities (Table IV) is uniformly lower in the foreign hops than in those from California, and approximates that in the hops from Oregon, Washington and New York. The variations in percentage are so marked that a partial identification of a doubtful sample from one of these localities could be made by determining the amount of ash. The questions as to the commercial value of the mineral constituents of the ash and the possible means of identification by the determination of the percentage of ash are still open and worthy of consideration.

Since the amount of moisture present in hops varies greatly with the method of storing, and since the samples employed in this investigation were stored in the laboratory for several days previous to extraction, the results of the moisture determination are not tabulated. They admit of no comparisons other than that among themselves each year. The average amount of moisture present, in all samples after storage in the laboratory for several days, was found to be 5.82 per cent.

SUMMARY

I—One 10-gram sample picked at random does not give a correct index to the amount of soft resins in a quantity of hops, nor does one 10-gram sample picked from selected cones.

II—The average from a number of determinations of 10-gram samples picked at random gives a true value of the amount of soft resins in a quantity of hops, as likewise does one large representative sample of approximately 1500 grams weight.

III—The methods employed in this investigation give accurate comparable results.

IV—The yield of soft resins varies from season to season in the same and in different localities making necessary the determination of the percentages of soft resins in every bale of hops at the time it is used.

V—The percentage of ash in hops varies in samples from different localities but remains approximately the same in samples from the same locality from year to year.

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## A COLORIMETRIC METHOD FOR THE DETERMINATION OF COPPER AND IRON IN PIG LEAD, LEAD OXIDES, AND LEAD CARBONATE

By BERNARD S WHITE

Received May 7, 1915

Most methods in use for the determination of the small percentage of copper contained in pig lead, lead oxides and lead carbonate are long and tedious. This is especially true in those instances where refined metal serves as the base for the finished product and the copper content being extremely low, many difficulties present themselves; these can be overcome by the use of this colorimetric method.

While the estimation of the iron content in these compounds can be readily carried out colorimetrically by a separate analysis,[1] it has been found that the following method, which combines the determination of both copper and iron colorimetrically in one analysis, adds greatly to the rapidity and accuracy in finding the percentages of these impurities. The method not only eliminates the use of hydrogen sulfide, but it shortens the time of a single analysis to 30 or 40 minutes, while the results attain the same degree of accuracy as those established by the longer and more complicated methods.

The method of procedure varies somewhat with the nature of the sample to be examined: hence, it will be necessary to make especial mention of red lead.

ANALYSIS OF PIG LEAD, LITHARGE AND LEAD CARBONATE

WEIGHT OF SAMPLE—In analyzing refined pig lead, or lead compounds made from refined metal, it is necessary, owing to the small percentages of copper and iron usually present, to use large samples. It has been found, by the use of this method, that smaller samples may be used with equally accurate results, thereby reducing the bulk to be handled and eliminating any errors which frequently result from the use of large volumes. A sample weighing 30 grams has been found sufficiently large for refined products, and not over 10 grams need be used for the crude, or unrefined material.

METHOD OF PROCEDURE—Weigh the finely divided sample into a 400 cc. beaker, and add small portions of

[1] THIS JOURNAL, 4 (1912), 659.

hot (1:1) nitric acid until solution is effected. If any basic lead nitrate has been formed, dilute slightly with warm water and boil. Add 32 cc. (1:1) sulfuric acid, stirring constantly while adding. Let the precipitate settle, and decant filtrate through a coarse filter paper. Wash four times by decantation, using small portions of warm, distilled water. Transfer the precipitate to the paper, wash again and allow to drain. Make the filtrate neutral with ammonium hydroxide and add 4 cc. excess. Boil for a short time and filter. Wash the precipitate well with warm water, and reserve for the determination of the iron. Render the filtrate acid with special C. P. hydrochloric acid, adding not more than two drops excess. Add six drops of (1:10) potassium ferrocyanide solution, filter through close filter papers using two to each funnel. Catch the filtrate and inspect for copper ferrocyanide. Let the precipitate drain well without washing. Dissolve the copper ferrocyanide off of the paper with alternate washings of small portions of ammonium hydroxide and hot water. Wash well and keep the bulk to 30 or 40 cc. Render slightly acid with hydrochloric acid, adding not over two drops excess. Transfer to a 100 cc. Nessler tube, and dilute to mark with distilled water. The copper is then determined colorimetrically according to a modification of the method of Carnelly.[1]

In another Nessler tube, place 10 cc. dilute ammonium chloride solution, two drops concentrated hydrochloric acid and 90 cc. distilled water, add, from a burette graduated to tenths of 1 cc., standard copper sulfate solution until the color matches the sample under examination.

*Standard Copper Sulfate Solution*[2]—"Dissolve 0.393 gram of pure $CuSO_4.5H_2O$, in one liter of distilled water. 1 cc. = 0.0001 gram copper," or 0.00033 per cent when using a 30 gram sample.

### ANALYSIS OF RED LEAD

Treat 30 grams of the sample with 40 cc. (1:1) nitric acid, using great care that the violence of the reaction does not cause the sample to froth over the beaker. Slowly add 30 to 40 cc. of 3 per cent hydrogen peroxide, stirring constantly. Boil until solution is effected, and proceed as directed under the ANALYSIS OF PIG LEAD.

Sodium sulfite C. P. may be used in place of the hydrogen peroxide for effecting the solution of lead peroxide, adding it dry in small portions and boiling until no brown lead peroxide is present.

### DETERMINATION OF IRON IN THE ABOVE COMPOUNDS

For the iron determination, use the precipitate of iron hydroxide removed from the copper solution, proceeding as follows: Dissolve the precipitate contained on the paper with (1:1) hydrochloric acid, collecting the filtrate in a 300 cc. volumetric flask. Wash the paper free from acid with hot, distilled water, dilute to mark, and mix thoroughly. Place 10 cc. in a 100 cc. Nessler tube, add three drops nitric acid, 10 cc. (1:15) ammonium sulfocyanide solution, dilute to mark and compare with a standard iron solution according to the method outlined by Schaeffer:[1]

"The color is compared with a blank made in the following manner: A solution of ferric ammonium sulfate of known strength is required. This is made by dissolving 0.7022 gram of ferrous ammonium sulfate in water. Acidify with sulfuric acid, heat to boiling and add a solution of potassium permanganate until all the iron is converted to the ferric condition. Only the very slightest pink tinge may be present after the addition of the potassium permanganate, as this tinge will fade away, while the presence of a pink color tends to vitiate the results. Allow the solution to cool and dilute to one liter. One cc. of this solution equals 0.0001 gram of iron.

"Prepare the blank by pouring into a 100 cc. Nessler cylinder, 10 cc. ammonium sulfocyanide solution, and three drops of concentrated nitric acid. Dilute to 100 cc. and titrate to the exact color developed in the sample under examination, by the addition of the standard ferric ammonium sulfate solution. One cc. of this solution equals 0.01 per cent iron as the 10 cc. removed from the flask contained 1 gram sample. It will be found that the color can be accurately compared to within 0.001 per cent of iron content."

### COMPARISON OF RESULTS ON COPPER

Table I shows the results obtained by the above method, as compared with the method set forth by Fresenius,[2] on two sets of samples and a copper sulfate solution of known strength.

TABLE I COMPARATIVE RESULTS (PERCENTAGES CU) BY FRESENIUS AND AUTHOR'S COLORIMETRIC METHOD

| | Pig Lead | | Litharge and Red Lead | | $CuSO_4$ Solution | | |
|---|---|---|---|---|---|---|---|
| No. | Fres. | Color | Fres. | Color | Fres. | Color | % Cu present |
| 1..... | 0.0009 | 0.00088 | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 |
| 2..... | 0.0013 | 0.0013 | 0.0008 | 0.0008 | 0.0008 | 0.0008 | 0.0008 |
| 3..... | 0.0009 | 0.00088 | 0.0009 | 0.00088 | 0.00066 | 0.00066 | 0.0007 |
| 4..... | 0.002 | 0.002 | 0.0007 | 0.0007 | 0.001 | 0.001 | 0.001 |
| 5..... | 0.001 | 0.001 | 0.0015 | 0.0015 | 0.00066 | 0.00066 | 0.00066 |
| 6..... | 0.0015 | 0.0015 | 0.0038 | 0.0038 | 0.0015 | 0.0015 | 0.0015 |
| 7..... | 0.0012 | 0.0012 | 0.00088 | 0.00088 | 0.00088 | 0.00088 | 0.00088 |
| 8..... | 0.0079 | 0.0079 | 0.00088 | 0.0009 | 0.0009 | 0.00088 | 0.0009 |
| 9..... | 0.0013 | 0.0013 | 0.0013 | 0.0013 | 0.0015 | 0.0015 | 0.0015 |
| 10..... | 0.0004 | 0.0004 | 0.00066 | 0.00066 | 0.0007 | 0.00066 | 0.0007 |

### PRECAUTIONS AND INTERFERING ELEMENTS

If the sample contains much ZINC, the following method may be used for removing it: The filtrate from the iron precipitation, before precipitating the copper ferrocyanide, is rendered slightly acid with acetic acid, and 5 cc. of an 8 per cent sodium ammonium phosphate solution are added; boil, cool, filter and treat the filtrate as before outlined.

LEAD, when present in not too large quantity, has little or no effect on the accuracy of the colorimetric comparison of copper. If a faint white cloud of lead ferrocyanide should develop in the sample under examination, the addition of a small amount of very dilute lead nitrate solution to the standard will overcome this difficulty.

REAGENTS AND INDICATORS—This method presupposes the use of absolutely pure reagents, especially free from iron and copper. Use litmus paper as an indicator, as all other indicators, once introduced, will affect the final color.

LABORATORIES OF PICHER LEAD COMPANY
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[1] Sutton's "Volumetric Analysis," p. 204.
[2] *Ibid.*, p. 205.

[1] THIS JOURNAL, **4** (1912), 659.
[2] Fresenius' "Quantitative Chemical Analysis," Vol. II, p. 584.

## NOTE ON THE IDENTIFICATION OF TRIVALENT MANGANESE IN GLASS

By S. R. Scholes

Received July 7, 1915

Manganese, introduced as the dioxide, is commonly used as a decolorizer for glass, since it imparts a violet tint, which effectively masks the green produced by iron. The literature of glass is not definite regarding the particular compound of manganese responsible for the color. Some of the best authorities, such as Dralle and Hovestadt, regard the trioxide, $Mn_2O_3$, as the essential constituent oxide, but, so far as the writer is aware, no definite experiments have hitherto been described, demonstrating the state of oxidation of manganese in the colored silicate.

Some results, giving evidence of the presence of manganese trioxide in a glass, were obtained by means of the following experiments:

A low-melting glass, but approximating the composition of a commercial glass, except in manganese, was made, using:

| Sand | Soda Ash | Red Lead | Manganese Dioxide |
|---|---|---|---|
| 10 parts | 5 parts | 6 parts | 1 part |

This glass had a deep violet color. By pulverizing a sample and treating it with hydrofluoric acid, a pink solution was obtained, which could be decolorized by oxalic acid and other reducing agents. A similar pink solution was obtained by prolonged boiling of the powdered glass with 30 per cent sulfuric acid.

In order to obtain this pink solution more readily, a more soluble glass was made, using:

| Sand | Potassium Carbonate | Manganese Dioxide |
|---|---|---|
| 5 parts | 5 parts | 1 part |

From this glass, by digesting with 30 per cent sulfuric acid, a strongly colored, pink solution was obtained.

It was thought possible that the pink color might be due to permanganate, but failure to get a colored solution by digestion with water alone, in which this glass slowly disintegrated, showed the absence of permanganates. There was also a difference in color, these pink solutions possessing a less violet tint than permanganate, for equal depth of color.

Manganic sulfate was then prepared by heating manganese dioxide to partial reduction to brown $Mn_3O_4$, and treating this material with sulfuric acid. In this way, a solution was made, closely resembling that obtained from the manganese glass. Upon diluting these solutions with several volumes of water, a light brown, flocculent precipitate appeared in both cases; also, their behavior toward oxalic acid was the same. These facts seem to indicate the presence of trivalent manganese in the glass.

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## SOME NEW ORGANIC COMPOUNDS OF VANADIUM

By A. T. Mertes and Herman Fleck

Received March 23, 1915

While searching for an organic electrolyte to render vanadium tetrachloride a conductor of the electric current, the writer found that a strong reaction took place when pyridine was mixed with vanadium tetrachloride. An attempt was made to separate and analyze the product formed, but without success.

Other ammonia derivatives were tried, and, in most cases, well defined compounds were obtained that could be easily separated and analyzed. The method of analysis and procedures in making the compounds are given below. The analyses appear in Table I.

Table I—Action of Some Organic Compounds on Vanadium Tetrachloride

| Vanadium Chloride treated with | No | Analysis of Compound % V | % C | % N | Calculated Percentages For | % V | % Cl | % N |
|---|---|---|---|---|---|---|---|---|
| Aniline | 1 | 8.97 | 24.54 | ..... | $4C_6H_5NH_2.VCl_4$ | 9.06 | 25.09 | ... |
| Dimethyl-Aniline | 1 | 7.97 | 20.7 | ... | $4C_6H_5N(CH_3)_2.VCl_4$ | 7.56 | 20.98 | ..... |
| Phenylhydrazine (excess) $VCl_4$ in excess | 1 | 7.75 | 21.4 | ..... | $4C_6H_5NHNH_2.VCl_4$ | 9.75 | 27.01 | ... |
| | 2 | 9.80 | 24.1 | ... | ... | ... | ... | ..... |
| Toluidine | 1 | 9.03 | 25.25 | ..... | $4C_6H_4CH_3NH_2.VCl_4$ | 8.25 | 22.82 | 9.02 |
| Diff. portion | 2 | 11.2 | 29.86 | 8.10 | $3C_6H_4CH_3NH_2.VCl_4$ | 9.96 | 27.58 | 8.18 |
| Ammonia | 1 | 15.3 | 40.7 | 19.15 | $4NH_3.VCl_4.4H_2O$ | 15.4 | 42.6 | 16.8 |
| Diff. portion | 2 | 16.15 | 42.2 | 19.1 | $5NH_3.VCl_4.3H_2O$ | 15.4 | 42.7 | 21.0 |
| Diff. portion | 3 | 15.5 | 43.2 | 19.9 | ... | ... | ... | ... |
| Methylamine | 1 | 12.6 | 35.6 | 19.8 | $6CH_3NH_2.VCl_4.H_2O$ | 12.9 | 35.7 | 21.1 |
| Diphenylamine | 1 | 11.75 | 30.35 | ..... | $3(C_6H_5)_2NH_2.2VCl_4$ | 11.46 | 31.75 | ..... |
| Benzol (6 weeks) | 1 | 29.2 | 53.0 | ..... | $C_6H_6.2VCl_3$ | 26.2 | 54.4 | ... |
| Shorter time | 2 | 32.7 | 57.4 | | $C_6H_6.V_2Cl_5$ | 28.7 | 49.7 | |
| Shorter time | 3 | 27.3 | 59.6 | | ... | ... | ... | |
| Anthracene (Reflux condenser, 2 hours) | 1 | 21.6 | 39.05 | | $C_{14}H_9.V_2Cl_5$ | 22.4 | 38.8 | |
| | 2 | 18.7 | 33.6 | | $C_{14}H_{10}.2(C_{14}H_9.V_2Cl_5)$ | 18.8 | 32.5 | |

### DETERMINATION OF VANADIUM AND CHLORINE IN ORGANIC COMPOUNDS

One-half to 1 gram of the substance is well mixed with finely powdered, chloride-free quicklime and transferred to a combustion tube about 50 or 60 cm. long and 1.5 cm. in diameter. The tube is heated in a combustion furnace for from 2 to 5 hours, depending upon the ease with which the substance decomposes. The contents of the tube are transferred to a beaker with about 300 cc. of water and nitric acid added to dissolve the lime. After filtering the solution and heating to boiling, silver nitrate is added to precipitate the chlorine. The silver chloride is filtered off, washed, dried and weighed. The filtrate is neutralized with ammonia, made slightly acid with acetic and lead acetate added to precipitate the vanadium as lead vanadate. This is filtered off, washed with water, dissolved in warm dilute nitric acid, and evaporated to white fumes with 10 cc. concentrated sulfuric acid. After cooling and diluting with water, the lead sulfate is filtered off and the filtrate received in a 500 cc. flask and water added to make a volume of 300 cc. Sulfur dioxide gas is passed into the solution until it smells strongly of sulfur dioxide. A few pieces of vitrified tile are added to prevent bumping and the flask boiled until the excess of sulfur d oxide gas is driven off: this requires about 15 minutes of vigorous boiling. The solution is titrated hot with $N/20$ potassium permanganate to a faint pink end point. It is again reduced and retitrated. The permanganate may be standardized against pure ammonium vanadate or iron wire.

### ACTION OF VARIOUS COMPOUNDS ON VANADIUM TETRACHLORIDE

Aniline—A freshly prepared benzol solution of vanadium tetrachloride is treated with an excess of recently distilled aniline dissolved in benzol. A black

precipitate is formed. This is filtered off and washed with benzol to remove the excess of aniline. The benzol is allowed to evaporate spontaneously or in a vacuum desiccator. The compound so obtained is a black powder unaltered by exposure to dry air and practically insoluble in water, but suffering a slight decomposition.

DIMETHYLANILINE—A benzol solution of dimethylaniline was treated with a freshly prepared solution of vanadium tetrachloride in benzol. A green precipitate or tar-like substance separated out on standing and adhered to the sides of the vessel. By adding absolute ether to the mixture, this separation was more complete as the compound appeared to be insoluble in ether. By shaking the mixture, most of the substance could be made to adhere to the sides of the vessel and the main portion of the liquid poured off. After rinsing the product a couple of times with ether, it was dissolved in alcohol and transferred to a beaker where the alcohol was allowed to evaporate spontaneously in a warm place.

PHENYLHYDRAZINE—When a freshly prepared benzol solution of vanadium tetrachloride is added to a solution of phenylhydrazine in benzol, a compound is formed. If the phenylhydrazine is in decided excess, the mixture is violet colored. By the addition of more vanadium tetrachloride, it takes on a darker hue. The precipitate was filtered off using suction, and washed with benzol.

TOLUIDINE—A solution of vanadium tetrachloride in carbon tetrachloride was treated with a solution of toluidine in the same solvent, and a black precipitate resembling the aniline compound was obtained. This precipitate was filtered off, washed with benzol and dried in a vacuum desiccator.

The analysis does not correspond with either of the formulae given in Table I, due, no doubt, to the compounds, as prepared, being insufficiently washed free from excess of vanadium tetrachloride. The compound containing the higher percentage of chlorine and vanadium showed a marked tendency to absorb moisture from the air and become tar-like, also due, probably, to an excess of uncombined vanadium tetrachloride.

AMMONIA—A current of ammonia gas was generated by heating ammonium hydroxide and passing the evolved gas through a drying tower containing solid caustic potash. This gas was passed into a benzol solution of vanadium tetrachloride and a precipitate formed. When saturated with ammonia, the precipitate was filtered off and washed with benzol. It was then dried in the air and analyzed. Portions 1, 2 and 3 were made at different times.

The compound is practically insoluble in water but decomposes on heating or on standing in water. Mineral acids decompose it with the formation of a bluish green solution. When heated alone in a closed tube, water is driven off and ammonium chloride sublimes and deposits on the cooler portions of the tube. The residue obtained after driving off all the volatile matter is black in color and earthy in appearance, and when analyzed was found to contain 63.05 per cent vanadium, showing it to be composed principally of vanadium tetroxide. By continued heating in the air it oxidizes to the pentoxide.

METHYLAMINE—Methylamine was prepared by heating a 33 per cent solution and passing the evolved gas through a drying tower containing solid potassium hydroxide. The gas was bubbled through a filtered solution of vanadium tetrachloride in gasoline and a yellow precipitate formed.

DIPHENYLAMINE—A carbon tetrachloride solution of vanadium tetrachloride was added to an excess of a solution of diphenylamine in carbon tetrachloride. An indigo-blue precipitate was formed which, when dried, was grass-green.

BENZOL—When vanadium tetrachloride is added to benzol, the mixture has a slightly darker color than vanadium tetrachloride alone. If the mixture is allowed to stand some time, a precipitate settles out and hydrochloric acid is formed at the same time. By pouring off the excess of benzol solution, filtering and washing with benzol, a purple colored compound is obtained which is unacted upon by dry air. By heating in a test tube, brownish vapors were given off. When added to water, it dissolves, with hissing, forming a brown colored solution. The compound was analyzed by dissolving in dilute nitric acid and proceeding in the manner previously described. Portion 1 was obtained after a mixture of benzol and vanadium tetrachloride had stood for about six weeks. Portions 2 and 3 were obtained by allowing the action to continue a shorter time.

ANTHRACENE—(1) When a solution of vanadium tetrachloride in carbon tetrachloride was mixed with a solution of anthracene in the same solvent, a black precipitate was immediately formed and hydrochloric acid given off.

(2) Another portion was prepared by mixing a carbon tetrachloride solution of vanadium tetrachloride with a solution of anthracene and heating under a reflux condenser for two hours.

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## THE COMPOSITION OF FROZEN ORANGES AND LEMONS[1]

By H D YOUNG[2]

Received June 21, 1915

There is very little information, so far as the author has been able to find with the limited library facilities at his command, as to the effect of freezing temperatures on the composition of citrus fruits. Whenever a freeze occurs in one of the citrus districts and the injured fruits begin to appear on the market, the daily press contains dispatches as to the findings of health officers in the larger cities, but very little, if any, records are to be found in the scientific journals. Following a very severe freeze in January, 1913, in Southern California, a large amount of work was done

[1] *Paper* No 9, Citrus Experiment Station, College of Agriculture, University of California, Riverside, California.

[2] Grateful acknowledgment is made to Mr. C. O. Smith and Mr. E. E. Thomas, University of California, and Miss Alpha Rasor, Winthrop College, Rock Hill, South Carolina, for their assistance

as to the effect of freezing on the composition of the juice of oranges and lemons, which is here presented. Among the points investigated were the specific gravity of the juice and of the fruit and the analyses of fruit picked at short intervals and of other samples from fruit picked and stored very shortly after the freeze occurred. The sugars were determined by Bertrand's method, the acid by titration, using phenolphthalein as an indicator and calculating to anhydrous citric acid. It may safely be assumed that the frozen fruit had approximately the same composition at the time of freezing as that of the unfrozen fruit of the date of January 13th, as the differences which take place in a week's growth are slight in the case of oranges and lemons.

## SPECIFIC GRAVITIES

The first two columns in Table I present the record of oranges picked on January 13th and kept in storage, the specific gravity of the different fruits being determined every four days. The average of the 20 unfrozen oranges was 0.876 on the date of picking and this had increased by February 27th to 0.936. The frozen oranges had an average of 0.850 at the date of picking (which was a week after the freeze), and by February 3rd this had decreased to —0.820, 0.820 being the lowest range of our method, which consisted in submerging the fruit in alcohol of varying density until the fruit was in equilibrium with a liquid of known density.

Columns 3 and 4 present the results of successive new lots of oranges picked every four days. The specific gravity of the sound oranges does not change appreciably, varying on both sides of 0.876. The frozen oranges on the tree decrease very rapidly,

DATA ON FROZEN AND UNFROZEN ORANGES AND LEMONS

TABLE I—AVERAGE SPECIFIC GRAVITY OF FRUIT

| | Navel Oranges | | | | Eureka Lemons | | | |
|---|---|---|---|---|---|---|---|---|
| | Stored lots(a) | | Different picks(b) | | Stored lots(a) | | Different picks(b) | |
| Date | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen |
| 1/14 | 0.876 | 0.850 | 0.876 | 0.850 | 0.890 | 0.860 | 0.890 | 0.860 |
| 18 | 0.876 | 0.840 | 0.872 | 0.846 | 0.907 | 0.833 | 0.879 | 0.834 |
| 22 | 0.884 | 0.838 | 0.874 | 0.834 | 0.926 | 0.807 | 0.889 | 0.803 |
| 26 | 0.885 | 0.832 | 0.870 | 0.820 | 0.930 | .. | 0.887 | .. |
| 30 | 0.884 | 0.821 | 0.864 | 0.810 | 0.941 | .. | 0.869 | .. |
| 2/ 3 | 0.894 | 0.812 | ... | .. | 0.953 | .. | .. | .. |
| 7 | 0.903 | ... | 0.873 | .. | 0.959 | .. | 0.881 | .. |
| 11 | 0.914 | ... | .. | .. | 0.966 | .. | .. | .. |
| 15 | 0.923 | ... | 0.880 | .. | 0.968 | .. | 0.873 | ... |
| 19 | 0.928 | ... | .. | .. | .. | ... | .. | .. |
| 23 | 0.936 | ... | 0.871 | .. | .. | .. | 0.863 | ... |
| 27 | 0.936 | ... | .. | .. | .. | .. | .. | .. |
| 3/ 3 | ... | ... | 0.869 | ... | .. | .. | 0.862 | ... |
| 11 | ... | ... | 0.866 | ... | ... | .. | 0.865 | .. |

(a) Fruit picked on January 13th.

TABLE II—AVERAGE SPECIFIC GRAVITY OF JUICE

| | Navel Oranges | | | | Eureka Lemons | | | |
|---|---|---|---|---|---|---|---|---|
| | Stored lots(a) | | Different picks(b) | | Stored lots(a) | | Different picks(b) | |
| Date | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen |
| 1/14 | 1.053 | .. | 1.053 | .. | 1.060 | .. | 1.060 | .. |
| 18 | 1.052 | 1.042 | 1.052 | 1.044 | 1.042 | 1.042 | 1.048 | 1.046 |
| 22 | 1.055 | 1.044 | 1.056 | 1.046 | 1.050 | 1.041 | 1.053 | 1.046 |
| 26 | 1.047 | 1.046 | 1.055 | 1.047 | 1.045 | 1.040 | 1.044 | 1.041 |
| 30 | 1.050 | 1.045 | 1.045 | 1.040 | 1.046 | 1.038 | 1.046 | 1.037 |
| 2/ 3 | 1.051 | .. | 1.045 | 1.043 | 1.046 | .. | 1.040 | .. |
| 7 | 1.056 | .. | 1.045 | 1.045 | 1.050 | .. | 1.045 | 1.038 |
| 11 | 1.053 | 1.044 | 1.050 | 1.048 | .. | .. | 1.044 | .. |
| 15 | .. | .. | 1.053 | 1.048 | 1.052 | .. | 1.042 | 1.038 |
| 19 | 1.048 | 1.050 | .. | .. | 1.051 | .. | 1.042 | 1.038 |
| 23 | .. | .. | 1.056 | 1.042 | .. | .. | .. | .. |
| 27 | 1.055 | 1.054 | .. | .. | .. | .. | .. | .. |
| 3/ 3 | .. | .. | .. | .. | .. | .. | .. | .. |
| 11 | .. | .. | .. | .. | .. | .. | .. | .. |
| Av., | 1.052 | 1.046 | 1.051 | 1.045 | 1.049 | 1.040 | 1.046 | 1.040 |

(b) Successive new lots picked on date given.

TABLE III—PER CENT TOTAL SUGAR IN JUICE

| | Navel Oranges | | | | Eureka Lemons | | | |
|---|---|---|---|---|---|---|---|---|
| | Stored lots(a) | | Different picks(b) | | Stored lots(a) | | Different picks(b) | |
| Date | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen |
| 1/14 | 10.56 | .. | 10.56 | .. | 3.39 | .. | 3.39 | .. |
| 18 | 9.18 | 6.54 | 8.92 | 7.86 | 2.85 | 2.47 | 2.64 | 3.16 |
| 22 | 8.87 | 7.08 | 9.43 | 7.51 | 2.88 | 2.12 | 3.12 | 2.89 |
| 26 | 8.07 | 7.28 | 9.39 | 7.44 | 2.07 | 2.41 | 2.94 | 2.47 |
| 30 | 8.32 | 7.29 | 7.50 | 6.38 | 2.83 | 2.33 | 3.67 | 2.95 |
| 2/ 7 | 9.11 | .. | 8.09 | 6.99 | 2.71 | 3.14 | 2.57 | 1.60 |
| 15 | 9.67 | .. | 7.85 | 7.01 | 2.69 | .. | 2.77 | 2.24 |
| 23 | 9.17 | 7.17 | 9.00 | 8.03 | .. | .. | 2.96 | 2.54 |
| 3/ 3 | .. | .. | 10.11 | 8.82 | 2.79 | .. | 2.57 | 2.11 |
| 7 | 9.28 | 7.96 | .. | .. | .. | .. | .. | .. |
| 11 | .. | .. | 9.41 | 6.94 | .. | .. | 3.30 | 2.21 |
| 15 | 8.42 | 8.63 | .. | .. | 2.97 | .. | .. | .. |
| Average, | 9.06 | 7.42 | 9.03 | 7.44 | 2.79 | 2.49 | 2.99 | 2.46 |

(a) Fruit picked on January 13th

TABLE IV—GRAMS OF SUGAR PER FRUIT

| | Navel Oranges | | | | Eureka Lemons | | | |
|---|---|---|---|---|---|---|---|---|
| | Stored lots(a) | | Different picks(b) | | Stored lots(a) | | Different picks(b) | |
| Date | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen |
| 1/14 | 7.2 | .. | 7.2 | .. | 1.3 | .. | 1.3 | .. |
| 18 | 5.3 | 3.6 | 5.0 | 4.3 | 1.0 | 0.7 | 0.8 | 0.9 |
| 22 | 7.9 | 3.4 | 6.6 | 3.6 | 1.2 | 0.4 | 1.1 | 0.5 |
| 26 | 4.9 | 2.2 | 7.3 | 3.2 | 0.8 | 0.3 | 1.2 | 0.4 |
| 30 | 6.2 | 2.9 | 6.4 | 3.8 | 1.0 | 0.2 | 1.3 | 0.3 |
| 2/ 7 | 5.8 | .. | 5.8 | 2.3 | 1.0 | 0.2 | 0.9 | 0.1 |
| 15 | 7.9 | .. | 6.3 | 2.3 | 0.8 | .. | 1.0 | 0.08 |
| 23 | 7.6 | 3.1 | 8.8 | 2.0 | .. | .. | 1.2 | 0.08 |
| 3/ 3 | .. | .. | 8.0 | 2.1 | 1.0 | .. | 1.2 | 0.2 |
| 7 | 7.0 | 1.9 | .. | .. | .. | .. | .. | .. |
| 11 | .. | .. | 8.5 | 1.9 | .. | .. | 0.9 | 0.08 |
| 15 | 5.1 | 1.8 | .. | .. | 0.9 | .. | .. | .. |

(b) Successive new lots picked on date given.

TABLE V—PER CENT INVERT SUGAR IN JUICE

| | Navel Oranges | | | | Eureka Lemons | | | |
|---|---|---|---|---|---|---|---|---|
| | Stored lots(a) | | Different picks(b) | | Stored lots(a) | | Different picks(b) | |
| Date | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen |
| 1/14 | 4.69 | .. | 4.69 | .. | 2.36 | .. | 2.36 | .. |
| 18 | 4.10 | 3.39 | 4.13 | 3.75 | 2.11 | 1.53 | 2.26 | 2.03 |
| 22 | 4.33 | 3.60 | 4.17 | 3.76 | 2.24 | 1.55 | 2.09 | 1.85 |
| 26 | 4.06 | 3.76 | 4.70 | 3.88 | 1.74 | 1.56 | 2.30 | 1.57 |
| 30 | 4.35 | 3.60 | 3.66 | 3.37 | 1.91 | 1.48 | 2.46 | 1.89 |
| 2/ 7 | 4.60 | .. | 3.49 | 3.57 | 2.26 | 2.09 | 1.98 | 1.30 |
| 15 | 5.16 | .. | 3.48 | 3.73 | 2.22 | .. | 2.35 | 1.73 |
| 23 | 4.88 | 3.56 | 4.00 | 3.71 | .. | .. | 2.30 | 1.79 |
| 3/ 3 | .. | .. | 4.77 | 3.85 | 2.25 | 1.42 | 1.99 | 1.50 |
| 7 | 5.18 | 3.35 | .. | .. | .. | .. | .. | .. |
| 11 | .. | .. | 4.11 | 3.45 | .. | .. | 2.66 | 1.74 |
| 15 | 4.87 | 3.95 | .. | .. | 2.42 | .. | .. | .. |
| Av., | 4.62 | 3.60 | 4.12 | 3.67 | 1.95 | 1.60 | 2.27 | 1.70 |

(a) Fruit picked on January 13th.

TABLE VI—PER CENT SUCROSE IN JUICE

| | Navel Oranges | | | | Eureka Lemons | | | |
|---|---|---|---|---|---|---|---|---|
| | Stored lots(a) | | Different picks(b) | | Stored lots(a) | | Different picks(b) | |
| Date | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen |
| 1/14 | 5.87 | .. | 5.87 | .. | 1.03 | .. | 1.03 | .. |
| 18 | 5.08 | 3.15 | 4.79 | 4.11 | 0.74 | 0.94 | 0.38 | 1.13 |
| 22 | 4.54 | 3.48 | 5.26 | 3.75 | 0.62 | 0.50 | 1.03 | 1.04 |
| 26 | 4.01 | 3.52 | 4.69 | 3.76 | 0.33 | 0.85 | 0.64 | 0.90 |
| 30 | 3.97 | 3.69 | 3.84 | 3.01 | 0.92 | 0.85 | 1.21 | 1.06 |
| 2/ 7 | 4.51 | .. | 4.60 | 3.42 | 0.45 | 1.05 | 0.59 | 0.30 |
| 15 | 4.51 | .. | 4.37 | 3.38 | 0.43 | .. | 0.42 | 0.51 |
| 23 | 4.29 | 3.61 | 5.00 | 4.32 | .. | .. | 0.66 | 0.75 |
| 3/ 3 | .. | .. | 5.34 | 4.97 | 0.54 | .. | 0.58 | 0.61 |
| 7 | 4.10 | 4.61 | .. | .. | .. | .. | .. | .. |
| 11 | .. | .. | 5.30 | 3.49 | .. | .. | 0.64 | 0.47 |
| 15 | 3.55 | 4.68 | .. | .. | 0.55 | .. | .. | .. |
| Av., | 4.44 | 3.82 | 4.90 | 3.79 | 0.63 | 0.84 | 0.72 | 0.75 |

(b) Successive new lots picked on date given.

TABLE VII—PER CENT ACID IN JUICE

| | Navel Oranges | | | | Eureka Lemons | | | |
|---|---|---|---|---|---|---|---|---|
| | Stored lots(a) | | Different picks(b) | | Stored lots(a) | | Different picks(b) | |
| Date | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen |
| 1/14 | 1.56 | .. | 1.56 | 1.38 | 5.81 | .. | 5.81 | .. |
| 18 | 1.56 | 1.60 | 1.45 | .. | 5.70 | 5.01 | 6.64 | 4.23 |
| 22 | 1.67 | 1.62 | 1.68 | 1.49 | 6.96 | 5.34 | 7.23 | 5.02 |
| 26 | 1.47 | 1.74 | 1.69 | 1.83 | 7.54 | 4.74 | .. | 4.67 |
| 30 | 1.68 | 1.88 | 1.53 | 1.59 | 7.67 | 4.98 | 6.49 | 3.66 |
| 2/ 7 | 1.68 | .. | 1.50 | 1.51 | 7.00 | 5.36 | 6.53 | 4.72 |
| 15 | 1.59 | .. | 1.31 | 1.34 | 6.72 | .. | 6.32 | 5.18 |
| 23 | 1.40 | 1.29 | 1.22 | 1.37 | .. | .. | 5.64 | 4.72 |
| 3/ 3 | .. | .. | 1.38 | 1.15 | 7.76 | 5.79 | 6.19 | 5.73 |
| 7 | 1.19 | 1.14 | .. | .. | .. | .. | .. | 5.23 |
| 11 | .. | .. | 1.20 | 1.21 | .. | .. | .. | 4.79 |
| 15 | 1.11 | 1.20 | .. | .. | 7.73 | .. | 5.65 | .. |
| Average, | 1.49 | 1.35 | 1.45 | 1.38 | 6.98 | 5.20 | 6.27 | .. |

(a) Fruit picked on January 13th.

TABLE VIII—GRAMS ACID PER FRUIT

| | Navel Oranges | | | | Eureka Lemons | | | |
|---|---|---|---|---|---|---|---|---|
| | Stored lots(a) | | Different picks(b) | | Stored lots(a) | | Different picks(b) | |
| Date | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen | Unfrozen | Frozen |
| 1/14 | 1.1 | .. | 1.1 | .. | 2.3 | .. | 2.3 | .. |
| 18 | 0.9 | 0.9 | 0.8 | 0.8 | 2.0 | 1.5 | 2.0 | 1.2 |
| 22 | 1.3 | 0.8 | 1.2 | 0.7 | 2.9 | 1.0 | 2.4 | 0.8 |
| 26 | 0.9 | 0.5 | 1.3 | 0.8 | 2.9 | 0.7 | .. | 0.7 |
| 30 | 1.2 | 0.7 | 1.3 | 0.9 | 2.8 | 0.4 | 2.3 | 0.4 |
| 2/ 7 | 1.1 | .. | 1.1 | 0.5 | 2.7 | 0.3 | 2.2 | 0.3 |
| 15 | 1.3 | .. | 1.0 | 0.4 | 2.0 | .. | 2.3 | 0.2 |
| 23 | 1.2 | 0.6 | 1.2 | 0.3 | .. | .. | 2.3 | 0.2 |
| 3/ 3 | .. | .. | 1.1 | 0.3 | 2.8 | 0.1 | 3.0 | 0.5 |
| 7 | 0.9 | 0.3 | .. | .. | .. | .. | 1.6 | 0.2 |
| 11 | .. | .. | 1.1 | 0.3 | .. | .. | .. | .. |
| 15 | 0.7 | 0.3 | .. | .. | 2.4 | .. | .. | .. |

(b) Successive new lots picked on date given.

however, from 0.850 on January 13th to —0.820 on January 30th.

Stored lemons show the same kind of changes as oranges, but of a greater degree, since sound lemons increased from 0.890 on January 14th to 0.968 on February 15th, and the frozen lemons decreased from 0.860 to —0.820 on January 22d. The fruit on the tree remained approximately the same if unfrozen, but decreased very rapidly in specific gravity if frozen.

The explanation of the different behavior of sound and frozen fruit probably is as follows: Freezing kills the protoplasm of the cells in the fruit and so changes the cell wall from a living, semipermeable membrane to a dead, porous mass similar to a sponge. In the frozen fruit, therefore, connection is established between the rind and the pulp, and the water which is evaporated from the outside is replenished from the pulp without the fruit suffering much diminution of volume. Losing weight and retaining approximately its original volume, it must, obviously, decrease in specific gravity. The unfrozen fruit, on the other hand, loses very little, if any, moisture, except from the rind, which shrinks down very markedly and so decreases the volume of the fruit: as the weight does not decrease proportionately, the specific gravity increases. The difference in the evaporation from the rind is shown very clearly by the following example: two oranges were picked on January 13th and stored for two months; they were the same size, $3^1/_{16}$ inch in diameter on picking; when cut, the sound fruit had decreased to $2^3/_4$ inches, while the frozen fruit had lost only $^1/_{16}$ in., measuring 3 inches.

The fact that the specific gravity of the juice of frozen fruit decreases, in spite of the large loss of moisture (as shown by the amount of juice which could be extracted), would seem to indicate that an actual destruction of the sugars and acids takes place (probably by fermentation).

### SPECIFIC GRAVITY OF THE JUICE

Because of the large number of samples used, it was not possible to make determinations on all of them each four days. The charts, therefore, present a rather irregular appearance. The specific gravity of the juice of unfrozen oranges in storage, Table II, does not seem to change appreciably, but it remains consistently greater than that of frozen oranges. The juice of frozen oranges has an average specific gravity of 1.046 throughout the greater part of the experiment, increasing quite markedly toward its expiration. The juice of the sound oranges has an average of 1.052 which remains approximately constant.

The oranges picked at different intervals, Table II, show about the same averages, except that the frozen ones do not show any constant increase toward the end of the experiment. The averages for the different picks is 1.051 for the sound fruit and 1.045 for the frozen, both figures being slightly less than for the stored lots.

The figures for the lemons show about the same thing; the juice of the sound fruit is heavier than that of the frozen. There are more irregularities in the tables for lemons, due to the difficulty of getting a sample of uniform ripeness. By January 30th, the frozen lemons in storage had dried out so completely that it was no longer possible to get enough juice to determine the specific gravity. On January 30th, 20 lemons picked January 13th yielded a total of only 31 cc. of juice.

### TOTAL SUGAR

The work on sugar and acid is presented in two different ways: *first*, the per cent in the juice, and *second*, the actual amount present in the juice of one fruit. While the latter figure is admittedly not exact because of the difficulty of extracting all the juice, yet, in view of the fact that the approximately same size oranges were used in all cases, it permits of a basis of comparison that is very striking.

Studying first the percentage composition of the juice in regard to the total sugar, Table III, the sound oranges in storage show considerable variation but in no definite direction. It is apparently only the variation of sampling. The frozen oranges show, however, a slight but definite increase. The average of the sound lots is 9.06 per cent and of the frozen 7.42 per cent throughout the experiment. The average of the fruit picked at different dates is 9.02 per cent for the good and 7.44 per cent, or (within the limits of error) the same as the average of the stored fruit.

The percentage of sugar in the juice of lemons shows the same kind of variation as in the case of oranges, the average of the determinations for stored lots of unfrozen lemons being 2.8 per cent and of stored frozen lemons 2.5 per cent. The determinations on samples picked at intervals show an average of 3 per cent for unfrozen lemons and 2.2 for frozen ones.

The actual amount of sugar present, Table IV, shows much greater differences. The stored sound oranges show considerable fluctuation, but no definite change. The frozen oranges, however, show a very marked decrease in the amount of sugar present, dropping to less than 2 grams of sugar per fruit, against an average for the sound ones of 6.5 grams.

The fruit remaining on the tree showed almost the same differences, dropping to the same point, the sound fruit showing a slightly greater average than the stored fruit, or 6.9 grams.

The lemons show again the same kind of variation as the oranges, but of different degree. The unfrozen stored lemons average 1.0 gram sugar per fruit, while the frozen ones decrease from 0.7 to 9.2 grams per fruit. The different picks show about the same amount of variation.

Tables V and VI, for invert sugar and sucrose, present data that are little different from those in the total sugar. In other words, there seems to be no change in the relative amounts of the different classes of sugar present.

### ACID

The percentage of acid, Table VII, in the frozen and and unfrozen oranges in storage decreased in almost the same degree. The average of both lots in storage was the same, 1.49 per cent. The fruit picked at intervals show the same character of change, but have a slightly lower average, the sound oranges showing

1.45 and the frozen 1.43 per cent. Turning to the actual amount of acid present in a fruit, Table VIII, a very marked difference is found. The frozen oranges show a very small amount of acid present, 0.3 gram against an average of about 1 gram for the sound oranges. Lemons have, of course, a much higher percentage of acid than do the oranges. They also show a greater variation between the sound and frozen fruit than the oranges do. The stored lemons which were unfrozen average 7.0 per cent acid throughout the experiment, while the frozen ones average 5.2 per cent. The fruit picked at different intervals averaged 6.3 per cent for nine samples of unfrozen lemons, and 4.6 for the same number of frozen samples. The comparison of the actual amounts of acid present in individual lemons shows the same striking differences between the frozen and unfrozen ones that oranges do: the amount in the unfrozen lemons, showing considerable variation, ranges from 2 to 3 grams: in the frozen fruit, however, it practically disappears.

SUMMARY

I—The principal change caused in citrus fruits by freezing is an excessive loss of moisture. This is shown by a marked lowering of specific gravity.

II—The percentages of sugar and acid decrease slightly but definitely.

III—Since the change in the composition of the juice is slight, its edible qualities are not impaired if it is not frozen so severely as to cause it to dry up.

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## THE IMPORTANCE OF FINENESS OF SUBDIVISION TO THE UTILITY OF CRUSHED LIMESTONE AS A SOIL AMENDMENT

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After experiments at the Pennsylvania Experiment Station and elsewhere had demonstrated the value of calcium carbonate in the form of pulverized limestone as a neutralizing agent for acid soils, many questions were addressed to the Station as to the conditions necessary for its successful use, and particularly with regard to the fineness to which it should be reduced for economical results. This subject was much discussed by the producers of crushed limestone who, naturally, were desirous of meeting the growing demand for this product at the lowest manufacturing cost compatible with its fitness for use.

Experiment Station writers differed in judgment as to the importance of this quality. Agricultural literature contained little that bore directly upon the question. The work of Bernard[1] and Heinrich[2] was not sufficiently broad in its scope to afford an answer to a question of so great economic importance. The experiment of Voelcker[3] at Woburn was too indefinite to add much to our knowledge. In none of these experiments, moreover, was the quantity of limestone used proportional to the acidity of the soil.

[1] Le Calcaire.
[2] Mergel u. Mergeln, p. 39
[3] *Jour. Roy. Agric. Soc. England*, **71** (1910), 349

To afford an answer to the question, two series of experiments were planned in the early summer of 1911 by Walter Thomas, B.S., under the writer's direction, and conducted during the fall of that year and succeeding months. The same lot of crushed limestone was used as the amendment in both series. The stone was obtained from the American Lime and Limestone Company, of Bellefonte, Pa., and was a good representative sample of the compact blue stone from the Trenton beds of that locality.

The crushed stone was carefully sifted through sieves of 20, 40, 60, 80 and 100 meshes to the inch. The part coarser than $^1/_{20}$ in. was rejected. The several lots of siftings thus obtained were separately analyzed to ascertain if they differed in composition. The fine siftings in this case contained 98.13 per cent, the coarser ($^1/_{20}$ to $^1/_{40}$ in.) 95.93 per cent of calcium and magnesium carbonates. The intermediate lots increased constantly in carbonate richness in their order from coarser to finer. The average of the five analyses was:

| Acid insoluble | $Fe_2O_3 + Al_2O_3$ | $CaCO_3$ | $MgCO_3$ | Total |
|---|---|---|---|---|
| 0.42 | 2.86 | 95.93 | 0.84 | 100.05 per cent |

Notwithstanding the slight differences in composition shown by these lots of differing fineness, each was used in these experiments in quantities strictly proportional to its (CaO + MgO) content.

### SERIES I

The soil used for this series represented Plat 32, of the General Fertilizer Series of Experiments, which had, every two years since 1881, received dressings of dissolved bone-black, muriate of potash, and nitrogen in the form of sulfate of ammonia. Owing, doubtless, to the influence of the last-named fertilizer ingredient, this soil had developed a highly acid condition, and produced low crop yields in consequence: its supply of fertilizer constituents was not deficient. The acidity of this soil, as used for this series of experiment, indicated a lime (CaO) requirement (Veitch) of 3,200 lbs. an acre—7 inches.

The culture experiments were made in small, paraffined wire-baskets, of $5^1/_2 \times 5^3/_4$ in. size, with medium red clover as the crop. The saturation capacity of the soil (water-free) was 19.0 per cent, and moisture to two-thirds that amount was supplied at the beginning of the experiment and carefully renewed, as need was shown by frequent periodic weighings during the course of the test. The weighed and moistened soil, previously well mixed with enough of the limestone to meet its lime requirement, was filled into each pot with the usual precautions to secure uniform compactness. Eighty clover seeds were sown in each pot, but the number was thinned to fifty after the plants were well established. Each lot of limestone was represented by three pots identically treated.

During the first six weeks of the experiment, the plants were kept out-of-doors, with cloth shelter for nights and rainy days. Owing to the lateness of the season, growth was slow. On Nov. 3rd the plants were removed to a greenhouse, with a temperature of 45–60° F. Thereafter they grew quite well, though

they suffered slightly from quite uniformly distributed, but short-period attacks of the white-fly, green aphis and red spider.

At the end of $8^1/_2$ months, the green tops were harvested, weighed, air-dried and reweighed. The roots also were carefully washed out from the soil, dried and weighed. The results in terms of the dry weights secured are given in Table I.

These figures show very clearly: (1) the need of the soil for amendment to fit it for clover production; (2) that the fineness of the limestone greatly affects its value as an amendment for many months after its application even to a highly acid soil, that is, a soil well suited to develop toward its maximum the rate at which calcium carbonate can act in neutralizing soil acidity. The improvement of the crop, which, for practical reasons, should be measured in this case by the development of its top, increased with the fineness of subdivision, up to the limits of fineness here tested. The rate of increase was not, however, uniform, as is better shown by the crop-ratios (Table I) in which that obtained with limestone finer than $^1/_{100}$ inch is taken as 100.

TABLE I—DRY WEIGHTS (GRAMS) OF CROPS FROM DIFFERENT TREATMENTS ON TWO SOILS

| Limestone Crushed Mesh—in. | Series I—In Soil from Fertilized Plat 32 | | | | | | | | | | | | Series II—In Soil From Run-Down Farm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tops | | | | Roots | | | | Entire Plants | | | | Crop Ratio (Last = 100) | Tops | Roots | Entire plats |
| | Triplicates | | | Av. | Triplicates | | | Av. | Triplicates | | | Av. | | | | |
| None | Plants died shortly after germination | | | | | | | | | | | | 0 | 1.89 | 1.71 | 4.30 |
| 1/20 to 1/40 | 0.47 | 0.79 | 0.49 | 0.58 | 1.5 | 2.0 | 0.8 | 1.43 | 2.29 | 2.47 | 1.29 | 2.01 | 11.9 | 2.03 | 3.66 | 5.69 |
| 1/40 to 1/60 | 2.15(*a*) | 3.34 | 3.12 | 2.87 | 2.45(*a*) | 4.20 | 4.10 | 3.58 | 4.60 | 7.54 | 7.22 | 6.45 | 59.1 | 2.16 | 3.92 | 6.08 |
| 1/60 to 1/80 | 3.64 | 4.65 | 2.89(*b*) | 3.73 | 5.00 | 4.93 | 3.53 | 4.49 | 8.64 | 7.58 | 6.42 | 8.22 | 76.7 | 2.22 | 3.97 | 6.19 |
| 1/80 to 1/100 | 4.87 | 4.99 | 3.94 | 4.60 | 5.36 | 5.46 | 4.13 | 4.98 | 10.23 | 10.45 | 8.07 | 9.58 | 94.7 | 2.23 | 3.33 | 5.56 |
| Finer than 1/100 | 5.10 | 4.65 | 4.84 | 4.86 | 6.40 | 5.33 | 4.93 | 5.55 | 11.50 | 9.98 | 9.77 | 10.41 | 100.0 | 2.38 | 3.75 | 6.13 |

(*a*) Only 40 seeds germinated. (*b*) Pot leaked.

The falling off in rate of increase in crop yield with materials finer than $^1/_{80}$ inch is in line with the previous observation of H. Yoyokama[1] that precipitated lime gave no better results than crushed limestone.

Taking into consideration the cost of effecting the highest pulverization, and the fact that stone of $^1/_{40}$ to $^1/_{60}$ inch in fineness produced only about three-fifths the effect secured with stone finer than $^1/_{100}$ inch, while stone of $^1/_{60}$ to $^1/_{80}$ inch caused more than three-fourths of the effect secured from the finest stone, it is judged that compact limestone of high purity should be crushed to a fineness of not less than $^1/_{60}$ inch, to fit it for economical use as a soil amendment. Less pure stones should, in view of the freight and handling costs and if sold at prices corresponding to their (CaO + MgO) richness, not fall below this degree of fineness for any considerable part of their weight. It is possible, however, that later tests may establish a less rigid requirement for soft, porous rocks than is here indicated for the compact Trenton stone.

### SERIES II

For this series of experiments, a different soil, obtained from a run-down farm long occupied by a succession of tenants, was used.

The tests were carried out as were those of Series I, but with four pots representing each lot of limestone added. The lime (CaO) requirement of the land was 1500 lbs. an acre—7 inches, that is, less than half that of the soil used in Series I. Despite the run-down condition of the soil, no fertilizer was added.

[1] *Jour. Coll. Agr. Imperial Univ. Tokyo*, **2** (1909), 181–182.

The results show quite clearly that acidity was not the limiting factor for the growth of clover. The differences between pots were less than in Series I. The averages of crop yields appear in Table I.

All the limestone dressings did a little good, yet in but one case did the crops of the treated pots, though grown with the same care, at the same time and in the same environment with those of Series I, approach the latter in yield. Since clover is an acidity-producing crop and the requirements for its larger development should be met, it is not believed that the results of this second series of experiments are as suitable for determining the question at issue, as are those of Series I.

It may be added that the results obtained in Series I are in accord with the results of similar experiments by Brehmer,[1] Gerlach[2] and v. Feilizten,[3] reported about the time our experiments were in progress.

The experiments here related should be regarded as preliminary. Others of like character, but involving the use of larger pots, affording opportunity for deeper root development and covering a much longer period for amending action have been planned and are being carried out by J. W. White, M.S., of this Section.

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## THE LIME: MAGNESIA RATIO IN SOIL AMENDMENTS

By WALTER THOMAS AND WILLIAM FREAR

Received June 25, 1915

In view of the prominence which the question as to the influence of the lime-magnesia ratio upon the vigor of plant growth had assumed, and of the very extensive use of magnesian limes and limestones as soil amendments in Pennsylvania practice, and also of the lack of established relationship, in experiments elsewhere conducted, between the degree of acidity of the soil and the quantity of the calcareous amendment applied, it was thought desirable to conduct experiments upon this subject in which correlation between acidity and neutralizing value of the amendment should be secured. The experiment here described was planned by Walter Thomas, B.S., under the writer's direction, and carried on at the same time with the experiments upon the influence of fineness of subdivision of limestone upon its use as a soil amendment, described in the preceding paper.

The calcium and magnesium were added to the soil in the form of hydroxides and carbonates. The materials used were prepared from calcite, magnesite and dolomite of the following percentage composition:

[1] *Illustrirte Landw. Zeitung*, **31** (1911), 832.
[2] *D. Landw. Presse*, **38** (1911), 409.
[3] *Svenska Mosskultorför Tidskr.*, **24** (1910), 95–98.

| | Acid-insoluble | $Fe_2O_3 + Al_2O_3$ | $CaCO_3$ | $MgCO_3$ | Total |
|---|---|---|---|---|---|
| Calcite | 0.16 | 1.93 | 97.81 | Trace | 99.90 |
| Magnesite | 0.41 | 1.21 | 2.67 | 95.81 | 100.10 |
| Dolomite | 0.58 | 1.11 | 52.98 | 45.55 | 100.22 |

The hydroxides were prepared by igniting the calcite and magnesite at low red heat in a muffle furnace until complete decomposition had been obtained, and adding to the oxides the amounts of water necessary for hydration. The several materials, carbonates and hydroxides, were at once pulverized, sifted through a 100-mesh sieve, and held in stoppered bottles.

The soil used was the same as that employed in Series II, of the experiment described in the preceding paper, *i. e.*, it was run-down soil of 1500 lbs. per acre—7 in. lime requirement, and all details of size of wire baskets, methods of soil preparation, addition of amendment, planting and environment during growth of the crop (medium red clover) were the same as in that experiment.

It may be added, as to the soil, that the land from which it came lies adjacent to the Pennsylvania Experiment Station farms, is of the same geological origin (Ordovician limestone of age earlier than the Trenton beds) of the same silty loam type, and probably of the same general composition as to its calcium and magnesium. The surface and subsoil of the unfertilized grass lands of the Station farm contain as shown by analyses made by J. W. White, in the Station laboratory:

| | Per cent CaO | Per cent MgO |
|---|---|---|
| Surface | 0.365 | 0.509 |
| Subsoil | 0.377 | 0.679 |

These percentages represent the action of hot concentrated hydrochloric acid acting for 10 hours (Official Method). The proportions of these bases soluble in weaker solvents have not been determined. If all the $CO_2$ present be reported as combined with CaO, the $CaCO_3$ represents only 18 per cent of that base soluble under the conditions above stated.

The CaO : MgO ratio in the acid-soluble materials is for the surface soil, 1 : 1.37; for the subsoil, 1 : 1.80. If, therefore, the ratios of these bases soluble in strong acid were a satisfactory criterion of the balance between these bases in the nutrient supply gained by plants from this soil, we should expect, from the findings of Loew and his pupils, a distinct disadvantage to the crop from the application of amendments increasing the proportion of magnesia available to the crops, and possibly also from such as very greatly raise the proportion of calcium to magnesium.

The amendments were added to the soil in amounts requisite for neutralizing its acidity, and in such mutual proportions as to secure in the amendments the CaO : MgO ratios stated below. Each treatment was represented by four pots.

During the period of growth the only point of distinct difference between the crops from high magnesian and high calcium treatments, respectively, was a retarding, by three or four days, of the germination of the clover seed where magnesian amendments were used.

At the conclusion of eight and one-half months, the clover tops were cut, weighed, air-dried and re-weighed, and the roots were washed out, dried and weighed. The root systems in all the pots containing amendments were more fibrous and showed better development of tubercles than those grown in the untreated soil. The air-dry crop weights from the several treatments were as given in Table I.

These results, like those of Series II in the preceding paper, indicate that acidity was not the limiting factor for clover growth on this soil. The yield from the carbonate treatment 168 : 40 was only half of that obtained from the corresponding fine limestone on the soil of Plat 32.

Nevertheless, all the treatments were attended by some crop increase. The CaO: MgO ratios represented do not include, at this time, any case in which the magnesia added exceeds the amount of lime added. These ratios were chosen to represent those found in numerous lime products on the market, rather than the possible extremes for such experiments.

It is true that the low magnesian dressings were attended by somewhat higher yields than those with the narrowest CaO : MgO ratio; but the yields from individual pots were overlapping in marked degree, and the differences between averages for the treatments not large. Moreover, the yield with $^1/_{100}$ mesh very low magnesian limestone, from crop grown on the same soil under identical conditions was 2.33 grams of air-dry top; less, that is, than the yield obtained from a mixture of equally fine calcite and magnesite applied in the ratio 168 : 40, so that the increase of yield with increase in calcium proportion in the amendment was not absolutely consistent.

TABLE I—CLOVER CROPS FROM DIFFERENT TREATMENTS, AND LIME : MAGNESIA RATIOS IN ASHES OF CROPS

| Treatments | CaO: MgO ratio in dressings | Air-Dry Crop Weights (Grams) | | | | | | | | | | | Ash in tops | Composition of Ash of Tops | | | | CaO : MgO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Tops | | | | | Roots | | | | | Entire Plant | Per cent | Per cent | | Weight in Grams | | Ratio in ash of tops |
| | | Determinations | | | | Av. | Determinations | | | | Av. | | | CaO | MgO | CaO | MgO | |
| Calcite | 1 : 1 | 2.10(*a*) | 2.26 | 2.00 | 1.87(*b*) | 2.06 | 4.26 | 4.23 | 3.18 | 4.06 | 3.93 | 5.99 | 4.90 | 32.44 | 13.31 | 0.0339 | 0.0139 | 1.7 : 1 |
| and | 2 : 1 | 1.90 | 2.15 | 2.12 | 2.30 | 2.12 | 4.00 | 3.65 | 4.20 | 3.55 | 3.85 | 5.97 | 5.10 | 33.95 | 12.44 | 0.0367 | 0.0134 | 2.0 : 1 |
| Magnesite | 3 : 1 | 2.69 | 1.80(*a*) | 2.33 | 2.94 | 2.44 | 4.20 | 4.00 | 4.05 | 4.21 | 4.11 | 6.55 | 5.10 | 35.20 | 10.09 | 0.0476 | 0.0136 | 2.5 : 1 |
| $Ca(OH)_2$ | 1 : 1 | 1.70 | 2.50 | 2.21 | 2.47 | 2.22 | 3.46 | 3.06 | 3.49 | 3.20 | 3.30 | 5.52 | 5.00 | 32.26 | 14.70 | 0.0358 | 0.0163 | 1.5 : 1 |
| and | 2 : 1 | 1.85(*c*) | 2.70 | 2.35 | 2.15 | 2.74 | 3.56 | 3.26 | 4.03 | 3.26 | 3.53 | 6.27 | 5.20 | 33.40 | 14.20 | 0.0417 | 0.0177 | 1.7 : 1 |
| $Mg(OH)_2$ | 3 : 1 | 2.73 | 2.75 | 1.96 | 2.18 | 2.90 | 3.26 | 4.20 | 4.13 | 4.00 | 3.90 | 6.80 | 5.20 | 36.44 | 11.00 | 0.0455 | 0.0137 | 2.4 : 1 |
| Dolomite | 1 : 1 | 1.54 | 2.18 | 2.20 | 1.91 | 1.96 | 2.68 | 2.77 | 2.56 | 2.60 | 2.65 | 4.61 | 4.70 | 33.15 | 9.41 | 0.0305 | 0.0087 | 2.5 : 1 |
| Untreated | .... | 1.84 | 1.52 | 1.39 | 1.52 | 1.57 | 2.72 | 2.82 | 2.66 | 2.67 | 2.71 | 4.28 | 4.40 | 30.10 | 9.47 | 0.0208 | 0.0065 | 2.3 : 1 |

(*a*) Coating cracked. (*b*) 42 seeds germinated. (*c*) Coating cracked; leaked.

The net results of the experiment on this acid, run-down soil, more highly magnesian than calcareous, may be expressed as follows:

1—The soil, despite its probable deficiency in plant food, was not too acid to yield a moderate clover crop.

2—Clover grown upon it was less responsive to calcareous amendment than when grown on soil of the same locality, long well fertilized.

3—None of the dressings, even that representing the most highly magnesian limestone to be found on the market, did any harm during the first year after its addition.

4—The most highly calcareous dressings showed,

in general, effects somewhat more beneficial than the highly magnesian dressings.

5—The yields from the hydrate applications all exceeded those from the corresponding carbonate applications, the average for the former being 2.62 as contrasted with 2.21 for the carbonates, exclusive of dolomite.

6—The dolomite was beneficial, but less so than the corresponding dressing of calcite and magnesite.

EFFECTS UPON ASH COMPOSITION

To determine in what measure the clover plants consumed the lime and magnesia thus supplied, the crops (tops) were analyzed, with the results given in Table I. The figures show that:

1—All the treatments increased the proportion of ash in the plants, the dolomite least, the hydrate most.

2—From dolomite, the plants took up less ash for each unit of dry matter increase, than did those receiving the other dressings. The CaO : MgO ratio of the ash increase was, however, 3.4 : 1; that is, from the dolomite the plants took calcium far more freely than magnesium.

3—From the other dressings, the plants took up magnesium much more freely than from the dolomite. From the low-calcium dressings they took proportionally more magnesium than they did from the most highly calcareous dressings—speaking with reference to molecular proportions.

4—The crops took relatively a little more magnesia than calcium from the hydrate *vs.* the carbonate dressings.

5—In general, the plants were not self-protected by an exclusion of the magnesia. It entered them, and, judging from the yields as compared with that obtained from the use of purely calcareous limestone, did them no detectable harm, except slightly delaying the germination. In no case, however, did the percentage of magnesia in the ash reach the amount stated by Wolff[1] for fully ripe clover, although for most of the treatments it exceeded the amount he gives for this plant at the time of bloom.

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## A NOTE UPON THE KJELDAHL METHOD FOR NITROGEN DETERMINATION

By PHILIP L. BLUMENTHAL AND G. P. PLAISANCE

Received May 17, 1915

In a recent number of THIS JOURNAL, Pickel[2] quoted results upon various substances analyzed by the Kjeldahl-Gunning-Arnold method, in which he heated the sample from 15 minutes to 3 hours. He stated that 30 minutes *total* heating gave excellent results.

The writers, while engaged in analyzing the carcasses of new-born pigs, experienced some little difficulty in obtaining concordant results by different methods in general use, and finally conducted a short series of analyses under varying conditions, to ascertain the maximum nitrogen yield. As a check upon the accuracy of the results, a sample of very pure casein (Hammarsten's) was analyzed at the same time. Table I shows the results obtained upon the animal carcasses, digesting for 5- and 3-hour periods *after* the solution became clear.

The Kjeldahl-Gunning-Arnold and the Gunning-Copper sulfate digestions cleared more quickly than those of the other methods tested, and were deemed preferable for the further tests. In the second series (Table II) casein and the pig sample were heated for various lengths of time and the results recorded.

A glance at these tables shows that 30 minutes' total heating does not suffice to fix all the nitrogen; in fact, a gain of over 3 per cent protein is obtained by a longer period of digestion. That this is not due to an error is evidenced by the figures on casein, in which the percentage of nitrogen is 15.68. The conditions followed were quite similar to those proposed by Pickel, except that it was necessary to add more sulfuric acid to prevent the solidification of the flask contents in the long digestions; in every case, therefore, 50 cc. of concentrated sulfuric acid were used at the start. It does not seem satisfactory to us to rely upon a definite time of *total heating*, because of variations in gas pressure, and in the efficiency of different burners. We prefer to heat for a definite length of time *after clearing*, and from the results quoted, this time should never be less than one hour.

An interesting point came to our attention during the work. Many chemists have noticed the formation of a black material, which tends to accumulate in the condensers and adapters of the distillation rack. Sometimes (where paraffin is used in digestion or distillation) this material is greasy or salve like. It was noticed that where this material was carried over into the receivers, higher results were obtained than with other determinations of the same set. The black deposit contains mercury and often paraffin: sometimes mercury globules are observed in the receivers.[1] We believe that this may be explained as follows: mercuric sulfate treated with a considerable *excess* of potassium sulfide and sodium hydroxide is first precipitated as mercuric sulfide, which is later partially or completely dissolved as a complex salt. The clearing of the dark-colored flask contents in boiling, a frequent occurrence, substantiates this view. Zinc is generally added to prevent bumping and the hydrogen generated by its reaction with sodium hydroxide, particularly when excess of these reagents is used, tends to liberate metallic mercury. This is fairly volatile at the temperature of the boiling solution, and paraffin may also be carried over under these conditions; the result is the black substance mentioned, which is quite difficult to remove from the condensers, and which is objectionable, even if no chemical action occurs with the ammonia liberated from the solution, or with the acid in the receiver. By substituting bits of unglazed porcelain or pumice, the bumping of the solution is decreased, and though these substitutes are not quite so efficient in preventing

[1] *Aschen Analysen*, **2** (1880), 122.

[2] THIS JOURNAL, **7** (1915), 357.

[1] Bosshard, *Z. anal. Chem.*, **24**, 199; also Pickel, see above.

TABLE I—COMPARISON OF METHODS USED

| Method number | Method Used | Digested 5 hrs. after clear: No. of detns. | Per cent nitrogen: Max. | Min. | Av. | Digested 3 hrs. after clear: No. of detns. | Per cent nitrogen: Max. | Min. | Av. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Kjeldahl (modified) Official: 50 cc. $H_2SO_4$ + 0.7 g. Hg + $KMnO_4$ | 4 | 8.38 | 8.34 | 8.36 | 5 | 8.30 | 8.22 | 8.26 |
| 2 | Kjeldahl (modified) Official: 30 cc. $H_2SO_4$ + 0.7 g. Hg + 20 cc. $H_2SO_4$ (added later) + $KMnO_4$ | 5 | 8.45 | 8.38 | 8.41 | 2 | 8.34 | 8.32 | 8.33 |
| 3 | Kjeldahl-Gunning-Arnold, modified by using $KMnO_4$ and excess $H_2SO_4$: 50 cc. $H_2SO_4$ + 0.7 g. Hg + 10 g. $K_2SO_4$ + $KMnO_4$ | 5 | 8.10 | 7.95 | 8.04 | 2 | 8.15 | 8.14 | 8.14 |
| 4 | Kjeldahl-Gunning-Arnold, modified by using $KMnO_4$ and excess $H_2SO_4$: 30 cc. $H_2SO_4$ + 0.7 g. Hg + 10 g. $K_2SO_4$ + 20 cc. $H_2SO_4$ (added later) + $KMnO_4$ | 5 | 8.29 | 8.20 | 8.26 | .. | .... | .... | .... |
| 5 | Kjeldahl-Gunning-Arnold, modified by using excess $H_2SO_4$ (no $KMnO_4$): 30 cc. $H_2SO_4$ + 0.7 g. Hg + 10 g. $K_2SO_4$ + 20 cc. $H_2SO_4$ (added later). | 5 | 8.28 | 8.19 | 8.22 | .. | .... | .... | .... |
| 6 | Kjeldahl-Jodlbauer (Official Kjeldahl to include nitrates): 50 cc. $H_2SO_4$ + 0.7 g. Hg + 2 g. salicylic acid + 2 g. Zn dust + $KMnO_4$ | 8 | 8.29 | 8.18 | 8.23 | .. | .... | .... | .... |
| 7 | Kjeldahl-Gunning-Jodlbauer: 50 cc. $H_2SO_4$ + 0.7 g. Hg + 2 g. salicylic acid + 2 g. Zn dust + 10 g. $K_2SO_4$ + $KMnO_4$ | 5 | 8.28 | 8.16 | 8.24 | . | .... | .. | .... |
| 8 | Dyer's modification of Kjeldahl-Gunning-Jodlbauer: 50 cc. $H_2SO_4$ + 0.7 g. Hg + 2 g. salicylic acid + 2 g. Zn dust + 10 g. $K_2SO_4$ + 1 g. sucrose + $KMnO_4$ | 6 | 8.33 | 8.21 | 8.27 | 3 | 8.28 | 8.27 | 8.27 |
| 9 | Gunning-Copper sulfate (modified by using $KMnO_4$): 50 cc. $H_2SO_4$ + 0.2 g. $CuSO_4$ + 10 g. $K_2SO_4$ + $KMnO_4$ | 5 | 8.41 | 8.04 | 8.23 | 5 | 8.30 | 8.20 | 8.24 |
| 10 | Gunning-Copper sulfate: 50 cc. $H_2SO_4$ + 0.2 g. $CuSO_4$ + 10 g. $K_2SO_4$ | 5 | 8.26 | 8.25 | 8.25 | . | . . | | . |
| 11 | Official Gunning: 50 cc. $H_2SO_4$ + 10 g. $K_2SO_4$ | 6 | 8.27 | 8.09 | 8.17 | .. | . . | . | .... |
| 12 | Vanadium-Gunning: 50 cc. $H_2SO_4$ + 10 g. $K_2SO_4$ + 0.2 g. $V_2O_5$(a) | . | .. | . | . | 6 | 8.12 | 7.96 | 8.06 |

(a) *Experiment Station Record*, **32**, 310.

TABLE II—PERCENTAGE NITROGEN IN CASEIN AND PIGS BY DIFFERENT TREATMENTS

| Determination: | | Nitrogen in Casein | | | | | | | Nitrogen in Lot II Pigs | | | | | | | Nitrogen in Lot II Pigs | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Method: | | Kjeldahl-Gunning-Arnold | | | | | | | Kjeldahl-Gunning-Arnold | | | | | | | Gunning-Copper Sulfate | | | | | | |
| | | Total Heating Minutes | | | | Hours heating after clearing(a) | | | Total Heating Minutes | | | | Hours heating after clearing(b) | | | Total Heating Minutes | | | | Hours heating after clearing(b) | | |
| Number | | 15 | 30 | 45 | 60 | 1 | 3 | 5 | 15 | 30 | 45 | 60 | 1 | 3 | 5 | 15 | 30 | 45 | 60 | 1 | 3 | 5 |
| 1 | A | 13.23 | 13.89 | 14.20 | 14.46 | 14.56 | 14.64 | 14.39 | 7.32 | 8.06 | 8.06 | 7.91 | 8.18 | 8.32 | Lost | 7.33 | 7.63 | 7.70 | 7.94 | 8.13 | 8.20 | 8.44 |
| | B | 13.36 | 13.87 | | | | 14.62 | 14.49 | 7.25 | 8.05 | 7.97 | 7.88 | 8.17 | 8.34 | 8.46 | | | 7.77 | | | 8.26 | 8.37 |
| 2 | C | 13.39 | 13.96 | 14.24 | 14.44 | 14.53 | 14.57 | 14.41 | 7.59 | 7.71 | 8.16 | 8.13 | 8.20 | 8.37 | 8.43 | 7.34 | 7.64 | 7.77 | 7.92 | 8.11 | 8.27 | 8.37 |
| | D | 13.49 | Lost | | | | 14.67 | 14.54 | 7.58 | 7.73 | 8.15 | 8.12 | 8.23 | 8.37 | 8.46 | | | 7.77 | | | 8.30 | 8.38 |
| Aver. | | 13.37 | 13.91 | 14.22 | 14.45 | 14.55 | 14.62 | 14.46 | 7.44 | 7.89 | 8.09 | 8.01 | 8.20 | 8.35 | 8.45 | 7.34 | 7.64 | 7.75 | 7.93 | 8.12 | 8.26 | 8.39 |
| Dry basis aver. | | 14.41 | 15.00 | 15.33 | 15.58 | 15.68 | 15.77 | 15.60 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |

(a) 35 minutes were required until clear

(b) 70 minutes were required until clear.

bumping, the usual frothing resulting from the use of zinc is obviated, and at the same time the distillation of mercury is eliminated. We experienced no further contamination of the condensers or receivers after making this change.

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## METHODS FOR THE DETERMINATION OF CARBON DIOXIDE AND A NEW FORM OF ABSORPTION TOWER ADAPTED TO THE TITRIMETRIC METHOD[1]

BY E. TRUOG

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A large number of different methods and forms of apparatus have been recommended for the determination of carbon dioxide. This is largely due to the fact that the determination is made for a large variety of purposes and under numerous different conditions. In the chemical analyses of soils and in the investigation of soil phenomena, the writer has had numerous occasions to determine carbon dioxide. In such work carbon dioxide is usually determined by one of the three following methods: gas-volumetric, gravimetric, and titrimetric. In order to secure sufficiently accurate results for most purposes with the gas-volumetric method, rather elaborate apparatus is usually required, and hence the method is not used as generally as the others.

[1] Publication authorized by the Director of the Wisconsin Experiment Station.

### THE GRAVIMETRIC METHOD

The gravimetric method, in which the carbon dioxide is absorbed in a KOH bulb or other absorbing tubes, gives very accurate results when the large number of precautions are strictly observed. These precautions and the disadvantages of the gravimetric method have been very completely set forth by J. R. Cain.[1] A precaution often ignored, but of great importance, is in the use of drying reagents of the same hygroscopicity at both ends of the $CO_2$ absorption bulb. The air must be dried to exactly the same degree, both when it enters and leaves the absorption bulb, or there will be an error due to loss or gain of water. In the writer's experience errors from this source may amount to as much as two milligrams. In the case of rapid aspirations of large volumes of gas so much absorbing and drying apparatus is needed that errors in weighing become serious.

### THE ALKALI TITRIMETRIC METHOD

Owing to disadvantages of the gravimetric method, various titrimetric methods have come into use. Of these methods the absorption of the carbon dioxide in a sodium or potassium hydroxide solution and determination of the carbonates by double titration with phenolphthalein and methyl orange has been the most widely used. This method for the absorption and determination of free carbon dioxide was first used by Brown and Escombe.[2] These investigators apparently

[1] *Technological Paper*, **33**, Bur. Standards, also THIS JOURNAL, **6** (1914), 465.

[2] *Phil. Trans.*, (*B*) **193** (1900), 289.

used the method very carefully, as several important precautions were given as follows: Pure sodium hydroxide free from iron and aluminum should be used. The volume should be kept low and in titration, loss of carbon dioxide locally should be prevented by thorough shaking. Contamination by carbon dioxide from the air should also be prevented by proper protection. They recognized the need of standard end points as a control and used vessels of the same shape, containing the same amounts of solution and indicators for the two end points, as were used in the regular analyses. In their check experiments in which varying known amounts of carbon dioxide were determined, the differences between the actual amounts present and those found range from 0.05 cc. to nearly 0.20 cc. of 0.1 *N* solution. This causes an error of 0.2 to 0.8 mg. of $CO_2$. These investigators, however, make no mention of the amount of indicator used or of the effect of carbon dioxide on the methyl orange end point. Later investigators have shown that these are considerations that need to be taken into account.

Küster[1] made an extended study of this double titration for carbon dioxide. He found that pure sodium bicarbonate reacts alkaline to phenolphthalein, even when present in small amounts. A rise of temperature makes the reaction more marked. An addition of sodium chloride depresses the reaction. He concludes that phenolphthalein is not suitable as an indicator for the accurate determination of alkali carbonates.

Noll[2] after an extended investigation comes to the conclusion that the correct results can be obtained only by use of phenolphthalein in the proper amount. The amount of phenolphthalein to be used is to be regulated by the amount of carbonates present. He also states that it is permissible to have only a small amount of carbonates present.

Auerbach[3] in studying the determination of carbonates in water states that the titration should only be made in case of small amounts of carbonates and with very dilute amounts of phenolphthalein, otherwise it is necessary to make a correction. He used 5 drops of a phenolphthalein solution which contained one gram in 500 cc. He used a dilution of about 300 cc., and states that higher concentrations of indicator require larger amounts of carbon dioxide to dispel the color, while higher concentrations of bicarbonate prevent to a certain extent the formation of the color.

The writer has investigated this double titration method to a certain extent. A solution of sodium carbonate was prepared as follows: Kahlbaum's sodium bicarbonate which gave no test for chlorides or sulfates was used. A 17 g. sample of this was placed in a platinum dish and heated at 300° C. to constant weight in an electric furnace. The sodium carbonate was dissolved in 2000 cc. of $CO_2$ free water giving an approximately 0.1 *N* solution. Measured portions of this solution were titrated against sulfuric acid solution of slightly less than 0.1 *N* strength. All measuring instruments used in this work had been carefully calibrated. The phenolphthalein solution used contained one gram in 100 cc. of alcohol. The methyl orange solution contained one gram in 1000 cc. of water. In the titrations of Table I two drops of phenolphthalein and one drop of methyl orange were used. The titrations were made in Erlenmeyer flasks, and the solutions were always diluted with such amounts of $CO_2$-free water as to make the final volume after titration close to 200 cc.

Standard end points for each titration were also used. The one for the phenolphthalein end point consisted of an Erlenmeyer flask similar to the one used in the regular titration, and to which was added 200 cc. of water and two drops of phenolphthalein. Since carbon dioxide has a very appreciable effect on methyl orange, it is necessary to vary this end point according to the amount of carbonates that are titrated. Carbon dioxide in amounts equal to those liberated in the titrations were added to 200 cc. of water containing one drop of methyl orange. The end points for each case were then made by adding 0.1 *N* sulfuric acid to 200 cc. of water until the color of the methyl orange indicated just a little stronger acidity than the corresponding one with carbonic acid. The end points with carbonic acid are not permanent because of escape of carbon dioxide, and hence it is necessary to make them with a non-volatile acid in which case they remain constant for several days.

In making the titration with phenolphthalein, the tip of the burette, which had been lengthened, was allowed to dip below the surface of the solution in the flask until near the end point, when it was raised. This procedure eliminates, largely, the possibility of escape of carbon dioxide due to local concentration of the mineral acid at the surface. This may also be accomplished by thoroughly shaking the flask and adding the acid very slowly. Such a procedure, however, may introduce other errors, since the vigorous shaking increases the opportunity for absorption of carbon dioxide during the first part of the titration; and may introduce an error in the opposite direction during the last part of the titration. An error due to the latter cause is apparently possible on considering the following: To 25 cc. of approximately 0.1 *N* $Na_2CO_3$ solution, diluted with water to 175 cc., were added two drops of phenolphthalein and then 0.1 *N* $H_2SO_4$ till the pink color was dispelled. The flask containing this solution was now placed in a Camp shaker and shaken for five minutes, when the solution was again distinctly colored. It took 0.3 cc. more of 0.1 *N* acid to change this color to the same shade as the blank which was not shaken. This is evidently due to loss of carbon dioxide. By simply letting the solution stand the same phenomenon will take place after several hours. After several days the solutions will become strongly colored. Table I gives a few of the results which have been obtained by following the procedure outlined.

If the method is to give correct results, then the titration with phenolphthalein should be just one-half

[1] *Z. anorg. Chem.*, **13** (1897), 127
[2] *Z. angew. Chem.*, **25** (1912), 998
[3] *Ibid.*, **25** (1912), 1722.

of the total on continuing to the methyl orange end point. From Table I it is evident that the method has given very good results when not over 25 cc. of 0.1 *N* $Na_2CO_3$, equivalent to approximately 50 mg. of $CO_2$, was present. If larger amounts of carbonates are present, then the end point with phenolphthalein comes

TABLE I—DOUBLE TITRATION OF SODIUM CARBONATE WITH $H_2SO_4$

All solutions approximately 0.1 *N* and all figures represent cc.

| $Na_2CO_3$ taken | Phenolphthalein | | Methyl orange | |
|---|---|---|---|---|
| | Calculated | Consumed | Calculated | Consumed |
| 10 | 5.53 | 5.48 | 11.06 | 11.05 |
| 10 | 5.53 | 5.50 | 11.06 | 11.10 |
| 25 | 13.81 | 13.76 | 27.62 | 27.68 |
| 25 | 13.81 | 13.75 | 27.62 | 27.55 |
| 50 | 27.62 | 27.20 | 55.24 | 55.15 |
| 50 | 27.62 | 27.15 | 55.24 | 55.00 |
| 75 | 41.43 | 40.91 | 82.86 | 82.76 |

too soon when only two drops of indicator are present. In two other trials not given above it was found as follows:

When 50 cc. of $Na_2CO_3$ were taken, it required four drops of phenolphthalein to bring the end point at the proper place. Similarly with 0.5 cc. of phenolphthalein and 50 cc. of $Na_2CO_3$ an excess of 1.10 cc. of acid was used.

Thus, if too little phenolphthalein is used in proportion to the amount of $CO_2$ present, then the end point comes too soon; and if the reverse condition obtains, then the true end point is overstepped. That such is the case can also be shown in the following simple manner: To 50 cc. of 0.1 *N* $Na_2CO_3$ diluted to about 100 cc. are added two drops of phenolphthalein and then acid till the color disappears. If more phenolphthalein is now added, the color will again appear, and the intensity will depend upon the amount of phenolphthalein added as well as the temperature and the amount of shaking and length of time the solution stands.

The results just given are in full accord with those of the investigators already cited. In order to obtain correct results it is absolutely necessary to regulate the amount of phenolphthalein used according to the amount of carbonates present. If precautions are not taken in regard to the use of phenolphthalein and to the effect of $CO_2$ on the methyl orange end point, then two errors enter into the determination; but since they are in opposite directions when only small amounts of phenolphthalein are used, they compensate to a certain degree. It is possible that because of this compensation, Brown and Escombe[1] were able to get as good results as they did, apparently without regard to these precautions. The evidence is conclusive that in order to be assured of correct results with the double titration method for carbonates, several precautions need to be carefully observed. To observe all these precautions causes considerable inconvenience.

It should also be noted that the end points, especially with phenolphthalein, are not at all sharp or positive, and thus it is possible to make the titration only under the best conditions of light. Even under such conditions many persons find it absolutely impossible to discern the true end points because of the gradual color change. The method thus leaves much to be desired.

[1] *Loc. cit.*

Bowser[1] recommends the use of KOH instead of NaOH for the absorption of the $CO_2$ and states that it is more satisfactory. The writer has found that this gives a slightly better end point with phenolphthalein than when NaOH is used, but the improvement is not sufficient to make the method satisfactory. Bowser also recommends the addition of 10 to 15 cc. of ethyl alcohol to further improve the end point. When solutions of $Na_2CO_3$ and $K_2CO_3$ to which phenolphthalein has been added are brought to the colorless point with acid and then allowed to stand, the resultant solution of $NaHCO_3$ regains its color much more rapidly than the solution of $KHCO_3$. This is undoubtedly due to the greater dissociation or breaking up of the $NaHCO_3$ and loss of $CO_2$ by dissipation to the air. The action of the alcohol probably consists in retarding this dissociation and preventing the loss of $CO_2$ to the air because of its greater solubility in alcohol than in water. The writer has found no advantage in the use of the alcohol and, as is well known, it decreases greatly the sharpness of the methyl orange end point.

### THE BARIUM HYDROXIDE TITRIMETRIC METHOD

In search of a better method the writer was led to try the method of absorption in a measured excess of $Ba(OH)_2$ in which the carbon dioxide is precipitated as $BaCO_3$ which is practically neutral to phenolphthalein. The excess of $Ba(OH)_2$ is then easily determined by titration, and thus by difference the amount of $CO_2$ is quickly determined. The principle of the method is essentially that of the C. Winkler titration method for carbon dioxide and carbonates. This method has the advantage of a good end point. The presence of the precipitate of $BaCO_3$ in the solution in which the titration is made may appear objectionable, but the experimental data show that the presence of the precipitate has absolutely no harmful effects. The precipitate, being pure white, aids rather than hinders the eye in detecting the end point. Küster[2] gives considerable data which show conclusively that carbonates can be determined with great accuracy by this method.

The writer has tested the method as follows: Measured quantities of standard $Ba(OH)_2$ were treated with excess of $CO_2$, and then boiled to expel the excess and change all bicarbonate to normal carbonate. Measured quantities of $Ba(OH)_2$ and four drops of phenolphthalein were added to these samples. Standard acid was then added till the color disappeared. The results showed that $Ba(OH)_2$ could be determined in the presence of $BaCO_3$ very accurately. The experimental results never varied from the calculated by more than one drop of 0.15 *N* acid and the end point was always good.

J. R. Cain[3] recommends the absorption of the $CO_2$ in $Ba(OH)_2$ and after filtering off and washing the $BaCO_3$, titrates it with standard acid. For very small amounts of $CO_2$ this is undoubtedly a very good method, and Cain has outlined a procedure for filtering and washing that has given excellent results. When larger

[1] THIS JOURNAL, **4**, pp. 203, also 765.
[2] *Z. angew. Chem.*, **13** (1897), 127.
[3] *Loc. cit.*

amounts of $CO_2$ are to be determined, then the washing of the precipitate becomes more troublesome, and there is nothing to be gained by this procedure over that of titrating the excess of $Ba(OH)_2$.

A serious objection to the method of titrating the excess of $Ba(OH)_2$ has been that of securing complete absorption in the case of rapid aspirations carrying considerable amounts of $CO_2$. The ordinary form of absorption towers with glass beads, as are used with alkali hydroxides, are not adapted for use with $Ba(OH)_2$ since in this case a precipitate is formed which prevents complete washing. When the aspiration is slow, and small amounts of $CO_2$ are to be absorbed, Meyer bulb tubes are a satisfactory form of absorption apparatus. Brady[1] has described an arrangement adapted for such purposes.

### A NEW FORM OF ABSORPTION TOWER

In an attempt to secure an absorption apparatus for use with $Ba(OH)_2$ that would be satisfactory for both slow and rapid aspirations, carrying either small or large amounts of $CO_2$, the writer has devised the absorption tower shown in Fig. I. This apparatus consists of a 500 cc. suction flask (A), a glass tube (B), of dimensions as shown, a 50 cc. dropping funnel, (E), and a soda lime tube (F), connected as indicated in the figure. A glass rod (C) with a head as shown is attached to the outlet and serves to break up any bubbles that may arise up into the tube. The outlet tube has a hole at (H).

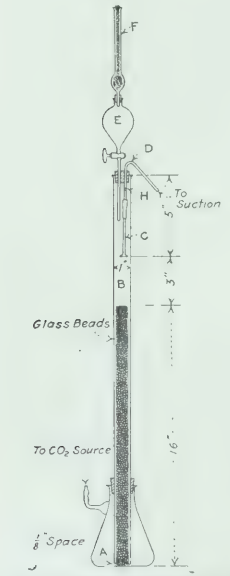


FIG. I ABSORPTION TOWER ADAPTED TO THE USE OF BARIUM HYDROXIDE FOR THE ABSORPTION AND TITRIMETRIC DETERMINATION OF CARBON DIOXIDE

The method of operation is as follows: Forty cc. of standard $Ba(OH)_2$ are run into the dropping funnel. The soda-lime tube is quickly replaced and the funnel is attached to the tower. After making the proper connections the apparatus is freed of $CO_2$ in the usual way. The $Ba(OH)_2$ is now allowed to run out of the funnel into the tower and the funnel stop-cock closed. The soda-lime tube is removed and 40–50 cc. of $CO_2$-free water are quickly poured into the funnel and the soda-lime tube is replaced. This water is now allowed to run into the tower, thus washing the funnel free of $Ba(OH)_2$. The suction draws the absorbing solution up into the tower. The apparatus is now ready for the absorption of $CO_2$. When the absorption is complete, the suction is closed off with a pinch-cock or stop-cock and the stop-cock of (E) is gradually opened allowing $CO_2$-free air to enter, when the absorbing solution settles into the flask. The flask is next disconnected from the source of $CO_2$ and after the solution has settled into the flask, the stop-cock of (E) is closed. The air in (E) is now free from $CO_2$ and ready for the next determination. The stopper at the top of the tower is raised and the extending tubes washed off into the tower with a little $CO_2$-free water. The tower is raised a few inches from the flask, when the beads slide out. If they stick to the tower, a little gentle tapping at the top suffices to make them drop. The inside of the tower is immediately rinsed with about 100 cc. of $CO_2$-free water poured from a beaker. The tower is raised and removed after also washing off the lower end on the outside. Four drops of phenolphthalein are added and the excess of $Ba(OH)_2$ is immediately titrated.

By following the directions as given, the flask and tower are filled with $CO_2$-free air previous to washing. The washing is quickly and easily made, and if the flask is then corked or the titration immediately made, there is scarcely any chance for contamination from the air. The $Ba(OH)_2$ is delivered directly from a burette into the funnel (E) which contains $CO_2$-free air. The soda-lime tube (F) is always replaced as quickly as possible. In the titration the flask is shaken continuously to prevent local action of the acid on the $BaCO_3$ and possible loss of $CO_2$. The glass beads cause no hindrance in the titration. A little $BaCO_3$ may stick to the sides of the tower, but this need not be completely washed out as it does not enter into the titration. After titration a little strong acid is added to the flask to dissolve the $BaCO_3$. The beads are then poured onto a scoop-shaped screen, washed under the tap, rinsed with distilled water and poured back into the tower, which has been replaced in the flask.

Perforated glass beads should be used in preference to the solid spherical kind, as they break up the bubbles more completely and increase the efficiency of the absorption. In the old form of towers, perforated beads could not be used advantageously, since they made complete washing very difficult. This objection is entirely done away in this form of tower. If solid spherical beads are used they should be mixed with some short pieces of glass tubing in order to leave sufficient pore space for the absorbing solution. Alkali hydroxides may be used also with this form of tower and the absorbed $CO_2$ may then be determined by double titration, or better, by adding an excess of $BaCl_2$ and then titrating the $BaCO_3$ after neutralizing the excess of hydroxide. The best plan of all is to use a standard solution of $Ba(OH)_2$ to absorb the $CO_2$. Solutions of $Ba(OH)_2$ free from carbonates are much more easily prepared than those of the alkalies. By using a sufficiently large tower there is no trouble in getting complete absorption with $Ba(OH)_2$ even with rapid aspirations. A tower of the height in the figure suffices for most purposes. If the aspiration is extremely rapid the column of beads should be increased to twenty inches in height. The precipitate of $BaCO_3$ aids in the absorption, by checking the movement of gas bubbles.

[1] THIS JOURNAL, 6 (1914), 843.

REAGENTS

STANDARD HYDROCHLORIC ACID SOLUTION—A 0.4 *N* solution is employed.

BARIUM HYDROXIDE SOLUTION—A 0.4 *N* solution is prepared as follows: Dissolve 80 g. of $Ba(OH)_2.8H_2O$ in 1000 cc. of water, heat to boiling and then filter with a Buchner funnel into a stock bottle which has been freed of $CO_2$. A double filter paper is carefully laid on the funnel and drawn down and then the funnel is never allowed to suck dry till the solution has all gone through. In this way a solution free of carbonates is much more quickly and easily prepared than by allowing the precipitate to settle and siphoning over. The burette and appropriate guards are then attached and the proper dilution is made after titrating against the standard acid.

PHENOLPHTHALEIN SOLUTION—One gram of the indicator is dissolved in 100 cc. of ethyl alcohol.

ACCURACY OF METHOD

In order to test the efficiency of the apparatus and technique in preventing the contamination of the $Ba(OH)_2$ by the $CO_2$ of the air, measured quantities of the $Ba(OH)_2$ were placed in the tower in the regular way, and after aspirating $CO_2$-free air through the apparatus for some time, the solution was removed in the regular way and titrated. The titrations disclosed no measurable quantities of $CO_2$, and hence the contamination is practically entirely prevented. In order to test the efficiency of the absorption with this tower, measured quantities of the $Ba(OH)_2$ solution were treated with $CO_2$ and after boiling to expel the excess of $CO_2$, the precipitate of $BaCO_3$ was transferred to an evolution flask and the evolved $CO_2$ drawn through the absorption tower and determined by titration. The results never varied from the calculated by more than a drop of 0.4 *N* acid, which represents less than 0.5 mg. of $CO_2$. The $Ba(OH)_2$ in the tower will absorb efficiently with rapid aspiration to nearly one-half saturation, which represents about 0.15 g. of $CO_2$. With slow aspiration still more may be safely absorbed. The tower is conveniently attached to almost any form of apparatus in which $CO_2$ is evolved for measurement. For more accurate determinations of small amounts of $CO_2$, more dilute solutions of $Ba(OH)_2$ and HCl should be used.

SUMMARY

I—The gravimetric determination of $CO_2$ by weighing of absorption apparatus gives accurate results in the case of small amounts of $CO_2$, slow aspiration, and due precautions in weighing and drying. In the case of rapid aspirations carrying considerable amounts of $CO_2$ the gravimetric method is troublesome.

II—The determination of $CO_2$ by absorption in alkali hydroxide and double titration has many disadvantages. The amount of indicator used needs to be carefully regulated and standard end points should be used. Under the best conditions, the end points are not sharp, making it absolutely unusable by some people. Good results can be obtained in the case of people having a good eye for color by observing the necessary precautions, but this leads to a great deal of inconvenience.

III—A new form of tower, described above, makes possible the use of $Ba(OH)_2$ as an absorbing medium for $CO_2$ under nearly all conditions. It also eliminates practically all contamination of $CO_2$ from the air, and greatly facilitates the washing. The titration has the advantage of a very good end point. The standard solution of $Ba(OH)_2$ is easily prepared free of carbonates.

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## THE AMINO ACID NITROGEN OF SOIL

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INTRODUCTION

The importance of the amino acids as the chief products of the chemical, and under some conditions, of the biological decomposition of protein material, makes desirable a quantitative knowledge regarding their occurrence in the soil. While there is, no doubt, present in the soil representatives of all the classes of compounds between undecomposed protein and ammonia and nitrates, yet there are no methods which have been applied to the quantitative determination of any of these classes of compounds except ammonia, nitrates, and nitrites, which together make up but a small proportion of the total nitrogen compounds. It would seem, therefore, that a more complete knowledge of the nitrogen of the soil is very important from an academic and a practical standpoint. In this investigation, our attention has been confined to the amino acid nitrogen. Many investigators have found amino acids in soil after subjecting it to hydrolysis, but there has been no quantitative determination of the amino acids as such. In fact, the only investigations showing the presence of amino acids in the soil were made by Shreiner and Shorey, who found histidine, arginine,[1] and lysine,[2] in a weak alkali extract of soil.[3]

Except for the work of Chardet, which has not been confirmed, the only proof there is of the presence of amino acids in the soil is the work of Schreiner and Shorey. Until quite recently, there has been no method sufficiently sensitive to permit of the accurate determination of the amino acids in the soil, but the copper method of Kober,[4] being capable of detecting, with considerable accuracy, one part of amino acid nitrogen in 500,000 parts of solution, has been found very suitable for soil work. By this method 5 to 30 parts of amino acid nitrogen per million parts of soil have been found, so it can easily be seen how the earlier methods would be entirely unsuited. The formol titration method of Soerensen[5] has been shown

[1] *J. Biol. Chem.*, **8** (1910), 382.

[2] U. S. Dept. Agric., Bur. of Soils, *Bull.* **88** (1913).

[3] Since the experimental part of this paper was completed, Chardet (*Rev. gén. chem.*, **17**, 137) reports the analysis of 4 soils for amino acid nitrogen by the Soerensen method. He found from 49 to 68 per cent of the total nitrogen was amino acid nitrogen. Following his directions, as given, we have been unable to find an appreciable amount of amino acid nitrogen in any of several soils examined.

[4] *J. Am. Chem. Soc.*, **35** (1913), 1546.

[5] *Z. physiol. Chem.*, **64** (1910), 120.

by Loeb[1] to be accurate to only one part in 1600, while the Van Slyke[2] method has been shown by its originator to be accurate to one part in 10,000, and besides is specific for the amino group, not for amino acids.

The reader is referred to the papers by Kober[3] and collaborators for the details of the copper method for amino acid nitrogen. In this report the term "amino acid nitrogen" is the nitrogen in the amino group in the $\alpha$ and $\beta$ position with reference to an unsubstituted carboxyl group; "free amino acid nitrogen" is the $\alpha$ and $\beta$ amino nitrogen in "free" amino acids; "peptide nitrogen" is the $\alpha$ and $\beta$ amino nitrogen of the amino acids from the hydrolyzed peptide.

## EXPERIMENTAL

The technique of the Kober method as recommended by its originator was followed, with some modifications, in all its essentials in this work. The cupric hydroxide was prepared in an ice mixture and centrifuged instead of filtered as Kober recommends. The buffer solution was titrated from time to time, and it was found to hold its original strength. The thiosulfate solutions were standardized from time to time against standard iodine solutions. S. and S. No. 589, Blue Ribbon filter paper was used throughout, instead of S. and S. No. 590, as recommended by Kober. The No. 590 paper, although more rapid, often caused trouble. Any other deviations from the original method are cited in the proper place.

It is well known that dilute acids in the cold dissolve only a small part of the soil nitrogen, yet it is known that 1 per cent HCl dissolves some organic nitrogen,[4] hence it was thought possible that any amino acids present would be dissolved. One hundred and fifty g. of a soil which contained 0.181 per cent nitrogen were shaken with 300 cc. of 0.2 *N* hydrochloric acid for one hour. The mixture was poured upon a paper filter, and 80 cc. of the clear filtrate were transferred to a 100 cc. flask: 7 cc. of a saturated solution of lead acetate and 7 cc. of ammonia (sp. gr. 0.90) were added and water to complete the volume to 100 cc. The mixture was thoroughly shaken and then filtered. To 75 cc. of the filtrate 25 cc. of a saturated solution of barium hydroxide were added, and the ammonia removed by boiling at a pressure of about 25 mm.[5] The liquid was then made up to 75 cc.; the barium carbonate filtered off and 50 cc. of the filtrate were transferred to a 100 cc. flask. The solution was then made barely alkaline to phenolphthalein, 40 cc. of "buffer" solution added, and after cooling for about two hours or more in the ice box, one cc. of a cold suspension of cupric hydroxide in water was pipetted in, the whole vigorously shaken, water added to the mark and the mixture filtered through S. and S. No. 589 Blue Ribbon filter paper: 50 cc. of the filtrate showed no trace of copper. Other soils treated in the same way gave the same result. Upon adding a small amount of alanine to some soils and then extracting with 0.2 *N* hydrochloric acid in the same way, no amino acid nitrogen was found. This result is somewhat in harmony with the fact that only from 60 to 70 per cent of small amounts of ammonia added to the soil are extracted with 0.2 *N* acid.[1]

Dilute alkali is known to dissolve more organic matter from the soil than any other of the milder reagents, therefore 2 per cent sodium hydroxide was next tried as the extraction agent and was found to be quite satisfactory. Much the same procedure was used here as for the acid extraction, except that 600 cc. of the alkali were used with 150 g. soil. It is almost impossible to filter this extract by any of the ordinary methods, so it was cleared by centrifuging in the machine described in a bulletin from this Station.[2] After whirling in this machine a few minutes, the clear but dark-colored solution was drawn off through the silver tube: 80 cc. of this solution were approximately neutralized with 1 : 1 HCl and then the same procedure carried out that was used in the acid extract up through the filtering off of the excess copper hydroxide. Although with all the soils tested copper was always found in this filtrate, yet there was present some reducing substance which took up the iodine liberated by adding potassium iodide. Hence, instead of titrating directly, 50 cc. were placed in a beaker, acidified slightly with nitric acid, heated to boiling and bromine water added until a permanent color was given. The solution was then boiled down to about 100 cc. and to make sure the last traces of free bromine were given off 30–40 cc. water added and again boiled down to 10 cc. The solution was cooled, neutralized with sodium carbonate, a very slight excess of 1 per cent hydrochloric acid added and after the addition of the potassium iodide and starch solution, the free iodine was titrated with 0.001 *N* sodium thiosulfate solution. Each cc. of this solution equals 0.0280 mg. of amino acid nitrogen, or 0.0140 mg. peptide amino nitrogen. For the determination of the free amino acid nitrogen, 40 cc. of the solution were used and Kober's directions were exactly followed.

As a check upon our work, analyses were run on some pure glycine and alanine solutions, and also known amounts of these substances were added to soil and the increase in amino acid nitrogen found. For the analysis of the pure amino acid solutions, the indicated amounts, obtained by aliquoting strong solutions, were placed in 100 cc. flasks, made up to about 80 cc. with sufficient sodium hydroxide to give a 2 per cent solution of the alkali and from then on run exactly as was the soil. The amino acids were added to the soil by aliquoting the same solutions, and then sufficient sodium hydroxide solution

[1] *Biochem. Ges.*, **46** (1913), 696.

[2] *J. Biol. Chem.*, **7** (1910).

[3] *Loc. cit.*, also *J. Biol. Chem.*, **13** (1912), 1; *Am. Chem. J.*, **48** (1912), 383.

[4] Kelley and Thompson, *J. Am. Chem. Soc.*, **36** (1914), 438.

[5] After this procedure, Kober found it necessary to remove lead either with potassium sulfide or sulfate. In our experience, the lead is entirely precipitated by the ammonia. This is in harmony with the statement found in text books that lead hydroxide is insoluble in excess of ammonia.

[1] Potter and Snyder, THIS JOURNAL, **7** (1915), 221.

[2] Stevenson, Wells and Coover, *Iowa Bull.*, **124** (1911). A glass tube was originally recommended for drawing off the solution. We are indebted to Prof. R. E. Smith for the suggestion of the use of a silver tube which has been found much more satisfactory.

to give 600 cc. of 2 per cent alkali, and after shaking two hours and centrifuging, 80 cc. of the extract were taken and the regular procedure carried out. The results are given in Table I and are calculated in every case to the amount of amino acid nitrogen in the 80 cc. of solution or extract.

TABLE I—AMINO NITROGEN ADDED, FOUND AND RECOVERED

| SUBSTANCE | ADDED Mg. | Amino N found Mg. | Av. | % | Amino N recovered Mg. | Av. | % |
|---|---|---|---|---|---|---|---|
| Glycine | 0.224 | 0.203 | | | | | |
| | 0.224 | 0.210 | 0.207 | 92.4 | | | |
| Soil A | | 0.168 | | | | | |
| | | 0.174 | 0.171 | | | | |
| Soil A and glycine | 0.224 | 0.370 | | | 0.199 | | |
| | 0.224 | 0.364 | 0.367 | | 0.193 | 0.196 | 87.5 |
| Alanine | 0.224 | 0.208 | | | | | |
| | 0.224 | 0.216 | 0.212 | 94.6 | | | |
| Soil A and alanine | 0.224 | 0.375 | | | 0.204 | | |
| | 0.224 | 0.380 | 0.378 | | 0.209 | 0.207 | 92.4 |

From the results set forth in Table I it is seen that by the analysis of the pure glycine 92.4 per cent of the theoretical quantity was found, while in the case of the alanine 94.6 per cent was found. Since the samples used were Kahlbaum's C. P. material, and since practically the theoretical amount of nitrogen was found in each case by the Kjeldahl analysis, the material is, no doubt, very close to 100 per cent pure. When it is considered what small amounts were dealt with in each case, the low percentages obtained are not surprising. In solutions of glycine containing approximately the same amounts, Kober found in one case 94.8 per cent and in another 95.7 per cent of the theoretical quantity. The recovery of the 87.5 per cent of the added glycine and 92.4 per cent of the added alanine, when the many operations through which the soil solutions must pass are considered, seems, on the whole, not unsatisfactory.

In order to determine if the amount of amino acid nitrogen found was influenced by the duration of the treatment with the alkali, samples of two soils were shaken for 1, 2, 4 and 6 hours with 2 per cent sodium hydroxide and the amino acid nitrogen was determined in the extract from each treatment. Within the experimental error the results for the four periods for each soil were the same. This was expected from the known stability with alkali of the amino acids and protein material as far as amino acid production is concerned.

In Table II are given the results for the various kinds of nitrogen for two soils. The differences are notable and the relations for other soils will be studied in the future in this laboratory.

TABLE II—NITROGEN IN P. P M. AIR-DRY SOIL (DUPLICATES)

| SOIL | Amino acid | | Free amino acid | | Total peptide N | |
|---|---|---|---|---|---|---|
| A | 8.1 | 7.8 | 5.6 | 5.3 | 32.6 | 30.4 |
| B | 23.0 | 23.2 | 15.0 | 14.4 | 30.0 | 31.8 |

The consistency with which the amount of amino acid nitrogen is so small in the soils reported above points to the fact that, as with ammonia, there is not much tendency for it to accumulate in soils. This is, perhaps, to be expected from the fact that amino acids are known to be very good nutritive media for bacteria.[1] It has also been shown by Jodidi[2] that those amino acids made up of aliphatic nuclei, when incubated at room temperature for from six to ten days with soils containing 18 per cent moisture, in amounts varying from 0.1 to 0.5 g. amino acid per 50 g. soil increased the amount of ammonia nitrogen in the soil by from 44 to 74 per cent of the amount of amino acid nitrogen added. The amino acids tyrostine and phenylalanine, containing carbocyclic groups, under similar conditions give rise to approximately 27 per cent less ammonia. As pointed out by Jodidi, the actual production of ammonia might have been really greater, because part of the ammonia produced might have been nitrified. No doubt, also, part of the nitrogen was assimilated by bacteria. The amount of amino acid added to the soil by Jodidi was far in excess of that actually present in any soil which we have examined, yet since he found the percentage transformations were about the same whether he added 0.1 g. or 0.5 g. of amino acid, no doubt the rate of transformation of still smaller amounts would be similar.

It is a well-known fact that the action of bacteria and boiling acids upon proteins gives rise to about the same products, namely, proteoses, peptones, peptides and amino acids, but as pointed out above, the action of bacteria does not stop with the amino acids. Another important factor to be taken into account when considering the transformation of soil nitrogen is the assimilation of the nitrogen by bacteria. While data are lacking on the chemical constitution of bacteria, usually present in soil, yet their composition is probably not far different from that of some of the pathogenic organisms. It has been shown by Cramer,[1] for instance, that the spirillum cholerae has a protein content varying from 45 to 65 per cent according to whether it was grown on a media poor or rich in protein material. Therefore, in soil there are two opposing tendencies, namely, the degradation of the complex nitrogenous material into its constituent parts and subsequent ammonification and nitrification of these parts, and then the assimilation of the degradation products by the microflora of the soil to give again material more or less complex than originally. Of course, there are other changes, such as assimilation of the nitrogen from the atmosphere and denitrification, but these and other changes need not be entered into here.

It is a well-known fact that the introduction of large amounts of fresh organic matter in soils causes a great depression or the complete disappearance of nitrates therefrom, and also prevents any appreciable formation and accumulation of nitrate nitrogen. Various explanations have been offered to account for this, such as denitrification, assimilation, or the depression of nitrification because of accumulated intermediate products of degradation. Whether there is a continuous production of nitrates which are subsequently assimilated, or whether the organisms get their nitrogen from the ammonia or amino acids[2] or other compounds cannot be definitely stated, but

[1] Czapek, *Hofmeister's Beit.*, **1** (1902), 538; **2** (1902), 557; **3** (1902), 47; Emmerling, *Ber. d. chem. Ges.*, **35** (1902), 2289.

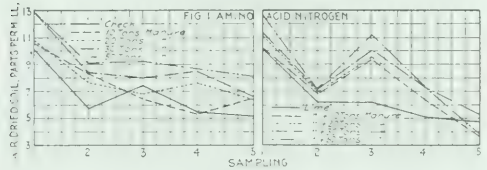
[2] *Iowa Research Bull.*, **9** (1912).

[1] *Archiv. f. Hygiene*, **12**, 157; **13**, 76; **16**, 171.

[2] It has been shown by Bierima (*Centr. Bakt. Parasitenk., II Abt.*, **23** (1909), 672) that amino acids, as well as ammonia are assimilated by soil bacteria.

in well aerated soils not too wet, one would certainly expect nitrification to be taking place, and for the same reasons, none or only a negligible amount of denitrification. The use of the term "acid soluble" by Jodidi[1] in the following statement has led to some confusion on this question: "The principal portion of the acid-soluble organic nitrogen contained in the soil herein investigated is made up of acid amides, monamino acids and diamino acids."

The Kober method for amino acids, as we have applied it to soils, will give definite information as to the amounts of amino acids actually present in




soil, and will, therefore, show whether under various conditions there is any tendency for these products to accumulate in soil. Interest in the question is also raised by the accumulating evidence that green plants may utilize amino acids[2] for their nitrogen nutrition. While it is not thought that green plants would utilize an appreciable amount of amino acid in the presence of nitrates and ammonia, yet it is possible that in soils temporarily deprived of nitrates, the amino acids, as well as the ammonia, might be used by the plant.

It was to study the problems suggested by the above discussion that the following experiment was performed: Several hundred pounds of Soil A, which was acid to litmus and showed a lime requirement of 3800 lbs. of calcium carbonate per 2,000,000 lbs. of soil by the Veitch[3] method and which contained 0.151 per cent of nitrogen, were procured. The sample was air-dried, shaken through a four mm. sieve and very thoroughly mixed. Twenty pot experiments, each pot containing 30 lbs. of air-dry soil, were run with this soil with the treatments indicated below.

TABLE III—TREATMENT IN TONS PER 2,000,000 LBS. SOIL

| Experiment No | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Pot No. | 11 | 3 | 5 | 7 | 9 | 11 | 13 | 15 | 17 | 19 |
| | 12 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 20 |
| TREATMENT: | | | | | | | | | | |
| $CaCO_3$ | 0 | 4 | 0 | 0 | 0 | 0 | 4 | 4 | 4 | 4 |
| Stable manure | 0 | 0 | 10 | 20 | 30 | 50 | 10 | 20 | 30 | 50 |

The manure used was collected from the stalls of horses and was made up of about equal parts of the droppings and of the wet straw. It was cut up, mixed while still moist and added to the soil in that condition. The object of adding the moist manure was to avoid too great a modification of the bacterial flora. Because of the condition of the manure, it was impossible to obtain a perfectly uniform mixture, or to mix it with the soil as well as was desirable.

Manure gathered as above was analyzed for total amino acid nitrogen, ammonia nitrogen and total nitrogen. For the amino acid nitrogen 100 grams were stirred with 400 cc. of 1 per cent sodium hydroxide for a few minutes, the coarser particles were strained out and the liquid was then filtered through a folded, dry filter. Aliquots were taken for duplicate determinations and the solution was then carried through precisely the same procedure as the soil extract.

For the ammonia determination, 50 g. of the manure were placed in 500 cc. Kjeldahl flasks, 200 cc. of water and about 5 grams of sodium carbonate added and the ammonia determined by aeration. Aeration was continued until practically no more ammonia was being given off. The total nitrogen was determined in 2-gram samples obtained by drying and grinding a larger sample. The results are given in Table IV.

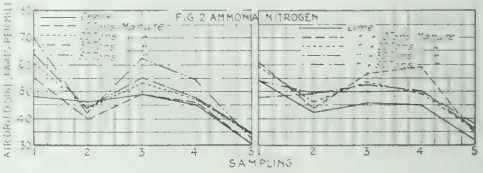
TABLE IV—NITROGEN IN P. P. M. WET MANURE

| | | | | |
|---|---|---|---|---|
| AMINO ACID | 31 0 | 24 7 | 32 6 | Average 29.4 |
| AMMONIA | 140 | 161 | 155 | 152 |
| TOTAL | 5100 | 4795 | 5460 | 5118 |

It should be pointed out that the determinations were made on separate samples; that is, ammonia and amino acids were not determined on the same sample. The discrepancies of the results illustrate the non-uniformity of mixing. The results are calculated to the wet basis, that is, just as it was added to the soil.

All of the pots were maintained as closely as possible at 20 per cent moisture by replenishment of the evaporated water every two or three days with distilled water. The experiment was started on May 15, 1915; the first sampling made May 18th and then every two weeks until in all fine samplings had been made. On each of the samples taken, amino acid, ammonia, and nitrate nitrogen were determined by the following methods:

AMINO ACID NITROGEN—At the first sampling, the moisture was immediately accurately determined, enough of the fresh soil taken to give 150 grams of dry soil was put in a bottle and sufficient water and 4 per cent sodium hydroxide to give 600 cc. of 2 per cent alkali, and after shaking two hours, the total amino acid nitrogen was determined. Then the fresh




soil, as soon as the soil had been withdrawn for the determinations of the amino acid nitrogen in the wet soil, was quickly dried, with the aid of an electric fan. The total amino acid nitrogen was then determined in the air-dry soil in the usual way. The results using the fresh soil and the air-dried soil were practically the same, so for the remaining samplings, air-dried soil was used. The dissolved copper was titrated with 0.001 *N* sodium thiosulfate. Duplicate determinations were always run.

AMMONIA NITROGEN—75 grams air-dried soil, 200 cc. distilled water, 10 grams magnesia and a small

[1] *Iowa Research Bull.*, **3** (1911), 121.

[2] Molliard, *Bull. Soc. botan. France*, **57** (1910), 541–547; Hutchinson and Miller, *J. Agr. Sci.*, **4**, 282.

[3] *J. Am. Chem. Soc.*, **24** (1902), 1120.

piece of paraffin were placed in a copper flask and distilled, 150 cc. of distillate being collected in 0.1 *N* acid.[1] The results by this method are, no doubt, high, but conditions were kept as nearly constant as possible, so the results are probably at least approximately comparable.

NITRATES—The phenoldisulfonic acid method as modified by Chamot[2] and collaborators was used throughout. As is well known, this method gives somewhat low results with higher amounts of nitrates: 100 grams of soil and 2 grams calcium carbonate were shaken for about a half hour with 200 cc. of water and immediately filtered and an aliquot of the solution so obtained immediately evaporated to dryness; treated with the phenoldisulfonic acid reagent and after dilution potassium or sodium hydroxide[3] added until the maximum color was produced.

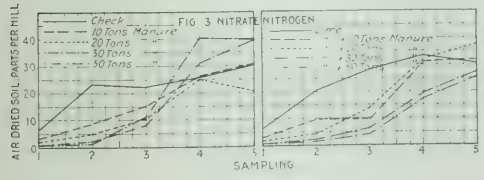
## RESULTS

In Table V, because of lack of space, only the averages of the results from the samplings of the duplicate pots are given. These results have been plotted (Figs. 1, 2 and 3) and the points so found have been joined by straight lines.

Table V.—Three Forms of Nitrogen (Results in Parts per Million Air-Dry Soil)

| Expt. No. | Sampling No. | Amino Acid Nitrogen 1 | 2 | 3 | 4 | 5 | Ammonia Nitrogen 1 | 2 | 3 | 4 | 5 | Nitrate Nitrogen 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 10.1 | 5.74 | 7.42 | 5.46 | 5.18 | 48.3 | 46.0 | 49.0 | 45.2 | 30.8 | 6.4 | 23.3 | 22.4 | 25.6 | 30.4 |
| 2 | | 10.0 | 6.16 | 6.16 | 5.04 | 4.76 | 53.9 | 41.8 | 45.5 | 44.5 | 31.5 | 6.4 | 20.3 | 28.2 | 33.6 | 30.4 |
| 3 | | 10.6 | 8.31 | 6.44 | 5.32 | 6.44 | 55.3 | 40.0 | 49.0 | 45.9 | 30.8 | 3.1 | 8.8 | 15.2 | 26.4 | 30.5 |
| 4 | | 10.8 | 7.70 | 6.86 | 7.84 | 6.44 | 60.9 | 44.1 | 53.2 | 47.3 | 34.7 | 2.2 | 4.8 | 10.4 | 25.2 | 20.8 |
| 5 | | 12.9 | 8.40 | 7.98 | 8.54 | 6.72 | 64.4 | 43.9 | 55.3 | 47.6 | 34.7 | 0.8 | 2.2 | 8.2 | 31.2 | 39.2 |
| 6 | | 12.9 | 9.10 | 9.24 | 8.68 | 8.12 | 70.4 | 42.0 | 62.3 | 54.3 | 33.6 | 0.6 | 1.45 | 11.3 | 40.8 | 39.2 |
| 7 | | 10.3 | 6.72 | 9.38 | 6.30 | 3.64 | 60.2 | 43.1 | 56.0 | 55.8 | 33.6 | 3.2 | 9.8 | 9.8 | 31.2 | 32.0 |
| 8 | | 11.0 | 6.86 | 9.52 | Lost | 3.71 | 58.8 | 45.9 | 53.2 | 49.0 | 35.4 | 1.9 | 4.5 | 14.0 | 32.0 | 37.6 |
| 9 | | 11.2 | 7.00 | 10.1 | 7.28 | 3.85 | 47.6 | 48.8 | 52.2 | 49.9 | 35.4 | 0.82 | 2.0 | 6.7 | 19.2 | 27.2 |
| 10 | | 12.5 | 7.00 | 11.2 | 7.28 | 5.32 | 53.2 | 49.3 | 49.7 | 49.3 | 37.5 | 1.0 | 1.5 | 4.4 | 17.6 | 25.8 |
| Differences between duplicates | | | | | | | | | | | | | | | | |
| MAXIMUM... | | 2.2 | 2.24 | 0.6 | 1.40 | 0.84 | 14.0 | 8.1 | 9.8 | 15.4 | 9.1 | 2.6 | 8.2 | 3.4 | 6.4 | 21.2 |
| AVERAGE... | | 0.7 | 1.27 | 0.23 | 0.6 | 0.37 | 4.2 | 5.4 | 2.7 | 4.1 | 3.3 | 0.4 | 1.7 | 2.0 | 3.7 | 5.9 |

In Fig. 1 it is seen that in general there is a decrease of amino acid nitrogen compounds. The values for the manured soils are but slightly higher than for the unmanured. This is, perhaps, the most striking fact brought out by the experiment. There is no tendency for an accumulation of these products under the conditions of the experiment. Another noteworthy fact emphasized by Fig. 1 is the greater consistency of the results for the limed pots. Perhaps a reason for this is that the microbiological activities proceed more normally in a medium of the reaction induced by the lime.




The ammonia results, plotted in Fig. 2, in a general way follow the amino acid results. When the experiment stopped, as with the amino acid, the ammonia content was decreasing.

In Fig. 3, which shows the nitrate results, the most striking thing brought out is that the curves for the unmanured soils are below the curves for the manured soils, in the case of the unlimed soils for the first three samplings and for the limed soils for the first four samplings. This points to denitrification or assimilation, or a combination of the two. If denitrification takes place to any great extent, it might be followed by total nitrogen determinations. In this laboratory at present some very carefully controlled experiments along this line are being carried out.

## CONCLUSIONS

1—The work of Chardet, who used the Soerensen method and found from 49 to 68 per cent of the soil nitrogen to be amino acid nitrogen, was not confirmed. Practically no amino acid nitrogen could be found in soil by this method.

The Kober method as applied to soils gave the following results:

2—No amino acid nitrogen could be found in the dilute acid extract of soils.

3—Upon adding small quantities of amino acid to a soil and extracting with dilute acids, no amino acid could be found.

4—Upon adding small quantities of amino acids to a soil and extracting with dilute alkali, practically the entire amount added was recovered.

5—There was found to be no difference in the quantity of amino acid nitrogen extracted by dilute alkali in one, two, four and six hours.

6—A few soils were analyzed for free amino acid nitrogen, total amino acid nitrogen and total peptide nitrogen, with the following results:

| Soil | Nitrogen—P. P. M. Air-Dried Soil: Total nitrogen Per cent of soil | Total amino acid | Free amino acid | Total peptide |
|---|---|---|---|---|
| A | 0.151 | 7.95 | 5.45 | 31.8 |
| B | 0.180 | 23.1 | 14.7 | 30.9 |
| C | 0.21 | 23.1 | | |

The conclusions to be drawn from the pot experiments are as follows:

7—There is no tendency for the amino acid to accumulate under the conditions of the experiment, namely in a limed and unlimed acid soil, in a heavily manured and limed, and a heavily manured unlimed acid soil.

8—The amino acid nitrogen was present in the soil in less amounts than the ammonia nitrogen, but in a general way it fluctuates with the ammonia nitrogen.

9—The soils with the higher amounts of manure show a decided decrease in the amount of nitrate nitrogen at first, but after from four to six weeks, there is a decided increase.

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[1] Since the experimental part of this paper was completed, the authors have worked out a method for the determination of ammonia in soils (*Loc. cit.*) which is much more satisfactory than the magnesia method.

[2] *J. Am. Chem. Soc.*, **33** (1911), 381.

[3] The original directions call for potassium hydroxide.

## THE OIL OF THE WILD GRAPE SEED, VITIS RIPARIA[1]

By Geo. D. Beal and C. K. Beebe

This oil has been examined in a series of studies which the senior author has been carrying out on the oils of the different members of the grape family. The source of the oil was the seeds from the wild grape, obtained during the manufacture of grape butter. The seeds, after freeing them from the dried pulp, were ground in a mill and extracted with low boiling petroleum ether; after evaporation of the ether, the oil obtained amounted to 19.38 per cent of the weight of seed taken. The oil had a greenish amber tint, tasted like castor oil, and had a peculiar acrid odor.

Physical and chemical examination of the oil gave the following data:

| Density at 15° C. | Refractive index at 15° C. | Saponification value | Iodine value | Acetyl value | Insoluble Per cent | Fatty acids neutralization value |
|---|---|---|---|---|---|---|
| 0.9425 | 1.4781 | 187.8 | 76.47 | 61.29 | 90.00 | 173.4 |

| Total Fatty Acids | Per cent | Iodine value | Mean molecular weight |
|---|---|---|---|
| Liquid | 95.00 | 91.8 | |
| Solid | 5.01 | 3.12 | 268.6 |

The low iodine value of the solid fatty acids may be assumed to be caused by the trace of liquid fatty acids which it is impossible to remove by the lead salt-ether method of separation. On the basis of the neutralization value of these solid acids and their calculated molecular weight, we have calculated that these were a mixture of 64.28 per cent of palmitic acid and 35.72 per cent of stearic acid.

The iodine values obtained for the liquid fatty acids are too low, and were probably due to oxidation during the process of separation. Another portion of the oil was treated for the removal of the liquid acids, these were brominated, and the linolic and ricinoleic bromides separated by fractional crystallization from petroleum ether. The bromides obtained by this method corresponded to approximately 44 per cent of oleic and ricinoleic acids, and 56 per cent of linoleic acid.

The quantity of oil available at the time was too small for further studies on its composition, or for any determinations of its physiological properties. We hope during the present year to obtain a further supply of the oil, and to continue the investigation.

The saponification value, iodine value, acetyl value and nature of the fatty acids all tend to place this oil in the group with the other oils of the grape family and with castor oil, with which the group is headed. We have hopes that it will present, though doubtless to a much less degree, the physiological properties of castor oil.

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## THE STABILITY OF NITROGLYCERIN TABLETS[1]

By Wilbur L. Scoville

Tablets of nitroglycerin for medicinal use, are manufactured from a 10 to 20 per cent alcoholic solution, or from a 20 per cent paste mixture containing sugar of milk or calcium carbonate. The body of the tablet is usually either sugar of milk or a mixture of this with cane sugar.

Since the tablets contain but a minute quantity of nitroglycerin (1/200 grain to 1/20 grain each), yet are quite powerful in action, it is necessary that the strength shall be accurately adjusted, and that the tablets shall not change in strength on keeping.

It has been found that there is a decided loss of strength in manufacturing, and this loss is now allowed for, the final adjustment being made by assay on a preliminary sample of tablets. The ratio of loss is not constant, and it is necessary to test each lot during the process of manufacture. This is a matter of detail which is easily adjusted, and tablets of nitroglycerin need not vary materially from the stated strength when first made. The question of permanence, however, has not yet been decided.

Until within four years a trustworthy method of estimating the minute quantity of nitroglycerin in tablets was not known. And the question of deterioration can only be settled by starting with tablets whose strength has been accurately determined.

About $3\frac{1}{2}$ years ago a series of sample tablets, freshly made and tested, was set aside for observation. These represented the usual market, and were stored, some in bottles of amber glass, some in white, some in bottles well filled and some partially filled, so that the varying conditions of light and air might be considered in the keeping qualities of the tablets. Table I shows the results.

Table I—Tests of Tablets of Nitroglycerin

| No. | Class | Strength Grain | Material | Date of manufacture | Test—Percentages When made | Jan. 1912 | June 1912 | June 1914 |
|---|---|---|---|---|---|---|---|---|
| 1 | Triturate | 1/20 | Paste | Sept. 1911 | 95 | 95 | 95 | 95 |
| 2 | Triturate | 1/25 | Paste | Feb. 1911 | 80 | 80 | . | 80 |
| 3 | Triturate | 1/25 | Paste | May 1911 | 100 | 100 | 100 | 100 |
| 4 | Triturate | 1/25 | Paste | Nov. 1911 | 100 | . | 100 | 100 |
| 5 | Triturate | 1/50 | Paste | Sept. 1911 | 95 | 95 | 95 | 95 |
| 6 | Triturate | 1/50 | Paste | Dec. 1911 | 100 | . | 100 | 100 |
| 7 | Hypodermic | 1/50 | Solution | Sept. 1913 | 100 | . | . | 85 |
| 8 | Hypodermic | 1/60 | Solution | Dec. 1913 | 100 | . | . | 80 |
| 9 | Triturate | 1/100 | Paste | May 1910 | 95 | 95 | 95 | 90 |
| 10 | Triturate | 1/100 | Paste | June 1911 | 100 | 100 | 100 | 100 |
| 11 | Triturate | 1/100 | Paste | Oct. 1911 | 105 | 105 | 105 | 105 |
| 12 | Triturate | 1/100 | Solution | Dec. 1912 | 105 | . | . | 90 |
| 13 | Hypodermic | 1/100 | Solution | Dec. 1910 | 100 | 80 | . | 80 |
| 14 | Hypodermic | 1/100 | Solution | Dec. 1910 | 100 | 50 | 40 | 35 |
| 15 | Hypodermic | 1/100 | Solution | Sept. 1911 | 105 | . | . | 70 |
| 16 | Hypodermic | 1/100 | Solution | Feb. 1912 | 105 | . | 100 | 85 |
| 17 | Triturate | 1/150 | Paste | Oct. 1911 | 100 | 95 | 85 | 50 |
| 18 | Triturate | 1/150 | Paste | Oct. 1911 | 100 | 100 | 80 | 50 |
| 19 | Hypodermic | 1/150 | Solution | Sept. 1913 | 100 | . | . | 55 |
| 20 | Triturate | 1/200 | Paste | Dec. 1911 | 100 | . | 65 | 60 |
| 21 | Triturate | 1/200 | Solution | Nov. 1913 | 100 | . | . | 90 |
| 22 | Hypodermic | 1/200 | Solution | Nov. 1912 | 100 | . | . | 80 |

It will be noticed that *all tablets containing less than* $^1/_{100}$ *grain each have deteriorated*, and, also, *all those made from solution of nitroglycerin, while tablets made from the paste, of* $^1/_{100}$ *grain or over, have maintained their strength.* Two explanations of this are possible:

(1) The solution may yield a finer attenuation of the nitroglycerin, exposing more surface and favoring volatilization. The chemists at the Bureau of Mines hold to the idea that nitroglycerin is slightly volatile at ordinary temperatures, and this view is largely accepted. The deterioration of the tablets containing less than $^1/_{100}$ grain each bears out this view, since in such tablets the nitroglycerin must be more highly attenuated than in the stronger, to secure

[1] Presented at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

uniform dosage. On the other hand, the amount of air-space in the containers does not appear to be any factor in the deterioration, since some tablets that showed a 50 per cent deterioration were stored in securely stoppered tubes which allowed only a very small proportionate air-space, and freshly opened tubes showed the same deterioration as had taken place in bottles furnishing a relatively large air-space.

(2) A second possible explanation is found in the two forms in which nitroglycerin is known to exist. Kast, in 1906, found that solid nitroglycerin is capable of existing in two isomeric forms—a labile form melting at 2.8° C. and a stable form melting at 13.5° C. H. Hibbert, in a paper read at the Eighth International Congress of Applied Chemistry, confirmed this, and found that freshly prepared nitroglycerin usually crystallizes in the labile form; but that on long standing, particularly after having been once frozen, it tends to change to the stable form; that the stable form is also promoted by mixing with wood pulp and sodium nitrate, accompanied by a trace of moisture; that rubbing with a glass rod also promotes the change in the cold; and that the labile isomeride melts at 2.0° C. and the stable at 13.2° C.

The nitroglycerin used in the above tablets was from one lot of paste, purchased in October 1908, and four lots of solution, purchased respectively in September 1910, July 1911, February 1912, and March 1912. They were stored in a small, unheated, and isolated building, in which the temperature is always very close to that of the outer atmosphere. Thus the paste had passed through two winters before being used in any of the series of tablets here reported, while the solutions had all passed through one winter's storage. In Detroit a temperature of a few degrees below 0° F. (—18° C.) occurs in most winters a few times.

Hibbert found that cooling to —40° C. and stirring with a glass rod was necessary to crystallize the liquid nitroglycerin, but when the liquid was "seeded" with a crystal of the form desired, a temperature of —5° C. only was necessary. He also showed a marked tendency of nitroglycerin to gradually change into the stable form, but did not succeed in reversing the process. He was unable to change a stabilized form to labile. He further showed that liquid nitroglycerin is much more susceptible to shock-decomposition than the solid, but that the stabile isomeride seems to persist in the liquid condition after it had been formed, and that slowly-frozen nitroglycerin differs in its properties from rapidly-frozen.

Thus in the paste form, we have nitroglycerin in the condition most conductive to forming the stable isomeride, *e. g.*, the presence of a hard-crystalline body (milk sugar) and of a trace of moisture; while in the alcoholic solution the conditions may be unfavorable to the formation of the stable form. Even the labile crystals do not form except in the presence of some sharp body and rubbing. Hibbert used ground glass and a glass rod to obtain the crystals.

Thus the nitroglycerin in those tablets which deteriorated may have been in the labile condition, with a greater tendency to decomposition than the others. Several tests were made for nitrites in the deteriorated tablets, which might show decomposition, but none were found. But if decomposition occurs, it is more likely to be an oxidation process than a reduction, hence a failure to find nitrites proves nothing.

The work on the isomerides of nitroglycerin is too recent to prove whether it is a factor in the deterioration of nitroglycerin in tablets or not, but three facts are established.

I—Tablets containing less than $^1/_{100}$ grain of nitroglycerin lose strength very markedly on keeping.

II—Tablets made from an alcoholic solution of nitroglycerin are less stable than those made from a paste.

III—It is probable that a nitroglycerin which has been slowly frozen and slowly thawed is better for tablet use than one freshly made.

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## ON CONSTITUENTS OF OIL OF CASSIA[1]

By FRANCIS D. DODGE AND ALFRED E. SHERNDAL
Received May 28, 1915

The essential oil of cassia, obtained in China by steam distillation of the bark and leaves of *Cinnamomum cassia*, is commercially one of the most important oils, yet its composition does not seem to have been thoroughly investigated. The chief constituent is the well-known cinnamic aldehyde, the amount of which, in pure oils, appears to vary from 75 to 90 per cent. In the last fractions of the oil, a crystalline compound has, at times, been noted: it was designated "cassia steroptene" by Rochleder who first observed it, and was later identified as the methyl ether of orthocoumaric aldehyde by Bertram and Kursten[2] who also synthesized the compound by the condensation of methyl salicylic aldehyde with acetaldehyde. In 1889, Schimmel and Co. isolated cinnamyl acetate as a constituent, and the presence of phenyl-propyl acetate was indicated by the boiling point of the alcohols obtained by saponification of the esters present. Cinnamic acid also occurs in small amounts, undoubtedly resulting from oxidation of the cinnamic aldehyde. In commercial oils, mineral oil and rosin are still found, evidence of the gross adulteration so long practiced.

Apparently pure oils generally show a slight rotation, in the polarimeter, but to what constituent this is due, has not yet been ascertained.

In the course of an examination of a sample of oil of cassia, it was found that when the alkaline solution obtained by shaking the oil with dilute sodium hydroxide was acidified and distilled with steam, the distillate gave an intense purple coloration with ferric chloride.

As this reaction could not be due to any of the heretofore recognized constituents of the oil, the test was applied to various samples of commercial oils, to determine if it were perhaps due to the presence of an accidental impurity. Fifteen cc. of oil were shaken with an equal volume of 2 per cent sodium

[1] Presented at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

[2] *J. prakt. Chem.*, [2] **51**, 316.

hydroxide and the mixture allowed to stand until the supernatant liquid was clear. The latter was then decanted, acidified, and distilled with steam. The first 5 cc. of distillate, which contained a little oil, and had the characteristic odor of salicylic aldehyde, gave, in every case, strong indications of the presence of phenolic compounds.

In order to identify the compound responsible for this reaction, and to determine approximately the amount present in the oil, 500 grams of a freshly redistilled oil, of undoubted purity, were worked up.

The oil had the specific gravity 1.050 at 25°, rotation +0.32°, and showed 88 per cent cinnamic aldehyde, by the usual method. It was extracted twice with 500 cc. portions of 2 per cent sodium hydroxide, the clear alkaline solution acidified, and extracted with ether. The ether solution was then extracted with 10 per cent sodium bisulfite solution, the latter neutralized with soda, distilled with steam, and the distillate again extracted with ether. The ether solution, on evaporation, left a colorless oil, weighing 1.66 grams, showing the characteristic properties of salicylic aldehyde, and yielding a crystalline semicarbazone, melting at 228°, with decomposition.

The first ether solution, after extraction with bisulfite, was washed with sodium bicarbonate solution to remove acids, and then evaporated. An oily residue, weighing 0.53 g., was obtained, which crystallized on standing, and was identified as coumarin (melting point, after crystallization from hot water, 67°). From the bicarbonate washings a small amount of crystalline acid was isolated, which melted, not very sharply, at 123°–128°, and showed, on titration, an acid value of 379 (calc. for cinnamic acid, 378.3; for benzoic acid, 459).

The experiment indicated, then, the presence of about 0.4 per cent salicylic aldehyde and about 0.2 per cent coumarin in the oil. The amount of the latter in the original material must, however, be considerably more, since coumarin is not readily volatile with steam.

In addition to the compounds mentioned, we found indications of other substances, in small amount, so that an examination of a larger quantity of oil seemed advisable. From 600 lbs. of oil we obtained an alkali-soluble portion amounting to 3 lbs. Of this, about 25 per cent was readily volatile in steam, and consisted principally of salicylic aldehyde; the last portion of the steam distillate was separated, by means of sodium carbonate solution, into an insoluble part, mostly coumarin, and an oily acid, which dissolved. The latter, when isolated in the usual manner, showed a molecular weight of about 175 by titration (assumed monobasic), and seemed to be unsaturated, as it readily reduced permanganate solution. A larger quantity of this acid, or acid mixture, was isolated from the portion of oil not easily volatile with steam, which was worked up as follows: Crystals of coumarin which had separated on standing were filtered off; on washing the oil with sodium carbonate solution, more coumarin crystallized out, and was separated. From the alkaline solution, by acidifying, a mixture of cinnamic acid and oil was obtained. The latter, on chilling, yielded more coumarin, and an oily acid mixture, which was distilled *in vacuo*. About 60 per cent of it came over between 145° and 200° (29 mm.), and the yellow distillate crystallized on chilling. The crystals were found to be salicylic acid.

The liquid portion of the distillate, which appeared to be the oily acid mentioned above, was esterified with ethyl alcohol, and yielded an ester mixture, boiling between 220° and 285°, and having the odor characteristic of the esters of the higher fatty acids. On fractioning this the first portion was lighter than water; the last, heavier, and apparently contained ethyl benzoate. The small quantity of substance prevented a further examination.

To sum up, the results of our examination showed that the oil of cassia contained at least 0.5 per cent soluble in dilute alkali, consisting of a mixture of about 25 per cent salicylic aldehyde, 60 per cent coumarin, 8–10 per cent cinnamic acid, and small amounts of salicylic acid, benzoic acid and a volatile liquid acid, not identified. No phenol, other than salicylic aldehyde, could be detected.

Although present in small proportion, salicylic aldehyde and coumarin undoubtedly contribute to the composite aroma of the oil. In fact, the presence of the former can be often detected by odor, in the first fraction of a redistilled oil, and it seems remarkable that these familiar compounds should so long have escaped observation.

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# LABORATORY AND PLANT

## LIME RECOVERY FROM SPENT CAUSTICIZING MUD

By James H. Payne

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In an article written for This Journal about a year ago[1] the writer dealt with this subject in an introductory manner, tracing roughly the state of the art and deducing, by methods of comparison with similar operations in lime and cement practice, what the fuel consumption and operating costs should be. From data covering the performance of several lime recovery plants which the writer has had the privilege of observing for a period of a year or more, it is now possible to deal with the subject more in detail, and also to suggest further improvements in design.

Every soda pulp mill, alkali works, and the larger soap works, carries on the causticizing operation and produces daily large quantities of spent lime mud. Miscellaneous chemical industries also produce quantities of this material. Mud of similar character is produced by the Steffen process of de-sugarizing molasses and in the manufacture of magnesia, acetone, etc., but in these cases the mud contains no caustic and is often of coarser grain and hence more easily freed from water.

In almost every case the removal and disposal of

[1] This Journal 6 [illegible]

this material is troublesome and expensive. Although excellent material for agricultural purposes, it has to compete with ground limestone at very low prices. It must first be dried, and drying costs nearly as much as burning to quicklime. From the standpoint, therefore, purely of disposal, the only feasible method is to reburn to quicklime and either use it over and over again to make a cyclical process, or where this is not possible, dispose of it in the form of quicklime, in which form it always finds a ready market. As will be shown later, from the standpoint solely of economy, regardless of any consideration of necessity, the proposition of reclaiming caustic mud and using it over and over again is a highly profitable one for tonnages exceeding 15 tons lime per day, and even where the quantity is as low as 10 tons the cost of reclaimed lime will generally fall below the cost of new lime by a good margin.

Lime recovery has been carried on successfully for the past year and a half at one of the large pulp mills in Maryland, and practically all the ammonia soda works are now recovering a large percentage of their waste lime. It has also been carried on for a number of years at several beet sugar plants in the West. The ammonia soda works and the beet sugar mills have usually their own limestone quarries from which they produce lime at $2.00 to $2.50 per ton, and the recovery process is competing successfully with these figures. The pulp mills and chemical plants, on the other hand, usually buy their lime, paying an average of about $4.50 per ton for it. It is, therefore, but a question of time before the adoption of the process will become quite general throughout the chemical industry.

### DESCRIPTION OF TYPICAL PLANT

While each plant varies in its details more or less, all those known to the writer employ the following general method, which may be regarded as typical: The mud in the causticizing tanks after the second or third wash water is drawn off is sent by centrifugal pump to an agitated storage tank near the filter. Its concentration is usually about 1 part solids: 1 1/2 parts liquid, in which condition it is readily handled either by gravity or pump to the filter tank. The filter is preferably of the rotary vacuum type, of metal construction, with the exception of the filter cloth, which may be of canvas or of asbestos cloth. On leaving the filter, where it may receive a third wash, if necessary, the mud consists of 100 parts solids to 45 parts liquid. It drops directly into a brick-lined cylinder of the cement type which may be 80 to 150 feet long, 6 to 8 feet in diameter, and may be fired with producer gas, natural gas or fuel oil. The time required for the material to travel through the kiln is 1 1/2 to 2 hours. From the kiln the burnt lime, in the form of small rounded lumps, mostly under one inch in size, drops into a suitable cooler which for small tonnages may consist simply of iron cars, but for large tonnages should be mechanical and arranged to deposit the lime in a steel bin whence it may be drawn into buggies for the causticizing room. The reclaimed lime is used in the causticizing room exactly as lump lime and goes through the system again and again. About ten per cent is discarded each day and replaced by new lime to prevent the amount of contamination, which is always present to a certain extent and is cumulative, from growing above the point where its action becomes deleterious. This contamination manifests itself largely in the form of unslakable lumps, much of which is too fine to be retained by the baskets in the slaking tanks. Instead of introducing ten per cent of new lime daily, a more effectual way of keeping up the purity of the mud is to remove these unslaked grains by means of any one of several types of classifiers now in use in metallurgy.

Two men per shift are required to operate the filter, producer, kiln and cooler. The operation is a continuous one, on a basis of 7 days a week. Repairs being rarely necessary, a recovery plant seldom needs to actually shut down, except twice a year for the necessary re-lining of the kiln and producer.

### FUEL REQUIREMENTS

As the item of fuel constitutes about one-half the operating cost, it is very important that definite data based on long periods of operation be established. Fuel requirements will vary with the tonnage, the water content of the mud when fed to kiln, and with the dimensions and design of the kiln.

Based on figures covering a number of months running time at several recovery plants using natural gas or producer gas, the fuel required to burn a ton of lime has been found to average 675 lbs. coal for producers (including steam for blowing same), or 9500 cu. ft. for natural gas. These figures assume kilns 7 ft. in diameter and 120 ft. in length, 45 per cent water in the feed, and 30 tons output per day. This bears out fairly well the estimate appearing in THIS JOURNAL a year ago[1] which was deduced from known cement and lime data. The estimate was 500 lbs. coal per ton of lime, but the same water content as in cement practice was assumed, 35 per cent. Actual practice in lime recovery has not yet been able to get lower than 45 per cent water in the feed. This difference of ten per cent in water content is equal to 85 lbs. coal, which brings the original estimate within 90 lbs. of the results actually obtained.

The drier the mud is when fed, the less fuel is required. Aside from fuel saving, there is a marked increase in kiln capacity and improvement in the quality of the lime, because the length of the burning zone is thereby increased. It is out of the question, however, to consider burning mud entirely freed of water, as this has met with failure in times past because of the excessive amount of dust produced. Feeding the material wet solves the dust problem completely.

### FACTOR OF EVAPORATION IN ROTARY KILNS

Some idea of what the proper factor of evaporation is for long rotary kilns may be deduced from the above data by comparison with known data for dry limestone. If we take 350 lbs. coal per ton lime as a fair figure for

[1] *Loc. cit.*

burning dry, crushed limestone in a similar kiln, the evaporation factor may be deduced as follows:

| | |
|---|---|
| Dry mud to produce one ton lime | 3400 lbs. |
| Water in same (at 45 per cent) | 1530 lbs. |
| Coal to burn one ton lime from mud (45 per cent water) | 675 lbs. |
| Coal to burn one ton lime from dry limestone | 350 lbs. |
| Coal to evaporate 1530 lbs. water (difference) | 325 lbs. |
| EVAPORATION FACTOR: 4.7 lbs. water per lb. coal. | |

The evaporation factor will of course vary with dimensions of kiln, stack draft, and temperature of outgoing gases. In this instance the kiln is 7 ft x 120 ft., the draft at base of stack is 0.3 of an inch, and the average temperature of gases leaving the kiln throat is 400° F.

### CONSIDERATIONS INVOLVING USE OF FILTER

To attempt to burn the mud without first removing by mechanical means all the water possible would be poor economy. The principal item of expense is fuel, and many of the modern types of filters or dewaterers will soon pay for themselves in fuel saved and capacity gained. Even in the case of a small plant, where the expense of installing a filter is proportionately very great, the omission of the filter would be a reversion towards conditions that have met with failure in former attempts to re-burn caustic lime waste.

Without a filter, a pulp of 1 water : 1 solids, or 100 per cent water, is about as thick as can be readily obtained by settling or fed uniformly to the kiln with any degree of economy. A good filter will reduce the water to 40 or 45 per cent, require little attention and act as an automatic feed to the kiln. To get a ton of lime, 1450 lbs. water must be driven off from filtered mud and 3400 lbs. from settled mud. At four pounds evaporation per lb. of coal, this means a difference of 490 lbs. coal, which at $3.00 per ton is 74 cents per ton of lime. The difference would actually be greater than this, because the long drying zone necessary within the furnace to drive off such a large quantity of water would restrict the burning zone to such a short distance that excessively high temperature and poorly burned lime would result.

Any of the modern filters may be used to advantage, but the continuous type is preferable because it gives an automatic feed to the kiln and is therefore better adapted to actual conditions. It is difficult to reduce the water below 45 per cent because at this point cracks begin to appear in the cake and further removal of water is practically stopped.

### QUALITY OF THE RECOVERED LIME

Reclaimed lime does not begin to slake as quickly as new lime, even in hot water, but once the hydration begins it goes on quite as rapidly as with average lime and shows a high percentage of causticity. This slowness in starting is probably due to the presence of a thin skin of silicate of lime on the surface of the lime particles. Once this is penetrated the slaking goes on very rapidly. No complications arise from continued re-use provided about ten per cent is replaced by new lime daily. Any time lost in slaking is made up in settling time, as the recovered lime settles very rapidly.

### ECONOMY OF THE OPERATION

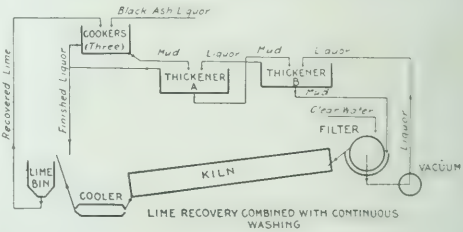
The cost of re-burning lime will vary with the tonnage and the cost of fuel, but even in a plant using 15 tons per day or less the cost is always considerably below the cost of new lime added to the usual loss in alkali and the expense and annoyance of disposing of the sludge. For a 30-ton plant the cost averages $2.00 per ton of lime and an installation will pay for itself in less than two years. In the case of a 15-ton plant the cost should range from $2.50 to $3.00 per ton. As new lime costs about $4.50 to such plants there is still a good margin of profit to be derived from a lime recovery installation. Even in the case of plants using only ten tons lime per day or less, where they are forced to keep their waste out of the streams, a lime recovery installation can be depended upon to solve the disposal and to recover lime at a cost well below the cost of new lime. Plants of this size usually pay $5.00 or more for their lime, and at this price a recovery plant turning out less than ten tons per day could be made to return a good profit.

### CONTINUOUS WASHING OF THE SLUDGE

Where conditions justify it, a marked improvement on the typical scheme as already outlined would be to put the washing of the sludge upon a continuous basis by the use of the continuous counter-current decantation principle now so widely employed in various hydro-metallurgical processes.

To be sure, this necessitates the use of larger tanks than are usually found in use in causticizing, which means that a certain amount of equipment already in use will have to be thrown out. The cost of making the change, however, is small, and it is but a question of time before the use of this principle will become general for the purpose of freeing the mud from the caustic, because it is so plainly a parallel case to those widely used metallurgical processes where valuable solutions are separated from solids in pulp form at extremely low cost and high efficiency. The new system eliminates weak liquor storage, reduces floor space, saves labor and loss of alkali, and fits particularly well into a continuous lime recovery installation.

A diagrammatic sketch or flow sheet is shown herewith illustrating a typical lime recovery plant with the addition of this continuous washing feature. A capacity of 20 tons lime per 24 hours is assumed. Of the tanks ordinarily in use according to the batch system of washing, enough are retained to take care of the "cooking" reaction between the lime and the soda ash. This generally means about one-fourth the total tank capacity, as washing time is usually three times the cooking time. The other tanks are removed and



LIME RECOVERY COMBINED WITH CONTINUOUS WASHING

replaced by two large tanks 20 to 30 ft. in diameter equipped with the thickener mechanism. When a batch of lime and soda liquor has been carried to equilibrium in one of the cooking tanks the contents are allowed to settle, the clear strong liquor is drawn off, and the sludge is sent to Thickener A as shown on sketch. On its way there it is mixed with the overflow of clear wash water from Thickener B. The underflow from Thickener A, consisting of one part solids to one part solution, is lifted continuously by a diaphragm pump to Thickener B, mingling on its way there with the wash water from the filter. Underflow from B goes to filter where it receives a wash of clear water and drops into the kiln with a water content of 45 per cent. The overflow from B goes to A and the overflow from A unites with the strong liquor from the cooking tanks to form liquor of the concentration desired.

By proper adjustment of the wash water used, the strength of the outgoing caustic liquor can be readily maintained at the concentration desired, and there is no necessity for storing any wash water. By providing several make-up tanks for the final liquor (which is customary practice) any slight variation from the concentration required may be corrected by adding the necessary amount of strong or weak liquor. From the kiln the burnt lime goes to a cooler, thence to a storage bin, from which it is drawn as desired and put through the circuit again. The lime should not contain over one per cent caustic when washed in this manner.

The thickening tanks being of great size allow of sufficient flexibility to enable the kiln to operate several hours without any material being sent into the system from the cooking tanks, and *vice versa*. Hence though the cooking is on an intermittent batch system, the washing is continuous and supplies the kiln with a uniform feed as desired. The entire installation could easily be run by three men per shift and the total expense of causticizing and lime recovery should not exceed $2.50 per ton of lime used.

### CONCLUSIONS

I—Prior to a year ago there was little public knowledge of caustic lime waste being successfully reclaimed, and the generally known failure of a pulp mill in New England and an alkali works in the West ten years or more ago to solve the problem had created much skepticism.

II—The results of several recovery plants that have been in operation for more than a year show that there are no practical or theoretical reasons preventing the general adoption of lime recovery even where the tonnage is as low as 10 tons per day.

III—The factors that have made for success have been mainly the adoption of long rotary kilns and filters for removing all water possible by mechanical means before feeding mud to the kiln.

IV—A further improvement upon the process as now carried on is to wash the sludge according to the continuous counter-current decantation principle, thereby further reducing costs in the causticizing department.

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## RAPID VOLUMETRIC PROCEDURES FOR DETERMINING COMBINED ALUMINA AND BASIC ALUMINA OR FREE ACID IN ALUMINUM SALTS

By WILFRED W. SCOTT

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In the manufacture of aluminum salts, the purity of the finished product depends upon the control analyses of the liquors after mixing and before evaporation to crystallization. The tests must not only be accurate but must be rapidly executed. The following procedures, based on well-known reactions, have been worked out at the Laurel Hill laboratory of the General Chemical Company, to meet these requirements. The method for determining basic alumina or free acid in liquors and salts of alumina is the writer's modification of Craig's fluoride process.[1] The determination of combined alumina depends upon the acid reaction of aluminum salts towards phenolphthalein indicator, titration being made in hot solutions as recommended by Schmatalla.[2] The author is indebted to Mr. W. S. Allen, Chemist-in-charge, Laurel Hill laboratory for criticism and valuable suggestions that have assisted him in this work.

The methods as finally worked out are as follows:

### DETERMINATION OF BASICITY OR ACIDITY OF ALUMINUM SALTS

The procedure is based upon the fact that an excess of neutral potassium fluoride decomposes aluminum salts in solution, forming two stable compounds which react neutral to phenolphthalein, while the free acid remains unaltered, the following reaction taking place:

$$Al_2(SO_4)_3 + 12KF + xH_2SO_4 = 2AlF_3.3KF + 3K_2SO_4 + xH_2SO_4.$$

The precipitate $AlF_3.3KF$ is insoluble in an excess of the potassium fluoride reagent, and is not appreciably attacked by acids or alkalies. Theoretically about 7 parts by weight of potassium fluoride are required for one part by weight of aluminum sulfate, but in actual practice it is advisable to use twice this amount.

REAGENTS REQUIRED—*Standard solutions of sulfuric acid and potassium hydroxide*—Half normal solutions have been found to be of suitable strength. Sodium hydroxide may be used in place of the potassium hydroxide.

*Phenolphthalein indicator*—Alcoholic solution containing 0.1 per cent of the reagent.

*Potassium fluoride*—The reagent may be prepared by dissolving 1000 grams of potassium fluoride in 1200 cc. of hot, $CO_2$-free water, then neutralizing the solution with alkali or hydrofluoric acid as the case may require, using 5 cc. of phenolphthalein indicator. Dilute sulfuric acid may be used in place of hydrofluoric acid, in the final adjustment, to get a neutral product: 1 cc. of the solution in 10 cc. of $CO_2$-free water should appear a faint pink. The concentrated mix is filtered, if necessary, and then diluted to 2000 cc. with $CO_2$-free water. The gravity will now be approximately 1.32 (about 35° Bé.): 1 cc. contains 0.5 g. potassium fluoride salt.

[1] T. J. I. Craig, *J. Soc. Chem. Ind.*, **30**, 185.

[2] Otto Schmatalla, *Ber.*, **38**, 4; *Chem. News*, **91** (1905), 2373, 236.

METHOD OF PROCEDURE

SOLIDS—3.4038 grams of the finely ground sample or an equivalent amount in solution (100 cc. sample containing 34.038 grams per liter) are taken for analysis. The powder is dissolved by boiling with 100 cc. of distilled water in a 4 in. casserole with clock glass cover. To the hot solution 10 cc. of $N/2$ $H_2SO_4$ are added, and after cooling to room temperature (20° C.), 18 to 20 cc. of the potassium fluoride reagent are added and $^1/_2$ cc. of phenolphthalein indicator. The solution is now titrated with $N/2$ KOH, added drop by drop until a delicate pink color, persisting for one minute, is obtained. This titration shows whether the product is basic or acid.

BASIC ALUMINA—This is indicated when the alkali back titration is less than the amount of acid added. *Free* $Al_2O_3$ = (cc. $H_2SO_4$ — cc. KOH) ÷ 4.

FREE ACID—In this case the back titration of the alkali is greater than the cc. of acid added. *Free acid* = (cc. KOH — cc. $H_2SO_4$) × 0.72.

LIQUORS—In works control of liquors the specific gravity is taken: 5 cc. are diluted to 100 cc. with $CO_2$-free water, 10 cc. of $N/2$ $H_2SO_4$ added and the solution boiled for about five minutes. After cooling, the potassium fluoride reagent is added, together with phenolphthalein and the titration with the standard alkali made as in case of solids.

BASIC MIXES—(Cc. $H_2SO_4$ — cc. KOH) × (0.0245 × 0.3473 × 100) ÷ (5 × sp. gr.) = *free* $Al_2O_3$.

ACID MIXES—(Cc. KOH — cc. $H_2SO_4$ × 2.45) ÷ wt. of sample = *free* $H_2SO_4$.

NEUTRAL MIXES—The back titration of the alkali is the same as the volume of the acid added.

NOTES

$CO_2$-free water must always be used in titrations with phenolphthalein indicator. This may be obtained by boiling distilled water to expel $CO_2$.

If the sample does not dissolve clear, digestion with 10 to 15 cc. of standard sulfuric acid is advisable. This may be accomplished by boiling the sample, 15 to 20 minutes, in an Erlenmeyer flask with reflux condenser.

Darkening of the solution during the back titration with the alkali indicates that an insufficient amount of potassium fluoride has been added. If this is the case it will be necessary to repeat the test with fresh solution and larger amount of potassium fluoride.

Ammonium salts, if present, must be expelled by boiling the sample with an excess of standard potassium hydroxide solution and this excess determined.

The end point may be readily seen by gas or electric light, as well as by daylight.

3.4038 = factor $H_2SO_4$ to $Al_2O_3$ multiplied by 4.
0.72 = factor $Al_2O_3$ to $H_2SO_4$ divided by 4.

DETERMINATION OF COMBINED ALUMINA

Aluminum salts react acid to phenolphthalein and are completely dissociated in hot solutions, any acid, combined or free, reacting readily with fixed alkalies forming neutral alkali salts. The end point of the reaction is indicated by the pink color produced by phenolphthalein with the excess of alkali. From the amount of caustic required the percentage of combined alumina may be calculated, the following reaction taking place:

$$Al_2(SO_4)_3 + 6NaOH = 2Al(OH)_3 + 3Na_2SO_4.$$

PROCEDURE

The factor weight, 3.4038 grams, of the salt is dissolved in a 4 in. casserole with 100 cc. of distilled water, 1 cc. of phenolphthalein indicator added and the sample titrated boiling hot with $N/2$ NaOH, added from a chamber burette, graduated from 50 to 100 cc. in tenths. If the sample contains less than 12.5 per cent $Al_2O_3$ a larger amount of the material must be taken if the chamber burette, graduated as described, is used. The solution is kept boiling during the titration and is constantly stirred. Towards the end of the reaction the alkali is added cautiously drop by drop until a permanent pink color is obtained, *viz.*, a color that persists for at least a minute with the solution boiling.

Cc. NaOH required divided by 4 = *per cent alumina*, $Al_2O_3$; or cc. $N/2$ NaOH × 0.0245 × 0.3473 × 100 ÷ wt. sample = *per cent* $Al_2O_3$.

CORRECTION FOR IRON—Since iron salts also dissociate and are titrated with aluminum salts by this method a correction has to be made for the ferric and ferrous iron present in the material. The true value of combined alumina is obtained by subtracting the per cent FeO × 0.47 + $Fe_2O_3$ × 0.64.

DETERMINATION OF FERROUS AND FERRIC IRON—A 5 gram sample is dissolved in water and the iron oxidized with a few drops of strong potassium permanganate, the reagent being added until the solution becomes a permanent pink. The excess permanganate is destroyed by addition of a drop or so of normal oxalic acid solution. Total iron is now determined by titration of the solution with standard stannous chloride. The total iron in the sample should be between 0.002 to 0.05 gram. The solution should contain about 50 cc. of hydrochloric acid, 1:1. This is heated to boiling and the standard stannous chloride added to the hot solution until the yellow color of the ferric salt just fades. Cc. of the reagent required multiplied by the factor in terms of $Fe_2O_3$ = *Total* $Fe_2O_3$ *in the sample*. On a separate 10 gram sample the ferrous iron is determined. This is best accomplished by dissolving the salt in an Erlenmeyer flask by boiling with 100 cc. of dilute HCl, 1:1, in an atmosphere of $CO_2$ to prevent oxidation. The ferric iron is titrated with stannous chloride as in the first case. The difference between the first titration results in terms of $Fe_2O_3$ and the second in terms of $Fe_2O_3$ percentages is due to ferrous iron in terms of $Fe_2O_3$. This result multiplied by 0.9 = *FeO*. The accuracy of the titration depends upon the absence of oxidizing agents, other than iron, which react with stannous chloride. The reagent should be carefully standardized against ferric ammonium alum. If 17.2 grams of this salt are dissolved in 2000 cc., one cc. will contain approximately 0.001 g. of iron. Titration of the sample should be conducted under

conditions of temperature, acid concentration, etc., similar to those of the standardization.

The amount of phenolphthalein used should be the same in each determination. An excess of the indicator causes low results. It has been noted in cases of alums, where iron does not interfere, that best results are obtained with three or four drops of phenolphthalein solution. Larger amounts of indicator are necessary if iron is present, in order to detect the end point.

COMBINED SULFURIC ACID—Provided no free acid is present, the combined acid is calculated from the titration for combined alumina. The titration multiplied by 0.72 = *combined sulfuric acid. viz.*, factor 2.8792 divided by 4. Should free acid be present, as determined by the first procedure outlined, its equivalent should be deducted from both the alumina and combined acid. This is best done by subtracting the equivalent volume in terms of $N/2$ solution from the total volume titration before dividing by 4 to obtain percentage of $Al_2O_3$ or multiplying by 0.72 to get combined $H_2SO_4$.

EXAMPLE—Titration of $N/2$ alkali due to free acid = 2.2 cc. (1st method).

Total titration of the hot solution (2nd method) = 80.6 cc. NaOH.

The 80.6 — 2.2 = 78.4 and 78.4 divided by 4 = 19.6 per cent $Al_2O_3$ or 78.4 multiplied by 0.72 = 56.45 per cent combined $H_2SO_4$.

Free acid = 2.2 divided by 4 = 0.55 per cent $H_2SO_4$.

Sulfuric acid combined with the fixed alkalies is not titrated.

## EXPERIMENTAL DATA

INFLUENCE OF IRON—Iron is invariably present in aluminum salts in ferric or ferrous form, generally a combination of the two. The amount seldom exceeds 0.8 per cent Fe so that comparatively large amounts of iron need not be considered here. Since the combined acid of iron in either state of oxidation titrates readily, this impurity will cause an appreciable error unless allowance be made for the amount present. The following results were obtained on a mixture of pure potash alum with varying amounts of iron as indicated, this impurity being added as ferric and ferrous sulfate. The quantity of alum taken was sufficient to give a titration of over 69 cc. of standard alkali. The factors 0.64 for ferric and 0.47 for ferrous iron to alumina were used as recommended in the method.

| Added iron | Titration | ¼ Titration | ¼ Titration Corrected for iron |
|---|---|---|---|
| 0 | 69.4 cc. | 17.35 | |
| 0.1% $Fe_2O_3$ | 69.8 cc. | 17.45 | 17.39 |
| 0.5% $Fe_2O_3$ | 70.85 cc. | 17.72 | 17.41 |
| 1.0% $Fe_2O_3$ | 72.5 cc. | 18.12 | 17.48 |
| 0.1% FeO | 69.6 cc. | 17.40 | 17.35 |
| 0.5% FeO | 70.65 cc. | 17.66 | 17.43 |
| 1.0% FeO | 71.5 cc. | 17.88 | 17.41 |

It is evident that with ¼ the titration representing per cent, iron present either as ferric sulfate or ferrous sulfate up to one per cent in terms of iron oxide causes no serious error, provided the corrections are applied for the titration of the iron. Ferric iron tends to cause high results.

The fact that ferric and ferrous sulfates are titrated is shown by the results given below. Ammonium sulfate and persulfate are also titrated, the fixed alkalies are not. Results are given in terms of the acid calculated from the titration.

| Salt used | Gram acid present | Gram acid calculated |
|---|---|---|
| $Al_2(SO_4)_3$ | 0.300 | 0.299 |
| $FeSO_4.7H_2O$ | 0.699 | 0.636 |
| $Fe_2SO_{43}$ | 0.483 | 0.612 |
| $(NH_4)_2SO_4$ | 0.742 | 0.658 |
| $(NH_4)_2S_2O_8$ | 0.860 | 0.850 |

Ammonia is expelled in the boiling solution as the alkali replaces it in combination.

Ferrous hydroxide occludes phenolphthalein indicator to a point of saturation. For example, it was found that one gram ferrous sulfate with excess NaOH would completely absorb 25 cc. of the indicator preventing it from giving the desired color with caustic, whereas an excess of the indicator above this amount produced the pink color with the excess caustic.

The following results were obtained with three standard aluminum salts by the usual gravimetric methods, and the results checked by the volumetric procedures outlined:

| Gravimetric Analysis | Per cent | Volumetric | Per cent |
|---|---|---|---|
| | Aluminum Sulfate | | |
| $Al_2O_3 + Fe_2O_3$ | 17.95 | Combined $Al_2O_3$ | 17.20 |
| $Fe_2O_3$ | 0.55 | Free $Al_2O_3$ | 0.36 |
| $Al_2O_3$ by difference | 17.40 | Correction for ferric and ferrous iron | 0.25 |
| | | Total $Al_2O_3$ corrected | 17.31 |
| | Recrystallized Potash Alum | | |
| Total $Al_2O_3$ | 10.77 | Combined $Al_2O_3$ | 10.68 |
| Iron | Trace | Free $Al_2O_3$ | 0.04 |
| | | Total $Al_2O_3$ | 10.72 |
| | Aluminum Chloride | | |
| Total $Al_2O_3 + Fe_2O_3$ | 20.97 | Combined $Al_2O_3$ | 20.45 |
| $Fe_2O_3$ | 0.023 | Free $Al_2O_3$ | 0.33 |
| $Al_2O_3$ by difference | 20.947 | Total | 20.78 |
| | | Corrected for iron | 20.765 |

The end point is sharp when iron is absent, but with amounts of iron exceeding 1 per cent the color of the precipitated iron hydroxide tends to mask the pink color due to the indicator. Ferric iron produces a reddish pink end point; with ferrous iron a purplish pink color is observed.

Four men working independently checked within 0.6 cc. in the titration for combined alumina, and within 0.1 cc. in the fluoride method for free alumina, making the limits of error due to the personal factor, 0.15 per cent for total $Al_2O_3$ and 0.02 per cent for free $Al_2O_3$.

| | | | | |
|---|---|---|---|---|
| A | 69.3 | 69.4 | 69.8 | 69.2 cc |
| B | 3.8 | 3.7 | 3.8 | 3.8 cc |

## SUMMARY

Rapid volumetric procedures for determining combined and free alumina in aluminum salts, followed by experimental data showing reliability of the methods, are given. Impurities such as commonly occur in these salts do not interfere, with exception of iron, for which correction must be applied as stated. The methods are of special value for works control of liquors during the process of manufacture of aluminum salts, and the analysis of the finished product in daily routine analysis.

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# RECOVERY OF AMMONIA FROM WASTE LIQUORS

By E. L. KNOEBLER

Received May 22, 1915

A recent investigation of waste products in the plant of the Welsbach Company brought to light a

solution containing about 1 per cent of ammonia, which was being discharged into the sewer. The investigation showed that this solution consisted of a mixture of three ammoniacal solutions containing, respectively, the following percentages of free and combined ammonia:

| No. | Per cent free $NH_3$ | Per cent combined NH |
|---|---|---|
| 1 | 3.5 | 0.17 |
| 2 | 0.5 | 0.025 |
| 3 | 0.1 | 0.005 |

When mixed together, as they appeared when run to waste, the mixture approximated 1 per cent free ammonia and 0.05 per cent combined ammonia. The solution was perfectly clear and recovery of the ammonia was found to be practicable by the usual methods of distillation.

The waste liquor was produced by the factory processes at practically a constant rate throughout the working day, and this consideration influenced the decision to recover by means of a continuous still.

In the selection and erection of the apparatus, the points of easy and inexpensive maintenance and operation were carefully considered, with special attention to low labor charges and small steam consumption.

With these points in mind the distilling outfit shown in Fig. 1 was so erected and set that the waste liquor flows by gravity from the factory processes to a large iron tank set in the ground just outside the still house, from which it is pumped to the storage tank set above the column of the still. This pumping is the only handling of any liquor during the complete cycle of operations—the storage tank supplying the liquid at a constant head at all times, whence it flows by gravity through the washer, the coils of the heat exchanger, the heater and the still—the waste passing around the coils of the heat exchanger and then to the sewer. The ammonia vapors pass through the condenser and into the absorber, from which the freshly distilled ammonia overflows into the storage

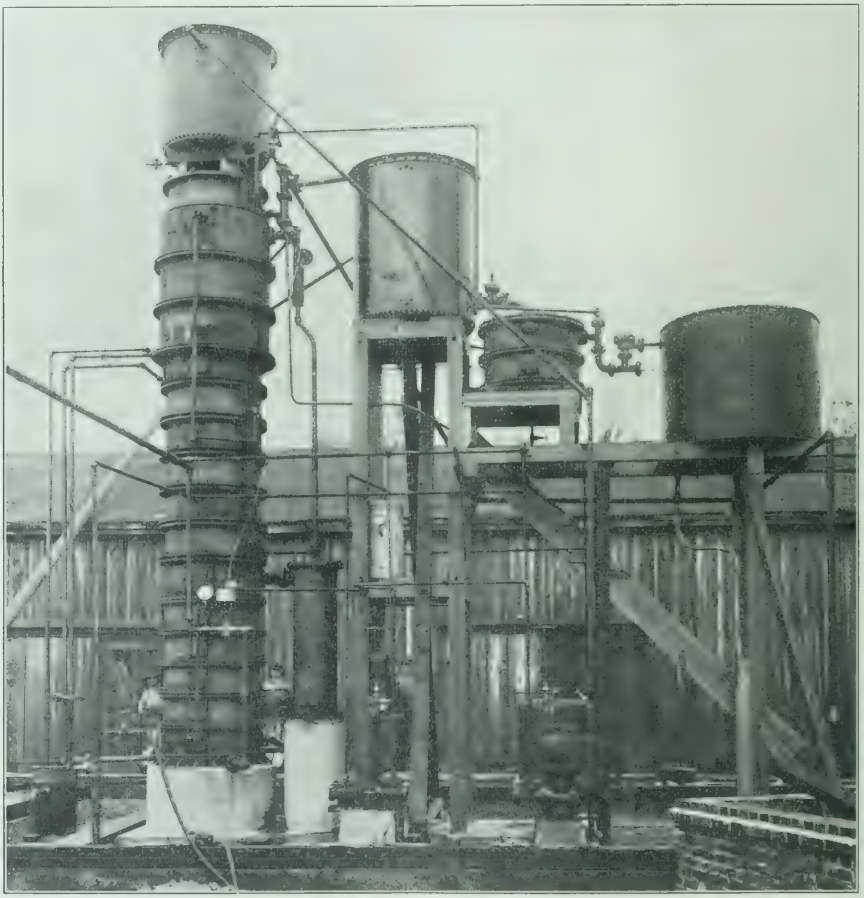


FIG. 1

tank. This tank is set at such a height that the fresh solution flows by gravity to the factory where it is available for use by simply opening a cock.

The steam supply for the still is automatically controlled, as is also the delivery of lime for release of the fixed ammonia, so that it is necessary for the attendant to look in only once each hour or two in order to see that the still is operating satisfactorily. The bulk of the heat in the waste liquor is saved by preheating the crude liquor in a heat exchanger and seal pot—the latter acting also as a constant flow automatic valve for the release of the waste. The consumption of lime is reduced to a minimum by keeping the milk of lime constantly and thoroughly stirred, and delivering it in small quantities and at frequent and regular intervals.

By these provisions for automatic operation, the cost of attendance and the handling of liquor, lime, etc., have been reduced to a minimum, the only still charges of any consequence being interest and depreciation, and coal for steam.

The operation of the still is extremely simple, and is as follows, references being to Fig. 2:

The weak liquor is pumped to the storage tank *A* by means of a small steam pump—the exhaust of which is led into the still to decrease the steam consumption. The liquor then flows by gravity at a constant rate, down through the washer *B* and then through the coils of the heat exchanger *C*, back up through the heater *D*, where it overflows through the pipe *E*, into the volatile still *F*, where the free ammonia is driven off. The liquor then passes out through the pipe *G* into the lime leg *H* where it meets and is thoroughly mixed with the milk of lime, when it passes back into the still for fixed ammonia, *I*. Here the fixed ammonia is released and the waste liquor passes down and out around the coils of the heat exchanger by means of the pipe *L*, and overflows to the sewer.

The ammonia vapor passes up through the still, bubbling through the down-coming liquors in its passage from one section to the next, and then passes out through the coils in the heater *D* and over into the condenser *J* by the lead pipe *M*. Here the water vapors are condensed, and a part of the ammonia is absorbed. The condensate then flows down into the absorber *K* where it is kept cool by means of water flowing through the coil *N*. Here the balance of the ammonia vapors are absorbed and the resulting ammonia solution passes over into the storage tank, from which it flows by gravity through lead pipes to the factory where it is used.

The milk of lime is made up and kept in an iron stir-

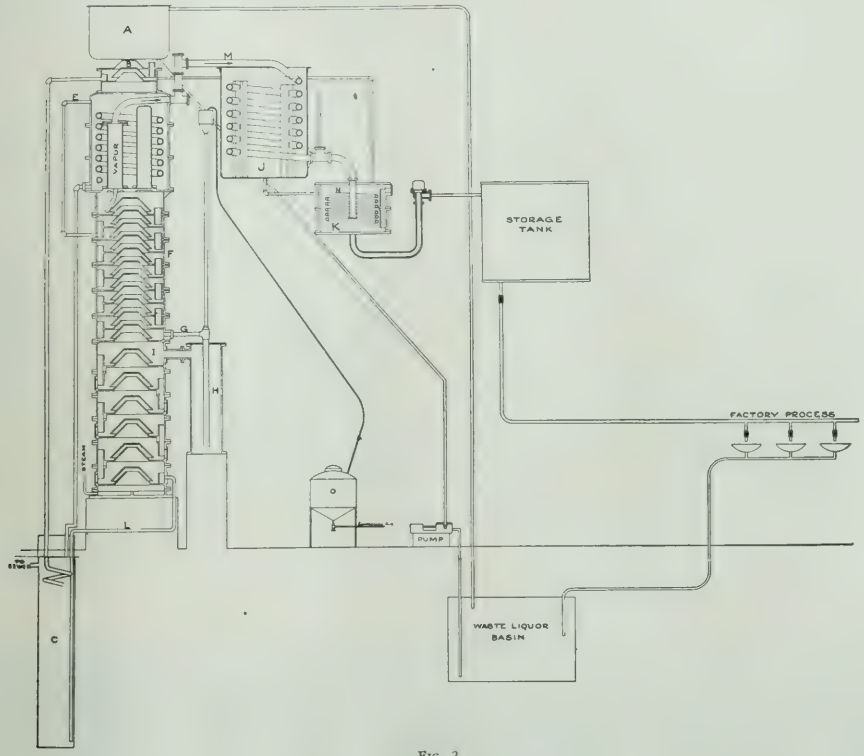



FIG. 2

ring tank, *O*, where it is agitated continuously by means of compressed air, which also operates the automatic valve, through which the lime is delivered to the still. The timing of this valve is regulated by a needle valve and by-pass between the top and bottom of a cylinder filled with kerosene, in which a piston descends and ascends. This makes it possible to supply the lime in small quantities and at frequent and regular intervals, making for uniform temperatures and regular operation.

Steam is supplied to the still through an automatic valve also operated by compressed air, the controller consisting of a thermostat, depending for its operation on the expansion or contraction of a liquid, the pressure thus generated serving to operate a small air valve which in turn controls the compressed air supply to a diaphragm valve through which steam is served to the still. The thermostat is adjusted to operate at the temperature of the top of the still, and serves to keep this temperature within a range of 2° F. of the predetermined point. The concentrate runs about 28 per cent $NH_3$ at all times and is diluted to the desired degree as used.

The cost of operation per 10-hour day runs approximately as follows:

| | |
|---|---|
| Steam, 12,000 lbs. | $3.00 |
| Labor and supervision | 1.23 |
| Lime | 0.20 |
| Repairs, paint, oil, waste, etc. | 0.35 |
| Interest and depreciation | 1.93 |
| | $6.71 |
| Output, 3,000 lbs. 26 per cent $NH_4OH$ | |
| Cost per 1,000 lbs. 26 per cent $NH_4OH$ | $2.24 |

The outfit has proved to be simple in construction and easy to operate and the results more than come up to expectations.

WELSBACH CO., GLOUCESTER, N. J.

## A NEW GLASS; AND AN APPLICATION OF THE LOW REFLECTIVITY OF GLASS FOR RADIANT HEAT

By E. C. SULLIVAN AND W. C. TAYLOR

Received August 19, 1915

A glass has recently been developed which is unique among borosilicate glasses in that it combines very low thermal expansion with great resistance to attack of reagents. It is of simple chemical composition, being free from heavy metals and metals of the magnesium-calcium-zinc group. Its characteristic properties are due, in part, to very high silica content which incidentally has necessitated special technique for its melting and working. Some of the measured properties of the glass are as follows:

Specific gravity 2.25.

Mean linear expansion coefficient (19–350°) 0.0000032.

ATTACK BY REAGENTS: Water at the boiling point dissolves several times as much from the best imported laboratory glass as from this glass.

SOFTENING POINT: A thread 1 mm. in diameter and 23 cm. in length suspended vertically and heated through the upper 9 cm. elongates of its own weight at the rate of 1 mm. per minute at 800° C.

Culinary ware made of the glass was found to bake food more rapidly than earthenware or metal. The reason for this lay in the case of the metal in the greater reflectivity of the metal for radiant energy. Magnus found that silver reflected 83 to 90 per cent, glass only 6 to 14 per cent of the rays incident at an angle of 45°,[1] while Hagen and Rubens[2] give 98 to 99 per cent as the proportion of heat reflected by silver and Coblentz's[3] curves indicate 3 to 11 per cent as the reflection by glass. The following experiment, devised by Dr. J. T. Littleton, showed that this difference in reflectivity is of practical importance in the baking process:

A baking dish was silvered on the outer surface in alternate quarters and a cake baked in it in an ordinary kitchen oven over a gas flame. Where the cake had been protected by the metal coating the bottom after baking was light colored, sticky, and imperfectly baked while in the other quarters it was brown and well done. Fig. I shows the interior of the dish with the cake adhering to it over the silvered sections, also the cake as it was turned out bottom up with the quartering plainly visible.

Experiments showing that bread bakes faster in glass than in tin were made by baking equal quantities of dough in two glass bread pans and two tinned iron pans of the same internal dimensions. The metal pans had been in service for some time and their outer surfaces were somewhat tarnished. The pans were placed in the oven of a gas stove, the two glass pans diagonally opposite each other and the metal pans diagonally opposite each other. All four were left in the oven the same length of time. When taken out of the oven the crust in contact with the glass was browner than the corresponding portions of the crust in the metal pans. The bread in the glass had

Fig. I—*a*. Dish Silvered in Quarters Outside Cake Has Adhered over the Silver
*b*. Where Protected by Silver, Cake is Light Colored and Imperfectly Baked; Brown and Well Done Elsewhere

FIG. II
BREAD IN GLASS AND TIN PANS AS REMOVED FROM OVEN

FIG. III
BOTTOMS OF LOAVES
Bread from Tin Is Lighter Colored

FIG. IV
HALVED LOAVES
Loaf from Glass Is Browner

[1] Poggendorff's *Annalen*, **138** (1869), 174.

[2] Drude's *Annalen*, **8** (1902), 1.

[3] "Investigations of Infra-red Spectra," Part 4, p. 88.

risen higher than that in the metal. On cutting the loaves the bread in the glass pans was found to be more thoroughly baked than that in the metal pans (see Figs. II, III and IV). This experiment was repeated with the same result.

A more accurate comparison of the rates of heating in various materials was obtained by placing the dishes containing one liter of water on the shelf in the oven for a definite time and noting the temperatures reached by the water. The determinations are given in Table I.

TABLE I—RATES OF HEATING WATER IN VARIOUS MATERIALS

| Test No. | Thin Glass | | Aluminum | Tin | Enameled earthenware | Thick Glass |
|---|---|---|---|---|---|---|
| 1 | 90° | 91° | 78° | .. | .. | .. |
| 2 | 88 | 86 | .. | 73 | .. | 86° |
| 3 | 89 | 89.5 | .. | 73 | 83 | .. |
| 4 | 89 | 89 | .. | .. | .. | .. |
| 5 | 94 | .. | 78 | 74 | 81 | 86 |
| 6 | 88 | .. | .. | .. | .. | .. |
| Average | 89.4 | | 78 | 73.3 | 82 | 86 |

The resistance of the glassware to fracture by blow was compared with that of crockery ("china") and enameled earthenware by dropping a 350-gram weight on the bottoms of inverted dishes of approximately the same shape. The height of drop was increased by 2-in. intervals until the dishes failed. The results appear in Table II and show that the glassware withstands a blow very much better than the other ware.

TABLE II—RESISTANCE TO FRACTURE BY BLOW

| Dishes Tested | Thickness of bottom | Result |
|---|---|---|
| GLASS: | | |
| 2-quart | 4.8 mm. | Cracked at 22 in. |
| 2-quart | 5.8 mm. | Not broken at 34 in. |
| 1-quart | 4.9 mm. | Cracked at 26 in. |
| 1-quart | 4.3 mm. | Cracked at 22 in. |
| ENAMELED EARTHENWARE: | | |
| German, 2-quart | 5.4 mm. | Cracked at 6 in. |
| Domestic, 2-quart | 8.1 mm. | Crazed at 8 in.; Shattered at 18 in. |
| German, 1-quart | 5.6 mm. | Cracked at 14 in. |
| CROCKERY: | | |
| New Jersey | 6.20 mm. | Broke at 16 in. |
| Domestic | 4.27 mm | Broke at 10 in. |
| English | 5.62 mm. | Broke at 12 in. |
| German | 2.76 mm. | Broke at 4 in. |

CORNING GLASS WORKS, CORNING, N. Y.

## THE REVERSED HEAT ENGINE AS A DRYING MACHINE

By PAUL J. FOX[1]

Received June 21, 1915

As far back as 1852, Lord Kelvin[2] called attention to the inefficiency of heating (*e. g.*, houses) by the direct combustion of coal. It would appear to common sense that, if all the heat escaping in any manner whatever from the combustion of the fuel were used for heating, perfect economy of the fuel would result.

"It is not my present object to determine how exactly in practice this degree of economy may be approximated to; but to point out how the limit which has hitherto appeared absolute may be surpassed, and a current of warm air at such a temperature as is convenient for heating and ventilating a building may be obtained mechanically, either by water power without any consumption of coals, or, by means of a steam engine, driven by a fire burning actually less coals than are capable of generating by their combustion the required heat;" ..... (even admitting that) "a very good steam engine converts about one-tenth of the heat generated in its furnace into mechanical effect."[3]

[1] Scientist in Soil Investigations, Bureau of Soils.

[2] Sir William Thomson, "Mathematical and Physical Papers," **1** (1852), 515.

[3] Lord Kelvin, *Loc. cit.*, pp. 516–517.

The suggestion seems never to have been adopted and that for reasons obvious enough. Anybody can burn coal in a stove or furnace. It requires neither expensive installation nor skilled attendance, and there are thermodynamic complications to be mentioned later. Besides, in the days when the extract given above was written, people did not go in for efficiency and conservation.

It seems to the author, however, that the ideas of Kelvin are well worth reviving at the present time, especially in view of conditions likely soon to come about in the electrochemical industry. Kelvin's proposal seems to have been confined to the application to house warming. This application might be valuable in the case of large buildings such as hotels, apartments, houses, and factories, where more or less elaborate installations of machinery are the rule. To the writer, however, an industrial use seems more interesting; that is, the use of large volumes of warm air for drying and evaporating operations on an industrial scale in cases where electrical or water power is cheap and coal expensive. In this way it would, in some instances, supplant heat for drying developed by electrical resistance methods, and in some instances render drying operations possible where resistance methods would be too expensive; and in some cases it might even be advantageous to generate the heat by this method, with the use of a steam engine. This is especially the case, since the drying engine includes a pump.

The writer will state the thermodynamic principles of the engine proposed, making use for this purpose, of various papers by Lord Kelvin,[1] but with present-day notation, and submit some observations and calculations as to how the machine would have to be modified to serve for drying. As is well known, a heat engine, *i. e.*, an engine for transforming heat into mechanical work, absorbs heat from a reservoir at a high temperature, transforms a part (relatively small) of it into mechanical work, and rejects a part (relatively large) into a heat reservoir (often the atmosphere) at a lower temperature. A large part of the heat is thus necessarily lost, even though the heat engine were a perfect transformer. The essential thing for operation is two heat reservoirs at two different temperatures. Conversely, when a heat engine is reversed, it can absorb a large amount of heat from the lower reservoir, have a relatively small amount of mechanical work performed on it, and deliver a large amount of heat at the higher temperature. These relations are most simply exhibited in a quantitative manner in the well known Carnot cycle. This consists of two adiabatic and two isothermal operations. The working substance, *e. g.*, air, expands at a high temperature, $t_1$, doing external work, and absorbing quantity of heat, $Q_1$. It then expands adiabatically, cooling itself to $t_2$ and doing external work. It is now compressed isothermally at $t_2$, but the compression results in the production of heat in the working substance, which must be ab-

[1] See especially, besides the paper cited, Sir William Thomson, "Mathematical and Physical Papers," **1** (1853), 326.

sorbed by the refrigerator (or heat reservoir at the lower temperature). Let $Q_2$ equal the amount absorbed. Finally, the working substance is compressed adiabatically to the same condition as it was in the beginning of the cycle. The work yielded by the first adiabatic operation is just sufficient to cancel the work necessary to apply to effect the second adiabatic operation. The work actually turned out by the machine is the difference between the work yielded by the isothermal expansion at the higher temperature, and the work required to effect the isothermal compression at the lower temperature. The working substance or gas in the machine remains in the machine and is considered part of it. If $Q_1$ is the heat given to the machine by the upper heat reservoir at $t_1$ and $Q_2$ is the heat absorbed from the machine by the refrigerator or lower heat reservoir at $t_2$, then $Q_2 = \frac{t_2}{t_1}Q_1$. The heat disappearing, $Q_1 - Q_2$, is the mechanical work done. It is unnecessary to develop these expressions here as they may be found in any text-book of engineering thermodynamics. The temperatures $t_1$ and $t_2$ are expressed on the absolute scale. If we apply this to an engine working between say 338° F. (100 lbs. gauge pressure) and 80°, we see that 67.7 per cent of the heat supplied is absorbed by the refrigerator. It is scarcely necessary to remark that no actual engine even approaches so small a loss.

The facts mentioned above have relevancy only as elucidating the operation of the proposed heat engine. The machine discussed above is reversible, *i. e.*, it may absorb heat from the refrigerator or lower heat reservoir, have a small amount of mechanical work done upon it, and deliver a relatively large amount of heat to the upper heat reservoir, which in this case is presumed to be the drying chamber. In this case, of course, precisely the same mathematical relations hold. We would scarcely use the drying engine, however, between the temperatures 338°–80°, *i. e.*, 338° would be higher drying temperature than ordinarily necessary. Consider the atmosphere at 60° and the drying chamber 125°. In this case, $Q_1$ or the amount of heat delivered to the drying chamber amounts to $Q_1 = Q_2\frac{t_1}{t_2} = 1.125\ Q_2$. The difference $Q_1 - Q_2 = 0.125\ Q_2$ is the mechanical work necessary to be applied. In other words, $Q_1$ consists of two parts, the greater one derived from the lower heat reservoir, as the air, and the smaller from the mechanical work applied to the machine. It is easily seen in the present case that 88.9 per cent comes from the atmosphere and 11.1 per cent from the mechanical work, *i. e.*, $Q_1 = Q_2 + 0.125\ Q_2$. Stated in another way, the heat obtained is 9.0 times the mechanical work done, or applied to the machine.

The Carnot cycle has been used above on account of its familiarity, and of the clearness with which it exhibits the essential thermodynamic principles of the engine. In practice, a different procedure would be followed. The gas would be cooled by expansion below the atmospheric temperature, allowed to come up to the atmospheric temperature at the reduced pressure by retention in a suitable vessel, and finally compressed again to atmospheric pressure, the compression resulting in an increase of temperature. Accordingly, the engine consists of three essential parts: (1) a large metal expansion cylinder with a piston; (2) a vessel in which the air in the machine is allowed to come to atmospheric temperature, and which we may call the "atmospheric heat;" and (3) a large metal compression cylinder, also with a piston. The two pistons are connected to one piston rod.

A single half stroke, or single complete movement of the piston in one direction completes a set of operations, and delivers to the drying chamber the weight of air taken in, which, in the following, is assumed to be one pound in all cases. The expansion cylinder takes in air at pressure $p$, specific volume $V$ and temperature $t$ on the left (for example) of the piston during a part of its stroke, and the ports being closed, expands it to $v_1$ and $p_1$ and cools it to temperature $t_1$. The amount of expansion will depend, of course, on the amount of heat to be added to the drying air. The expansion is assumed to be adiabatic. On the right of the piston, at the same time, the air which has been expanded in the previous stroke is discharged into the atmospheric heater.

The atmospheric heater is merely a vessel for allowing the cooled and expanded air to come to atmospheric temperature. It would naturally be a long tube or block or coil of tubes of thin metal to conduct heat to the enclosed air as rapidly as possible, and to avoid mixing warm and cool gas. The tube would be of larger bore where the temperature difference between the atmosphere and the atmospheric heater was greatest. There would be a progressive increase of temperature and specific volume as the air passed through the heater, but only such slight pressure gradient as was necessary to move the air along. Water might be used to bring the temperature of the heater up to atmospheric temperature, by circulating the water as in a condenser. In the house warming engine proposed by Lord Kelvin, it is implied that the expansion of air *in the cylinder* should be isothermal, which would, of course, require less power to operate, by the difference between adiabatic and isothermal expansion. However, considering the slowness with which heat is communicated to a gas, the operation would be substantially adiabatic, at least if the engine is operated at the speed common now. It is assumed adiabatic in the following. The atmospheric heater, then, is essential to bring the cooled and expanded air up to the atmospheric temperature. As the reduction in pressure amounts to only a few pounds, the walls of the heater would not have to be very heavy. In the heater the air expands from specific volume $v_1$ to $v_2$ and passes from temperature $t_1$ to $t$.

In the compression cylinder, on the left, for example, of the piston, air is taken from the atmospheric heater, throughout the whole stroke. On the right, the air taken from the heater during the previous stroke is compressed during part of the stroke from $p_1$ to $p$ (the atmospheric pressure) and heated by the compression from $t$ to $t_3$, the drying temperature. The

return half-stroke completes another cycle of operations as is sufficiently obvious.

In order to make the thermodynamic calculations for the drying engine, it is necessary to use the following constants, where $p$, $v$, $t$ mean the pressure in lbs. per sq. in., $v$ specific volume in cu. ft. per lb., and $t$ temperature in degree Fahrenheit (or abs., absolute Fahrenheit). Unit weight (one lb.) of air is considered throughout.

$p$, of outside atmosphere and of drying chamber.
$v$, $t$, of outside atmosphere.
$v_1 t_1$, on entering atmospheric heater.
$v_2 t$, on leaving atmospheric heater.
$p_1$ of atmospheric heater throughout.
$v_3 t_3$ on leaving the compressor, and in drying chamber.
$\gamma$ = ratio[1] of specific heat at constant pressure to specific heat at constant volume = 1.406.

[1] For dry air. Corrections would have to be made for moist air.

$R$ is the gas constant 53.37 for the English-American units. Of these constants, $p$, $v$, $t$ are fixed by the outside conditions, and $v_3$ can be found immediately by the ordinary characteristic equation of a gas $PV = RTm$, when we have decided on the drying temperature. The air is raised to the desired temperature by compression, and to compress it to a given temperature at a given (atmospheric) pressure, it is necessary previously to have brought it to a condition of lower pressure and temperature. The lower temperature in this case is fixed by the atmosphere; *i. e.*, the air before heating by compression is brought to atmospheric temperature in the atmospheric heater. Hence we must first find $p_1$ or the pressure in the atmospheric heater, by the formula for the adiabatic expansion of a gas.

$$PV^\gamma = K, \text{ where } K \text{ is a constant.}$$

Applying this to the present case, we have

$$p_1 v_2^\gamma = p v_3^\gamma.$$

But $v_2$, or the specific volume on leaving the atmospheric heater, by the characteristic equation amounts to $\left(\frac{Rt}{p_1 144}\right)$. Hence we have $p_1\left(\frac{Rt}{p_1 144}\right)^\gamma = p v_3^\gamma$, in which only $p_1$ is unknown.

The number 144 is inserted merely because $R$ in the characteristic equation is the constant when $p_1$ is expressed in lbs. per sq. ft. (not sq. in.). The equation yields for $p_1$

$$p_1 = p^{\frac{1}{1-\gamma}} \left(\frac{144}{R}\right)^{\frac{\gamma}{1-\gamma}} \left(\frac{v_3}{t}\right)^{\frac{\gamma}{1-\gamma}}.$$

Of these, the first two are merely constants depending on the units used and the atmospheric pressure. This latter we take as 14.7 lbs. per sq. in., which yields 0.001334 for $p^{\frac{1}{1-\gamma}}$ and 0.03222 for $\left(\frac{144}{R}\right)^{\frac{\gamma}{1-\gamma}}$ or 0.00004298 for the product. Let this constant $= B$.

The expression $\left(\frac{v_3}{t}\right)^{\frac{\gamma}{1-\gamma}} = \left(\frac{t}{v_3}\right)^{3.463}$ so that

$$p_1 = B\left(\frac{t}{v_3}\right)^{3.463}.$$

Knowledge of $p_1$ (with $t$) gives us the data to calculate $v_2$ or the volume on leaving the atmospheric heater.

To find $v_1$ and $t_1$, however, it is necessary to apply the $pv^\gamma = K$ formula again, and $pv^\gamma = p_1 v_1^\gamma$ where $p$, $v$, and $p_1$ are known. This yields

$$v_1 = \left(\frac{p}{p_1}\right)^{0.7113} v$$

which in turn gives $t_1$ by the $PV = RTm$ formula. Thus we have all the constants in the list.

To apply the above to a concrete case, take the atmospheric temperature $t = 519$ absolute or 60° F. nearly, and suppose we desire to dry at 100° F. or 559° absolute, then $p = 14.7$, $v = 13.085$, $t = 519$, $t_3 = 559$. The formula $p_1 = B\left(\frac{t}{v_3}\right)^{3.463}$ gives $p_1 = 11.40$; and $v_1 = \left(\frac{p}{p_1}\right)^{0.7113} v$ gives $v_1 = 15.68$. The characteristic equation $PV = RTm$ gives $v_3 = 14.093$, $v_2 = 16.87$, and $t_1 = 482.2°$ absolute. We may also find $t_1$ by the equation $t_1 = \left(\frac{v}{v_1}\right)^{.406} t$, which gives a neat check on the whole calculation.

We can now discuss quantitatively the thermodynamic operation of the engine. The operations may be summarized as follows, each pair being correlative processes. It is convenient to give a plus or minus sign to each process, the plus sign being given when the process tends to turn the machine in the same direction as the power applied, and the minus sign when it opposes the power.

1 + is the taking of air from the atmosphere by the expansion cylinder.
1 — is the delivery of air by the compression cylinder to the drying chamber.
2 + is the expansion of the air in the expansion cylinder.
2 — is the compression of the air in the compression cylinder.
3 — is the discharge from the expansion cylinder to the atmospheric heater.
3 + is the discharge from the atmospheric heater to the compression cylinder.

Thus there are three pairs of correlative processes, each pair containing one positive and one negative member. The handling in pairs also greatly simplifies the work of computation.

OPERATION 1—The work amounts simply to the volume times the pressure, the latter being constant. For taking in air $W_1 = pv$. For rejecting air to the drying chamber $W_2 = pv_3$.

Since the specific volume after heating at constant pressure is larger, the network for operation 1 is negative and is

$$W_3 = p\,(v_3 - v)144.$$

OPERATION 2—The work is given by the usual formula for the expansion or compression of a gas

$$W = \int_{V_a}^{V_b} P dV$$

which integrates into the following

$$W = \frac{R\Delta\theta}{\gamma - 1}, \text{ if for } PV, \text{ its equivalent } RT \text{ is substituted, and } \Delta\theta \text{ is the temperature difference before and after expansion. In the present case we have for the expansion } W_4 = \frac{R\,(t - t_1)}{\gamma - 1}, \text{ and for the com-}$$

pression $W_5 = \frac{R(t_3 - t)}{\gamma - 1}$; $W_4$ is + and $W_5$ is , but $W_5$ is always larger than $W_4$. This latter may be shown by using the adiabatic expansion formula $tv^{\gamma} =$ constant, calling the new temperature $t + \Delta t$ and the new volume $v + \Delta v$, and repeating the process with a new $\Delta t$ and $\Delta v$. It is also clear from the consideration that the temperature of the air is warmer at the same pressure at the end of the operation than at the beginning.

$$W_5 - W_4 - W_6 = \frac{R(t_3 - 2t + t_1)}{\gamma - 1}.$$

OPERATION 3—This is the delivery into and taking from the atmospheric heater. As the atmosphere heats the air (previously cooled by expansion), at constant pressure, not only is the temperature of the air raised, but a certain amount of work is done on it, *i. e.*, its volume is increased. Thus, a certain amount of work is yielded by the heater on account of the greater specific volume of the air on leaving the atmospheric heater than on entering. The work involved on entering is negative and is $W_7 = p_1 v_1$, and on leaving is positive, $W_8 = p_1 v_2$; $W_9 = p_1(v_2 - v_1)144$, the 144 being added since $p_1$ is expressed in lbs. per sq. in. and the work is desired in foot pounds.

Let us now apply the calculations to the concrete case before supposed, namely, that the atmosphere is at a temperature of 60° F. and we wish to dry at 100°. The volumes, pressures and temperatures have been stated above, and the heat and energy relations are now given. The work and heat are given in foot pounds or in British thermal units.

OPERATION 1: $W_3 = p(v_3 - v) = 2116.8 \times 1.008 = -2133.7$, $p$ being expressed in lbs. per sq. ft.

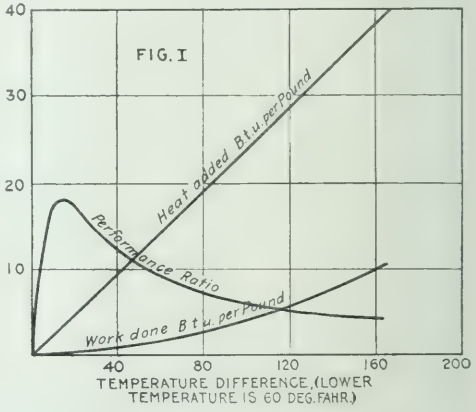
OPERATION 2: $W_6 = \frac{R(t_3 - 2t + t_1)}{\gamma - 1} = -427.2$.

OPERATION 3: $W_9 = p_1(v_2 - v_1) = +1960$, $p_1$ being expressed in lbs. per sq. ft. From the above we see that there is a net negative work of 601 foot pounds or 0.7725 B. t. u.

The specific heat of air at constant pressure is 0.2375. Hence we have added $0.2375 \times 40 = 9.50$ B. t. u. to the one pound of air at an expenditure of 0.7725 B. t. u. in the form of mechanical energy, which gives a coefficient of performance of 12.3; *i. e.*, we obtain 12.3 times as much heat as the heat equivalent of the mechanical energy consumed. Stated in another way, 8.1 per cent of the heat came from the power, and 91.9 per cent from the atmosphere in this case.

In the accompanying curve, the temperature differences are plotted on the axis of abscissas, 60° F. being considered the lower temperature. The vertical axis gives the British thermal units for the "heat added" curve—which is merely the specific heat at constant pressure multiplied by the temperature difference—and also for the work done on the engine. For the performance ratio curve, the units on the ordinate axis are mere numbers equal to the ratio of heat added to work done. One pound of gas in each case is considered the unit. It is more economical, generally speaking, to heat the air through as few degrees as possible; this is in accordance with the thermodynamic economy in avoiding as far as possible an irreversible drop of temperature.

It will be noted that the process is not cyclic, hence the formula $\frac{t_2}{t_3 \quad t}$ cannot be used to find the performance. In fact, it may be worth while, incidentally, to mention an apparent violation of the second law of thermodynamics in this connection. It serves to emphasize the necessity of being sure a process is cyclic before applying the maximum efficiency law. Take again our standard temperatures of 60° and 100°. Imagine air at atmospheric pressure and 60° F. in a cylinder, the whole enclosed in a vacuum. Let the air expand isothermally, absorbing heat from the atmosphere, until its volume is doubled. Since in isothermal expansion $W = Rt \log r$, where $r$ is the ratio of expansion, the work yielded in such isothermal expansion amounts to 19,220 foot pounds, for unit mass of gas. But 15,012 foot pounds of work is sufficient to compress the air adiabatically to the




original atmospheric pressure of 14.7 pounds, at the same time heating it to 174° F., thus leaving 4208 foot pounds in excess. In other words, the gas has heated itself to the temperature of 174°, at the same pressure, with the heat of the atmosphere only. The second law requires, however, that the process be cyclic, and it is not in this case.

A matter of the first importance in connection with the drying engine, is that, when the air is cooled in the operation 2+, the temperature, in many cases, will go below the saturation temperature of aqueous vapor, that is, the dew point, and water will condense out. In adiabatic expansion of air saturated with aqueous vapor, while the volume of course is increased, and hence there is more space for aqueous vapor, the temperature reduction much more than compensates the increase in volume. For example, in cooling air by adiabatic expansion from 60° to 23°, the ratio of expansion, *i. e.*, the ratio of the new volume to the old is 1.20, while the vapor pressure drops from 13.2 to 3 millimeters of mercury. Hence in this there would doubtless be much condensation of water, even if the air was far from saturated with aqueous vapor

initially. All this means that the air is dried in passing through the machine. The great importance of this from the drying point of view is obvious. The fact is that in any case, dry air or relatively dry air is the real drying agent. This production of dry air must be regarded as one of the most substantial advantages of the machine as a drying agent, and would be an argument for running the machine relatively fast, in order to approximate adiabatic conditions. On the other hand, the production of ice, by the freezing of the condensed water, might hinder the operation of the engine or make it necessary to accomplish the cooling in steps. Finally, as a house heating engine, while the large volumes of warm and especially moving air would facilitate ventilation, if the expansion was adiabatic, the resulting air might be drier than considered advisable in houses, though again, it might be remoistened by appropriate arrangements.

It is hardly necessary to state that the calculations are of a strictly thermodynamic character, and do not consider losses by friction, both mechanical and gaseous, nor the other losses—avoidable and unavoidable—in actual engines. These losses vary so greatly according to the size and construction of the installation, that a general discussion is not very profitable. We must remember, however, that the other methods of drying fall far short of complete efficiency, and few processes in practice even approximate the calculated possibility. In particular, the production of heat by the transformation of the electric current is far from an efficient process, if we are to judge by the data furnished in the papers on electric furnaces at the September, 1914, meeting of the American Institute of Metals (especially papers by G. H. Clamer and Carl Hering, H. G. Dorsey, and H. W. Gillett and J. M. Lohr).

On the practical side, however, it may be said that the common objections to air as a working substance do not apply. Air has a low specific heat, which causes the cylinders to be bulky. But if drying is to be effected, the dry air must be pumped or introduced in one way or another into the drying chamber even if only by inefficient diffusion, and the machine suggested acts also as a pump. The same consideration applies also to friction, whereas in a steam engine expansion can be stopped when counterbalanced by friction. The difficulty of communicating heat to air, unless the direct combustion products are brought into contact with the substance to be dried, is a strong argument in favor of the engine, for in it the air is heated evenly and to the temperature desired. Again, heat loss can be minimized. In a direct acting heat engine, as a steam engine, the heat proceeds from in outwards, and all loss of heat by radiation, etc., is a loss of efficiency. In the drying engine, however, the heat passes from out inwards, and all gain of heat is gain in efficiency. This applies to the expansion cylinder and atmospheric heater. So far as the compression cylinder is concerned, there is no reason why it should not be placed *inside the drying chamber*, and thus utilize for drying the various heat losses by friction, etc., occasioned by heating the air.

For drying chemical products, the avoidance of local excessive heating, aside from its wastefulness, is of the first importance for the production of a uniform product. Not only is the temperature uniform, but the circulation of the air, *i. e.*, the drying medium, does not depend upon accidental temperature differences, but can be thoroughly controlled. Besides, the uneconomical irreversible drop of temperature is avoided. A chamber of particular construction, nor one fitted with electric resistance arrangements, nor with closed pipes, is necessary. Again, by drying at the lowest temperature possible, the loss of heat by radiation from the drying chamber is minimized. The low temperature drying is especially valuable in the case of organic materials as fertilizers, where it is important that chemical changes should not take place.

The most serious objection to the plan is doubtless found in the variation of temperature in the external atmosphere, since the machine heats the air through a fixed temperature difference for a given valve setting. This condition might prevent its use in certain places of extreme temperature variation. It may be said, however, that by adjusting the valves and varying the speed of operation the engine could be adapted for different temperature ranges; or a number of machines could be set in series—each machine lifting the air through a certain temperature difference—and a varying number of them used as the atmospheric temperature changed. Or again, the machine could be set in a closed, heated room and the temperature range of the outside air compensated by other means, leaving the final temperature lift and the drying and circulation of the air to the reversed heat engine, used as a drying machine. Or, finally, the drying air could be heated higher than necessary, and adjustment made from time to time by adding varying quantities of cool atmospheric air.

BUREAU OF SOILS, WASHINGTON, D. C.

# ADDRESSES

## THE UNIVERSITY AND INDUSTRY[1]

BY NICHOLAS MURRAY BUTLER

At the outset I wish to disabuse your minds of any notion that you may have that I have been invited to speak at this conference because I am a chemist. All the chemistry I know is such recollection as remains to me, after 35 years, of Dr. Chandler's most admirable and stimulating lectures. But I have an impression, somewhat strengthened by the number of journals and periodicals which come to my table day by day, that there have been some changes in chemical knowledge during that 35 years, and I am afraid that if I were to attempt to reproduce any of his excellent instruction you might think me a student not of chemistry but of archeology.

The reason why I have been requested to speak is, I think, because in our University we have some very definite and long-considered ideas as to the general problem of which this question

[1] Address before the New York Section of the American Chemical Society, Chemists' Club, November 12, 1915.

before you is a specific instance. It is something that has been on our minds for a long time and about which I am very glad indeed to be able to have an opportunity to speak for a few minutes before giving way to those who have special and technical knowledge of the field of your immediate interest.

This problem is really one phase of the many-sided problem of social evolution. We are confronted by a peculiar condition which is the result of developments that have been going on in education and in industry for one or two hundred years. Different stages of development have been arrived at in different nations according to their needs, their opportunities, their national temperaments and the practical demands which have been made upon them. The events of the European war have forced us to compare and to contrast these various stages of development, and they have brought to the attention not only of the man of science and the chemist and the manager of a great industry, but to that of the public and the nations of the world, the varying stages of advancement which have been reached in dealing with this great problem.

The problem—if I may use a military term—is from one point of view a problem of mobilization of resources, of men, of facilities, of opportunities for a peaceful war in the interest of science and of industry. The problem from another point of view is a problem of conservation—the conservation of our natural, our human and our institutional resources. From still another point of view it is a problem in efficiency engineering, applied on a great national scale through an organized undertaking to care for the thousand points of contact between theoretical knowledge and practical life. You are dealing here with mobilization; you are dealing with conservation; you are dealing with practical efficiency. You are bringing your minds to bear, on this particular occasion, on the question how the highest type of educational institution—the University—can coöperate with and serve the practical industrial needs of a civilized people. If you mobilize them, you call them out ready and equipped for service; if you conserve them, you see that they are not wasted or abused; if you follow the efficiency engineers, you make sure that they coöperate to the fullest extent with the least number of waste processes and on the lowest scale of expenditure.

In dealing with this particular question our minds have been somewhat confused and misled in this country by the fact that we are very loose in our use of the word "University." You know, I suppose, that in almost any state, except New York, Pennsylvania and one or two more, any three gentlemen may meet together and organize a University under the General Corporation law in a very few minutes: the consequence is that the name has been used in such a way as to confuse the public mind as to the thing and as to the purposes for which real universities are organized. Naturally, you would hardly expect the sort of coöperation between University and Industry of which you are thinking, if by "University," for instance, you mean a doubtless very admirable institution once located in a not distant part of this Borough and known as "Columbia University of Horseshoeing." I suppose that often where the name University is used for a college, or for a high school, or for a group of professional schools of one sort or another, the question is asked, why does not this University serve Industry? The reason is because it is not a University. It could not possibly serve Industry because it has a wrong name, and while the thing which it is trying to do is doubtless a very excellent and admirable thing, it is not the thing which corresponds to the name it bears. Of course the word "University" has a little different significance in various locations, but the significance which it is coming to bear here in the United States in the minds of those best fitted to judge, is, I think, on the whole a richer and better conception of the term than has yet prevailed anywhere in the world—even in Germany, England or France—because we are beginning to see that a University is not primarily a place where young persons are taught, but that it is primarily a Public Service Institution for the conservation, the extension and the publication of knowledge and for the stimulus of the youth who engage in those undertakings; that is to say, in a University the student is subordinated to the aim of conserving, extending and spreading abroad human knowledge. In secondary school and in college, human knowledge is bent to the development of the student; he is being given information; he is being disciplined and trained as an end in itself; he is being formed to go higher, to go out into practical life, or perhaps to become a research student. In the University, on the other hand, the emphasis is laid on the extension of knowledge and on public service through its application. That is why a school of law that does nothing but train lawyers, even though they may be the best lawyers, is not a University School of Law. It becomes a University School of Law when it contributes to the science of law, when it investigates and publishes and stimulates investigation and publication. The same is true of a school of medicine. You may train students to be the best physicians, but a medical school is not a University School of Medicine unless in training its physicians it is also extending and widening medical knowledge and multiplying its practical applications. In order to be a real University Department or a real University School of Law, Engineering, Medicine or Chemistry, it is absolutely necessary that it shall be inspired and directed by the spirit of investigation, the restless spirit of research, and by that curiosity which has been the driving power in the whole development of civilization. When a University is a true University, it is animated first of all by that spirit of inquiry, of investigation and of the extension of knowledge, and next by the desire to relate itself to the public interests. There we come to the great question which is forced upon us by contemplating some of the lessons of the European war. We all see now, and we know, what it means to organize and to order the resources of a nation; what it means for men owing allegiance to one form of government, revering one flag, representing one set of traditions—we see now what it means for them to be able, and we also see what it means for them to be unable, to organize their resources, to mobilize, to conserve, to develop practical efficiency in the attainment of the national ideal.

There are two ways in which that can be done, and both of those we understand: they are made very plain to us by the events of the last sixteen months. That may be done, first, by the heavy hand of Government. The power of the State may be laid upon the individual institution, or the individual human being, or the individual industry, and it may order those individuals and institutions and industries to take their places in a great national organization. Or it may be done by the voluntary coöperative effort of institutions, individuals or industries. This is the method that is consonant with our American traditions and ideals and that is consistent with the preservation of our principles and habits of life. The great problem before the people of the United States to-day—a problem of which your particular question is a phase—is how, without the sacrifice of the voluntary principle or the freedom of individual initiative or our own individual liberty, we can organize, conserve, mobilize our national resources, intellectual and industrial, for this carrying forward of a great national purpose and a great national ideal. If we are not to resort to the heavy, and often very clumsy and harsh hand of government, then we as individuals, as institutions and as organizations of industry, must, of our own accord, set about the task of effecting this greater organization.

I remember a story that was told some years ago in a political campaign in this city—I think it was by the late Mr. Henry George. It has always seemed to me to be very striking and significant. Mr. Henry George used to tell about a man

who desired a trench dug about his farm. Then he was taken with some sort of illness, and his physician said that he needed a certain kind of physical exercise and that he ought to go out every day and dig, and that if there were not anything in particular to dig, he ought to go out and dig a hole one day and the next day go out and fill it up, so as to get the necessary exercise. So this good farmer, while paying money to a laborer to dig his trench, went out each day to dig a hole and fill it up. "Why my good man," said a neighbor, "why don't you take your exercise in digging something that needs to be dug; why don't you dig your own trench?" There is a lesson here for a University. Why do things solely for exercise when there are things waiting to be done for use and for practical application, that themselves give admirable exercise?

There is a device which seems to me a practical one to bring about the coöperation which is ready at hand; the spirit is there; the desire is there, but there is lack of familiarity with the proper methods. I am quite convinced that every great University should closely associate with its work a group of men from practical life, to be in constant touch with its expert scholars and investigators in a given field. For example, in the Columbia University School of Architecture—one of our great and important schools—we have a committee of visitors made up of nine well-known practicing architects in this country. It is their duty and function to visit the school, to observe the methods in use, to make suggestions for the improvement of the work, as well as to relate more closely the work of the School of Architecture to the profession of architecture in the city of New York. In other words, men are called from their profession to make a link between the public and a University School. We need similar links with all of our great schools in a University given over to research and higher instruction. You probably do not realize that in the course of a year there are between 5,000 and 6,000 advanced students—graduates of colleges, scientific schools and other similar institutions in all parts of the world—who spend a longer or shorter time in receiving training at Columbia University. Why should not those who are looking toward this great branch of industry that you represent, have the benefit of contact with a representative body of visitors, advisers and counsellors drawn from that industry itself? Why should not those who are controlling and organizing the work of the students have that benefit? And why should not the lines of inquiry into which these young men are being guided, be the lines of inquiry that the needs of your profession and the needs of a country demand at the moment? That is done in individual cases. Many of our professors and many men in other Universities are, as individuals, in close contact with industrial leaders and with industrial needs. We have always thought it wise at Columbia University, to encourage such a relationship. We have wanted the things that were done for the students to be the things that needed to be done to meet the requirements of the public. A University like ours could do infinitely more than it is doing if two conditions were fulfilled. The first, of course, is the possession of adequate resources for the purpose, and the second is contact with and coöperation from the organized bodies of practical men who are concerned with the management of the industries of the country. If those men would familiarize themselves with what the Universities are doing, if they would see by a short visit how a research laboratory is organized and conducted—what particular problems it is carrying on at the moment—what has been its success over a given period of past time, there would be a great gain. An immense amount is being done in the very direction of which I am speaking, but it is being done haphazard and it is being done at endless sacrifice, for we have not yet developed to a point where we have our voluntary organization well enough in hand to enable us to use it in this field in ways that quickly and effectively result in national profit.

In my judgment the day has gone by when the tariff will ever again be used as it was so long used during the period following the civil war. I think the time will soon come when the tariff will be used as a scientific instrument for filling up the gaps and strengthening the weak places in our national organization. It will not be used to care for the weak and inefficient, but it will be used to make compact and complete the groups of industries and undertakings that are needed to fill out our national equipment in given fields. We must bend our very best energies to this investment in national organization. We have heard voices calling us to do this for years before this war broke out. We have watched the using up of our unsettled territory. We have watched the running to waste and the passing into private hands of our water power. We have watched the cutting down of our great forests. We have been telling ourselves for years that here was a national problem to be solved, but not until we received the shock and the stimulus of the European war did general public opinion come to see what was meant by national organization, or by the interlacing and the dovetailing of our resources. The place to begin is where the ground lies rich to be tilled. Whatever of this has been done within the past few years has been done haphazard; it has not been done as the result of consistent and thought-out policy. I believe the time has now come for the organized movement of which I speak. It is time to see whether a democracy, without departing from the principle of individual initiative, without giving up civil liberty for a bureaucracy, can of its own accord and because of its own convictions organize its resources in the public interest, as well as any other nation or any other form of government that exists in the world. The Universities—and I am sure I am speaking for others as well as my own—are ready and willing to help. All they need is the stimulus of coöperation—practical contact with the leaders of industry. What the leaders of industry need is a better appreciation of the spirit that is animating the Universities. If we could show the people of the United States that a group of Universities and a group of industries were ready, of their own accord, to march forward in this splendid campaign of effective organization, the result would be an immense enhancement of our national prosperity, and a great enrichment of our national life.

COLUMBIA UNIVERSITY, NEW YORK

## CHEMICAL PATENTS—IV

### IV—ACTIONS FOR INFRINGEMENT

By SEABURY C. MASTICK[1]

#### I—THE CASE OF THE LOWER COURT (*Concluded*)

I have stated previously that a suit was brought in 1891 by the Cowles Company against the Pittsburgh Reduction Company for alleged infringement of certain Cowles patents and that, before the taking of testimony had begun in this suit, a patent had issued to Charles S. Bradley on an application filed by him on February 23, 1883. As a matter of fact the original Bradley application was divided, Patent No. 464,933 dated December 8, 1891, and Patent No. 468,148 dated February 2, 1892, both being issued on the original application. Of these two patents No. 468,148 was the broader and was the one chiefly discussed in the subsequent patent litigation.

Before discussing this later litigation we must first consider how these Bradley patents came to the ownership of the Cowles Company, therein seeing the application of certain of the rules as to assignments and contractual rights heretofore discussed.

In 1885 the Cowles Company had encountered Charles S. Bradley, who was a joint applicant with Francis B. Crocker, in a patent interference involving certain Cowles applications and a joint application of Bradley and Crocker. In a conference relating to the purchase by the Cowles Company of the joint

[1] Special lecturer on Chemical Patents, Department of Chemical Engineering, Columbia University, 1915.

application of Bradley and Crocker, the latter produced their application which contained the following reference to the application by Bradley alone, upon which the two patents which became the subject of so much litigation were subsequently issued.

"In an application for letters patent of the United States now pending (filed February 23, 1883, serial number 85,957), Charles S. Bradley, one of the present inventors, has described an electrometallurgical process in which an electric current is employed to perform two functions: *First*, to effect the electrolytic decomposition of the materials treated; and, *second*, to supply the heat necessary to maintain said materials in the fused state while they are being electrolyzed. The present invention resembles the above to a certain extent, but in the present invention the electric current which we employ performs no electrolytic action, the reaction which takes place being solely to develop the heat which is a necessary condition of the reaction. For this reason, our invention does not require the use of a continuous current of electricity. An alternating current may be employed, if desired, which is an advantage, since large alternating current dynamos may be constructed more cheaply than the continuous current machines, and it is also less trouble and expense to run them."

This reference to the application of Bradley, of 1883, was brought to the attention of both Eugene and Alfred Cowles, and was the subject of discussion between them and Bradley and Crocker before the contract was finally drawn and signed. At the time the contract was signed, Bradley and Crocker had no other application than the one then declared to be in interference by the patent office authorities with the Cowles application. They owned no patent of the United States for any invention. Bradley at that time had pending only one application in addition to the Crocker and Bradley application in terms assigned by the contract, and that was the application for the patents in controversy. The Cowles brothers proceeded with the Bradley and Crocker application, omitting the general claims which interfered with the Cowles application, and obtained a patent for the particular apparatus described by Bradley and Crocker in their application which might prove to be an improvement on or useful variation from the Cowles patent. This patent was issued to the Cowles brothers as the assignors of Bradley and Crocker. No claim of title to the Bradley application of 1883 was ever made by the Cowles brothers nor did they ever attempt to prosecute it to a patent. As a matter of fact, although it was not then known to the Cowles brothers, at the time of the execution of the contract of assignment in May, 1885, the application of Bradley of 1883 stood rejected, as not involving a patentable process. The application lingered along in the patent office, retained there by the filing of amendments until 1891. The main application was finally rejected by the examiner, and was then carried on appeal to the board of Examiners-in-Chief in the patent office, which reversed the decision of the examiner, and allowed the issuance of a patent in 1892. After their issuance the patents were assigned by Bradley to Grosvenor P. Lowrey.

The salient features of the contract between the Cowles Company and Bradley and Crocker are as follows:

"This agreement entered into this 18th day of May, 1885, between F. B. Crocker, of New York City, N. Y., and C. S. Bradley, of Yonkers, N. Y., constituting the first party, and the Cowles Electric Smelting and Aluminum Company, of Cleveland, Ohio, a corporation organized under the laws of the state of Ohio, constituting the second party, witnesseth that whereas, the first party have made certain discoveries and inventions relating to electric smelting processes and furnaces, and have made some applications for patents therefor in the United States patent office; and whereas, second party is desirous of becoming the owner of all such discoveries and inventions: It is therefore agreed between the parties as follows: (1) For the consideration hereinafter mentioned, the receipt of which, to our full satisfaction, is hereby acknowledged, the said (first) party does hereby sell, assign, and set over to the said second party all interest in any and all discoveries and inventions relating to electric smelting processes and furnaces, and all patents they have obtained therefor, and all applications now pending, and caveats on file, in the United States Patent Office, relating to electric smelting processes and furnaces, which do or may interfere with any applications for patents made by Eugene H. and Alfred H. Cowles, of Cleveland, Ohio, now pending in the United States Patent Office. It is understood and agreed between the parties that this clause also includes the application of the first party, now pending in the United States Patent Office, and designated serial number 158,805, and filed March 14, 1885. (2) Said first party also sells, assigns, and sets over to said second party their entire interest in all inventions, patents, and applications for patents, in all foreign countries, for the discoveries and inventions mentioned in the preceding clause of this agreement."

Upon this general statement of facts Lowrey brought suit against the Cowles Company alleging that he was the owner of the two patents (464,933 and 468,148) by virtue of the assignment to him by Bradley and asking that the Cowles Company be enjoined from claiming any title thereto by virtue of the assignment of May 18, 1885 (quoted above), signed by Bradley and Crocker. The Cowles Company answered by asserting their title under the assignment last mentioned and by a cross-bill prayed that Lowrey be enjoined from claiming title to the patents by virtue of Bradley's assignment to him.

The main question in the case was whether the assignment by Bradley and Crocker to the Cowles Company, dated May 18, 1885, covered and included the two patents in question.

The decision in the lower court was rendered on April 23, 1895 (68 Fed. Rep. 354), the Court stating in part through Taft, Circuit Judge, as follows:

"In 1885, the Cowles brothers were convinced that they had made a great discovery—one which would revolutionize the art of winning the rarer metals, like aluminum, from their usually refractory ores. As they were forming their company, they learned that some one else had made a similar discovery. They wished to buy peace, as their counsel says, and so they proposed to buy from Bradley and Crocker the invention which threatened to destroy the value of their own, and, to make themselves perfectly secure, they secured the assignment of all other inventions or discoveries of the assignors which would tend to interfere with the monopoly they hoped to enjoy from their own. They were seeking insurance from invasion by the assignors, and so the assignment was made to cover patents, applications, and discoveries which never were, and which the assignors, of course, knew had no existence. Bradley and Crocker were willing to make the language thus broad, because, as it could convey nothing it did them no injury. The intention of the Cowles brothers was not only to secure the application which had interfered, but also to have a most sweeping guaranty from Bradley and Crocker that they had no other discovery which would interfere with the Cowles discoveries. This is the only explanation possible of the assignment of European patents and applications, and of the reference to inventions, applications, and patents all in the plural, in addition to the application specifically assigned. It is not claimed that Bradley and Crocker represented that they had other inventions and discoveries which would satisfy the words of the assignment. It is manifest that the general and indefinite language was used only to secure the Cowles Company against possible and undisclosed inventions, and not for the purpose of including inventions known to both parties to be in existence.

"With the general purpose of the parties in the framing of the contract well understood, we come to the question whether they intended to include in the assignment Bradley's electrolytic process of 1883. The evidence establishes beyond controversy that when the assignment was drawn and executed the Cowles brothers knew that Bradley had applied for a patent for a process of reducing metals by electrolysis in which the current also effected the necessary fusion. They knew this from the Bradley and Crocker application which they were buying, in which the Bradley process was not only described, but the patent office number was given. It was discussed by them. Had the Cowles

Company then intended that it should pass by the assignment, it is not possible that it would not have been specifically mentioned therein. The Bradley and Crocker application was identified in the assignment by number and otherwise. Why not Bradley's? On its face, the assignment purported to convey Bradley and Crocker's applications, patents, and discoveries. This was the stronger reason, if an individual application of Bradley was to pass, to make the reference to it free from doubt. The Cowles Company was using general terms to describe patents and applications in the assignment for fear that the assignors might have others undisclosed. But here was one brought to its attention while the contract was being drafted. Surely the failure to mention it specifically is strong evidence that it did not intend or wish to acquire it. Otherwise, why did not the Cowles Company at once take steps to prosecute the application to a patent as it did in the case of the Bradley and Crocker application? For eight years it made no claim of title to the Bradley application. It is suggested that, at the time of the assignment, it stood rejected. But the Cowles Company did not know this, and, even if it had, rejections are not final in the patent office, as the many rejections of this very application abundantly show. It is fair also to infer that Bradley did not suppose he had included his application of 1883 in the assignment, because from 1885 until the issuance of the patent, in 1892, Bradley pressed for its allowance.

"The circumstances present convincing evidence that neither of the parties to the assignment thought that the Bradley application of 1883 was within its terms. But this conclusion does not dispose of the case. It was the purpose of the parties to this assignment that a certain class of discoveries, applications, and patents, if owned by the assignors, should pass to the assignee. The description of them *ex industria* was made general so that it might include individuals of the class whose existence was not known. If, now, it appears that there was an application which must be included within the general description to effect the purpose of the assignment, can the court exclude it from the operation of the grant, because both parties at the time of the assignment knew of its existence, but were ignorant that it was within the description of the class to be conveyed? It does not seem so. The question of construction is, what did the assignors intend to convey? If a class, then all the individuals fairly within it must be included in the assignment. The very object in a class description is to avoid the necessity of mentioning individuals, and to include individuals which might otherwise be omitted. It follows that the mistake of the parties in thinking that a certain individual is not of the class conveyed will not exclude it from the grant. But the fact that both parties do not think the individual to be in the class described may be a pregnant circumstance to show in what sense the words describing the class are used, if those words are capable of several meanings. This, then, brings us to the question whether the Bradley application of 1883 is fairly included within the words of the grant. The important words are:

"'any and all discoveries and inventions relating to electric smelting processes and furnaces, and all patents they have obtained therefor, and all applications now pending and caveats on file in the United States patent office relating to electric smelting processes and furnaces, which do or may interfere with any applications for patents made by Eugene and Alfred H. Cowles, of Cleveland, Ohio, now pending in the United States patent office.'

"It is clear that Bradley's application of 1883 was not included in the grant, unless it related to electric smelting processes and furnaces, *i. e.*, unless the process described therein was an 'electric smelting process,' as that term might reasonably have been understood by the parties when the assignment was executed. * * * *

"From the whole record, I feel sure that the parties to the assignment of 1885 did not use the term 'electric smelting processes' in the wide sense claimed on defendant's behalf, and that, in their minds, processes solely electrolytic were not embraced within it. Therefore, the Bradley process of 1883 was not conveyed to the Cowles Company by the assignment, and it never acquired title. * * * *

"For the reasons given I am satisfied that the Bradley patent was not intended to be conveyed by the assignment of May 18, 1885, and that it was not, in any view, included within the general terms of that assignment."

The case was promptly appealed by the Cowles Company and the United States Circuit Court of Appeals rendered its decision February 15, 1897 (79 Fed. Rep. 331), reversing the decision of the Court below. The Court said in part as follows, speaking through Severens, District Judge:

"Coming now, to the interpretation of the contract, it is contended on the part of the appellee that Bradley and Crocker, the parties of the first part in the contract, agreed to sell only such of their joint property as fell within the description of the subject of their grant, that no express mention was made therein of any individual property of either of them, and, therefore, that Bradley's individual application did not pass. On the other hand, the appellants insist that the general language employed, when considered in the light of the evident purpose and the reasons of the parties actuating them, includes, not only the joint property of Bradley and Crocker of the kind described, but also the individual property of each of them of the same kind, by plain intendment. The Court below held that the latter was the proper view to be taken of the question, and in that we concur. Undoubtedly, if there are in any such case no circumstances which would change the primary grammatical construction, the terms employed would support the appellee's contention; but the grammatical rule raises only a *prima facie* presumption, and does not preclude the settling of the meaning by detracting somewhat from the exactness of the language in order to give effect to more cogent reasons of another sort. And the cases are very numerous in which this principle has been applied, and the plural language of the agreement has been held to cover and include the singular also. * * *

"It is conceded by counsel for the appellee that the reference in another place in this contract to 'applications for patents made by E. H. & A. H. Cowles' would include the application which was made by A. H. Cowles alone, although he says that if he were disposed to stand upon a small point of verbal criticism he could say that the latter application was not within the terms of the agreement in controversy. We think that is a just as well as frank concession, and that the reason for it is equally applicable to the construction of the language we are now considering.

"Much stress is laid by the appellee upon the fact that the contract of May 18, 1885, did not in terms enumerate as coming within the grant, the Bradley application, notwithstanding that it had been brought to the notice of the Cowles Company by the reference thereto in the Bradley and Crocker application, which was present at the time when the contract was made. This reference to the Bradley application was made for the purpose of stating the difference between that and the Bradley and Crocker application. In the reference, the general characteristic of the Bradley invention was stated, but not the details; and it is now strenuously insisted that the omission of any special mention in the contract, of the Bradley application, whose existence was known, in connection with the fact that the Bradley and Crocker application is specifically mentioned, furnishes strong evidence that it was not intended by the parties that the Bradley invention should pass; and this consideration appears to have had great weight with the court below in determining the construction which ought to be put upon the contract. Now, one of the applications of Cowles and Cowles, for a patent for improvement in electric smelting furnaces, which had been

filed on February 24, 1885, was pending at the time of this contract. The details of the apparatus proposed by it were those suggested by their previous application, filed December 24, 1884, of which the one now mentioned was a divisional application. The claims were for combinations of such apparatus. After some changes in the specifications and claims, it was declared at the patent office to be ready for allowance on May 1, 1885, but it was at the same time declared that the case must be withheld from issue, because of the fact that the main case was in interference with the Bradley and Crocker application. And a little later, on May 6th, this Cowles application was declared suspended, because of the following facts stated in a notice directed to Cowles and Cowles, which stated that 'the caveat of C. S. Bradley and F. B. Crocker, pending at the date of the filing of this application, is found to cover substantially the apparatus herein claimed; and, as provided by rule 196 the caveators have been notified to file a complete application. This application must be suspended in view of the above action.' This notification was mailed to Cowles & Cowles on May 7, 1885, and, by due course of mail, must have reached them a week or more previous to the date when the parties met and concluded the agreement of May 18th. And its previous reception was probably the reason for the mention of caveats as one of the class of things desired by the Cowles in a letter written to Bradley and Crocker, May 11, 1885. The Cowles brothers must, therefore, have had quite as ample notice, not only of the existence of the caveat, but of its substantial nature, as they had of the Bradley application and its contents. The Bradley and Crocker caveat, therefore, stood directly across the path of one of the Cowles applications, and was obstructing the path of the applicants in the same way that the Bradley and Crocker application was obstructing that of another one. Yet the caveat was not distinctly mentioned in the contract, and is not included, unless it is included in the general terms. No one can doubt that the caveat must be regarded as within the scope of the contract. It is obvious, therefore, that the parties cannot be deemed to have excluded inventions and claims simply because they knew of their existence and did not include them in terms.

"The above-mentioned argument of the appellee appears to have had much weight with the Court below in determining the proper construction to be put upon the contract; for, as we gather from the opinion there given, it was the main consideration upon which the Court held that the parties did not actually suppose that Bradley's invention was included (68 Fed. 368). It is probable that the condition of the case on the application of Cowles and Cowles of February 24, 1885, at the date of the contract, was not brought to the attention of the court, as no reference was made thereto in its opinion. The manner in which this caveat was dealt with in the contract confirms the impression which is strongly induced by the general and sweeping terms of the contract as a whole when construed in the light of existing facts, that impression being that it was the purpose of the parties to bring under the operation of the contract every existing thing in the nature of inventions and applications which might tend to defeat any of the Cowles inventions and applications. * * *

"The result is that it must be held that the individual application of Bradley then pending in the patent office was included in the grant, if it is, in other respects than with regard to its ownership, within the description of the things intended to be conveyed. * * *

"A point is made upon the descriptive words of the grant, 'discoveries and inventions relating to electric smelting processes,' and the endeavor is to establish that Bradley's process is not correctly described if we designate it as 'electric smelting,' and, therefore, was not included. But we think it was an apt and proper description of it. * * *

"This brings us to the question of the interpretation of the following language in the contract:

"'And all applications now pending and caveats on file in the United States patent office relating to electric smelting processes and furnaces which do or may interfere with any application for patents made by Eugene H. Cowles and Alfred H. Cowles, of Cleveland, Ohio, now pending in the United States patent office.'

"It is urged upon us that we should accept as a test in the construction of this language that the parties intended it to be employed in a sense restricted to its technical signification—such a signification as would be given to the same expressions in the patent office. This is based upon the suggestion that they were scientific men dealing with a scientific subject in the crisis of an interference. But, when we attend to all the circumstances, we doubt whether such a mode of dealing with the construction of the contract would be just, although in the end it does make a vital difference whether we adopt the test suggested or not. It is to be observed that one of these parties was a corporation which was just being launched upon a manufacturing business. The patents which it was expected would be obtained upon the inventions which it had secured were an adjunct necessary to their business operations. The company was buying its peace, and endeavoring to obtain and secure an indubitable title to the inventions which they intended to employ. They were not engaged in a hand-to-hand contest in the patent office or in the Courts. They were endeavoring so to shape their affairs as to relieve themselves from the necessity of making such contests. They stood outside of any such place of controversy, and were dealing with the subject-matter on business principles. For these reasons we think there is much reason for believing that when they employed the general language, all inventions and discoveries, patents, applications, and caveats, which did or might interfere with their own applications for patents, they intended to gather in all which the other party had which would furnish any reasonable ground for claiming that they infringed. These facts and reasons are equally well calculated to show that the other party had an equivalent intention in making the grant; or, at all events, that they must have known that that was the understanding of the grantee when they closed the contract, and this would bind them to the agreement having that interpretation. It is a well-established doctrine that a party must be deemed to have assented to the contract in such a sense as he knew the other party intended it to signify, provided the language employed is capable of such a meaning. And we have no doubt that for the purpose of construing this contract we must suppose that the parties intended to deal with existing things, and in the form and character in which they existed. The leading purpose was to clear the way of all obstructions, so that the Cowles applications might proceed without any contest on the part of the other parties, with whom they were making the contract. It is difficult to suppose that these purchasers were intending to secure what might ultimately be determined to interfere with or defeat their claims, either upon a contest in the patent office or by judicial decree, as the result of litigation. It would rather seem that the proper test to be applied in the solution of the question, whether any invention or any application is to be included within the terms of the grant, is this: whether the invention or application was of such a character that it might interfere with the prosecution of their own applications; and by that we mean, of course, not an obstacle which had no substance or foundation on which a contestation could reasonably be based, but such as would furnish a reasonable ground for raising a controversy. We do not find it necessary, however, to give the contract so broad a scope. In our opinion it did, without doubt, include all inventions and applications of Bradley and Crocker which would in fact afford sufficient ground for declaring an interference or would tend to defeat a patent on any

of the Cowles applications if such a patent should, without any declared interference, be issued. Any other construction more favorable to the appellee would tend to defeat the leading and manifest purpose of the whole transaction. * * *

"Recurring to the situation of the applications of the several parties, it is impossible for us to hold that the Bradley patent was not or might not constitute an interference with any of the Cowles applications. * * *

"Something is sought to be inferred from the subsequent conduct of the parties to aid in the construction of the contract. Where the instrument is of dubious import, proof of this kind is receivable in order to show in what sense the parties understood it. But such proof is liable to open up a controversy in regard to what the conduct of the parties really was, and can be resorted to only when the contract, read in the light of surrounding facts, leaves the construction in doubt. But, if such doubt existed in the present case, the action of the parties here referred to gives nearly equal ground for opposite conclusions. It is urged that the Cowles Electric Smelting & Aluminum Company did not prosecute the Bradley application, but allowed it to lie dormant in the patent office for many years. On the other hand, Bradley himself did not move again upon it for nearly two years after the contract was made. And we think it may fairly be said that the Cowles Company, finding their own and that of Bradley and Crocker sufficient for their purposes, had no special requirement for the Bradley application, which at that time stood rejected though such rejection was not final. While, on the other hand, if Bradley supposed his own application still available for his own advantage, it is somewhat singular, knowing that it related to a then rapidly developing industry, that he should have left it so long neglected. * * *

"Upon the whole case, we are satisfied that the inventions covered by the Bradley application were intended to be included by the terms of the contract; that Bradley's unauthorized proceedings thereon, whereby he procured his patents, must be held to inure to the benefit of the Cowles Electric Smelting & Aluminum Company. The result is that the decree below should be reversed, the original bill dismissed, and the relief prayed by the cross bill should be granted."

Promptly upon the rendering of the decision giving the Cowles Company title to the Bradley patents, the Cowles Company (Electric Smelting and Aluminum Co.) brought suit against the Hall Company (Pittsburgh Reduction Co.) for infringement of said patents. The case was decided in the lower Court on October 22, 1901 (111 Fed. Rep. 742), the Court holding that the Hall process of Patent 400,766 did not infringe said Bradley patents. The decision was in part as follows:

"*Hazel, District Judge.* This is a suit in equity by the Electric Smelting and Aluminum Company against the Pittsburgh Reduction Company to restrain the infringement of two United States letters patent for a process of separating aluminum and for a process of obtaining metals from their ores or compounds by electrolysis. The patents are owned by the complainant under several mesne assignments. The original application for patent was filed by Chas. S. Bradley, February 23, 1883; on December 8, 1891, patent No. 464,933 was issued on a division of the original application; and on February 2, 1892, patent No. 468,148 was granted to him. Both patents relate to a process for the reduction of highly refractory and non-conducting metallic ores or compounds in an unfused state by electrolysis; that is, by subjecting the ores or compounds to the action of an electric current, resulting in a fusion of the entire mass of ore, and, while in a state of fusion, by conjoint and simultaneous action of the electric current to separate, disassociate or decompose the fluid mass, so that the metal contained therein will be gradually deposited at the cathode, then to be drawn from the bottom of the receptacle or basin in which it is contained. Claims 1, 2 and 3 of patent No. 468,148 cover and control the process broadly, while Claims 4, 5 and 6 cover and control the process described as specifically applied to the separation of aluminum from its ores. Patent No. 464,933 relates to the same process, but confines its claims to a particular structure used and a special mode of practicing the process. The answer sets up various defenses, among them want of novelty and non-infringement. * *"

The patent contains six claims, the first three being intended to cover the process as applied to the separation of metals from any highly refractory ores or compounds. Of this group Claim 1 may be taken as an example. It is as follows:

"(1) The process of separating or dissociating metals from their highly refractory ores or compounds, non-conductors in an unfused state, of which the ores and compounds of aluminum are a type, which consists in fusing the refractory ore or compound progressively by a source of heat concentrated directly upon it rather than by an external furnace and as it becomes fused effecting electrolysis by passing an electric current therethrough between terminals which are maintained in circuit with the fused bath, whereby the process is rendered continuous, substantially as set forth."

The last three claims are limited to the application of the process to separating aluminum from its ores or compounds. Of this group Claim 4 may be taken as an example, as follows:

"(4) The process of separating or dissociating aluminum from its ores or compounds, consisting in fusing and maintaining the fusion and electrolytically decomposing the ore or compound by the passage of the electric current therethrough, substantially as set forth."

"The case is of very great importance. The questions involved are of such magnitude and complexity that a great deal of time has been consumed in becoming familiar with the voluminous testimony, consisting of about 3,000 printed pages, including exhibits. The court has proceeded, however, in the hope that, when a decision is rendered, the propositions involved may have received such careful consideration as their importance requires. The claim of the complainant and the various defenses interposed are of a difficult and technical nature. The testimony of the expert witnesses, men of a high reputation in chemistry and electrometallurgy, is of widely divergent character as to the application of important scientific and electrical principles. A knowledge of the complicated and intricate subjects of chemistry and electricity, and the application of their laws, would seem necessary to a proper disposition of this case. The evidence consumes great space, and should make the questions at issue clear of comprehension. The arguments of counsel generously amplify the copious and discursive opinions of the expert witnesses. Everything appertaining to the discovery for which the patents were granted has been clearly set forth, so that in the consideration of the facts and the law applicable thereto the task of the Court may be as clear as the subject will admit. Some of the facts are obscured in more or less uncertainty, and are difficult of solution; but it is hoped that a sufficient understanding of the questions involved has been reached for a proper determination of the controversy.

"The process by which aluminum is extracted from its ores has been completely revolutionized. The patent of Hall, used commercially by the defendant, and claimed by complainant to infringe its patents in suit, is No. 400,766 issued April 2, 1889, for a process of reduction of aluminum by electrolysis. This patent unquestionably resulted in the phenomenal reduction in the price of aluminum. In 1886 its price ranged from $5 to $8 per pound, while in 1897 it was from 25 to 30 cents. The entire consumption of aluminum in the United States is supplied by the defendant. From an extremely rare and only occasional employment of this metal in the commercial world, it has become useful in the manufacture of articles for which theretofore brass, copper, and tin only were known to be serviceable. Its price being reduced to that of copper and brass resulted in the advantageous use of aluminum for many purposes made possible only by the lowered cost of manufacture. It is

not seriously disputed that this result was due to the discovery of the Hall process and its subsequent operation. Indeed, immediately after the defendant began its use commercially, manufacturers using other processes ceased to work on account of their inability to make aluminum profitably at the price for which the defendant was able to place the product on sale. What brought about this revolution in the art? Hall's answer is that he was the first to discover a suitable bath material, which, when fused, on account of certain properties contained therein, would at a low temperature freely dissolve alumina; that his bath contained a higher chemical stability than the dissolved alumina itself, so that, by the passage of the electric current, the alumina would be decomposed, and the bath material and its properties left unaffected. * * *

"What does Bradley claim? His invention consists in the regulation of the heat generated by current energy to perform three functions. He utilizes the electricity developed between electrodes placed in a mass of refractory ores—nonconductors in an unfused state. He maintains the necessary current energy communicated from the initial point throughout the entire mass, thus securing fusion and simultaneous electrolysis, and progressively holds a mass of ore in a continuously fused state, resulting in its reduction. Thus the pure aluminum will be deposited at the bottom of the cavity or basin, whence it may be withdrawn. To produce this result, the electric energy must be applied according to the method specified by the patent, and stated in complainant's brief to be:

"'(1) Melt and maintain melted the material in the initial line of flow. (2) To apply the current in such a manner that the melted material will spread its heat, so as to propagate sufficient heat to liquefy the surrounding material. (3) Decompose or separate the atoms of the fused mass, made a conductor of electricity by the diffusion of the heat generated.'

"The main object of the invention, the patentee says, 'is to dispense with the external application of heat on the ore in order to keep it fused.' This he proposes to accomplish by the employment of 'an electric current of greater strength or intensity than would be required to produce electrolytic decomposition alone.' The decomposition or disassociation of refractory ores by electrolysis is not claimed to be new in the art. The utilization of a sufficient quantity of heat from a center of fusion throughout a mass of non-conducting and refractory material, of which cryolite is a sample, by means of an electric current concentrated upon a portion of such mass, is claimed to have been unknown, and that Bradley is a pioneer in the art.

"Complainant claims that its process is not limited to any particular class of ores. The patent covers the extraction of metals from their compounds, and is not restrictive in its scope. Therefore, the Hall process is the same as Bradley's, although more economically performed, because Hall uses a well-known flux or solvent for the alumina, which facilitates fusion and consequent electrolysis. I am quite satisfied that it was not a well-known flux for this purpose. The utility of electricity as a potent agent for the transmission or diffusion of heat was well known for fusing refractory ores. Various anticipatory patents will be hereafter discussed. The mere application of this agent to decompose alumina, after it has passed through an intensely heated cryolite bath, does not necessarily fuse the alumina. Hall does not endeavor to do this. Instead of using a fusing process, he creates a bath by which alumina is dissolved. This is done by charging it into the fused bath, resulting in the process of solution. This distinction, claimed to exist between fusion and solution in the chemical and metallurgical arts, has been the basis for considerable expert testimony, extremely contradictory in its nature. * * *

"This very same question, which is regarded with so much importance, was decided in the Circuit Court for the Northern District of Ohio in the case of Pittsburgh Reduction Co. *v.* Cowles Electric Smelting and Aluminum Co. (predecessor of complainant) 55 Fed. 301. That was a suit brought by the defendant in this case against the Cowles Electric Smelting & Aluminum Company, a corporation then in existence and engaged in the manufacture of aluminum alloys, to restrain infringement of the Hall process on the part of the Cowles Company. * * *

"Hall maintained, and the conclusion of the Court was that the novelty of the process consisted in that the alumina dissolved in a fused double fluoride of sodium and aluminum as freely as sugar dissolves in water; that, until he discovered that alumina would thus freely dissolve in this bath, it had never been known, and that no one had ever before succeeded in disrupting the constituent elements of alumina by an electric current; and, therefore, the patent was a pioneer patent, entitling it to liberal construction. * * *

"I am constrained to hold that Hall's invention was not a mere alteration in the Bradley process, or the substitution of one ingredient for another, which was well known at the time. The subsequently conceived process of Hall is substantially different from the former of Bradley, and the addition of the alumina in the cryolite flux tended to perform a different function, not covered by the Bradley process. It tended towards the solution of an ore which, if operated upon by the Bradley process, construing it broadly, and not limiting it to any particular class of ores, would have necessitated its fusion with the contents of the bath, and would, therefore, have required an extremely high electrical voltage to perform the office of disassociating the aluminum. * * *

"Hall's claims do not say what heat shall be employed to fuse the bath. The process described by his patent speaks of dissolving alumina in a fused bath, composed of fluorides of aluminum and a metal more electropositive than aluminum, and then passing an electric current through the fused mass. With reference to obtaining the required temperature to maintain the bath the patent says:

"'This crucible is placed in a suitable furnace, B, and subjected to a sufficient heat to fuse the materials placed therein, such materials fusing at approximately the same temperature as common salt.'

"From this it is deduced that Hall never intended, certainly that he did not conceive, the plan of internal heating by current energy, and that its present use for bath fusion and electrolysis is an infringement of Bradley's process. The latter describes a method for maintaining both fusion and electrolysis by continuous and simultaneous action of the electrical current applied to his bath. The specifications declare:

"'The main objec tof my invention, therefore, is to dispense with the external application of heat to the ore in order to keep it fused. In order to accomplish this object, I employ an electric current of greater strength or intensity than what would be required to produce the electrolytic decomposition alone, and I maintain the ore or other substance in a state of fusion by the heat developed by the passage of the current through the melted mass, so that by my invention the electric current is employed to perform two distinct functions, one of these being to keep the ore melted by having a portion of its electrical energy converted into heat by the electrical resistance offered by the fused ore, and the other being to effect the desired electrolytic decomposition, by which means the heat, being produced in the ore itself, is concentrated at exactly the point where it is required to keep the ore in a state of fusion.' * * *

"Was the conception of the application of electrical heat, in the art as it existed at the date of the application for the Bradley patent, such a discovery as to entitle the patentee to the protection of the patent laws? * * *

"Prior to 1884 Messrs. Cowles were engaged in the reduction of metals, aluminum alloys. By their process, the refractory and non-conducting material was mixed with carbon or other similar conducting, although highly resisting, material. At this time the diffusion of electrical heat throughout the mass of material in the furnace, invented by Cowles, was justly re-

garded as a remarkable process, marking an era in practica metallurgy. Bradley's application for a patent was then on file. The general adoption of the practice of internally heating the baths by the current, from the failure of external heating unquestionably, is due directly to Messrs. Cowles. Doubtless great credit is due to their enterprise and progressive commercial foresight. Nevertheless it was known that Sir Humphrey Davy, in a lecture delivered before the *Royal Society of London* in 1807 and published in the *Philosophic Transactions* for 1808, used this language:

"'I tried several experiments in the electrization of potash rendered fluid by heat, with the hopes of being able to collect the combustible matter, but without success, and I attained my object only by employing electricity as a common agent for fusion and decomposition.'

"This was a mere experiment, possibly, but it was an account of a process that was complete and capable of practical operation. Bradley admitted, in the proceedings at the patent office, in his second brief on appeal to the commissioner, that:

"'Sir Humphry Davy's reduction of potassium and sodium, as described by him, on an infinitesimal scale, was the process described and claimed by Bradley.'

"I cannot agree with the argument that Sir Humphry Davy's process revealed nothing to the world. His laboratory operations with reference to a process for reduction have since been carried out on a larger scale. They have been proven practical by successive improvements, and his method has been tested by actual use. Castner's patent, No. 452,030, granted May 12, 1891, is cited as an improvement in the process described by Davy. Siemens invented a mode of initial fusion, using the arc, which made Davy's process applicable to other fusible electrolytes than those upon which he experimented.

"It is vigorously contended by complainant that Davy's experiment did not demonstrate that electric heating could be practically applied internally by conduction to surrounding non-conducting and refractory substances; that his experiment consisted of its operation on minute quantities; and that soda and potassa, Davy's material, does not justify a similar operation with materials of different character. Dr. Morton, expert for complainant, says, in speaking of the Davy experiment, after declaring that a battery analogous to that of Davy ought to be used to ascertain the conditions which existed in his case:

"'I have no doubt that Davy's experiment may be successfully carried out, even with a battery, as in the experiment that I made, or with a dynamo machine and adjustable resistance properly manipulated.'

Dr. Chandler met with fair success in his trial experiments for use in this case by his substantial repetition of Davy's process. In 1881 the Compagnie Generale Belge, in its French patent, spoke of the use of the electric arc for heating substances. Nothing is said of reduction, but it is suggestive of the use of electrical heat for fusion of metals. Prof. Howe in 1882 published a paper in the regular annual volume of *Transactions of the Society of Mining Engineers*, and copies thereof were distributed as early as May, 1882. In this paper Prof. Howe speaks of fusing his material before decomposing it by electrolysis. Bunsen fused chloride of magnesium, and electrolyzed it with the aid of electrodes, and demonstrated the necessity of a definite voltage. The United States patent of Ball & Guest, No. 236,478, described the application of an electric current for carbonizing arcs of paper or other materials while confined in a case of non-conducting material. Siemens' British patent No. 2,110 of 1879, to which I have already referred, describes the use of the electric arc for the fusion of metals. It makes no reference to decomposition, but it is clearly stated by the patent that the electric current is applied to produce intense heat for the fusion of electrolyzable substances. Two carbon rods, fitted to slide towards each other horizontally, within water-cased tubes, are employed. The substances to be fused are introduced in the crucible, and the carbon rods are advanced sufficiently near each other to form an arc within the crucible. Dr. Morton says that with modern dynamos, generating large currents, Siemens' apparatus, which was useful only on a small scale, could be enlarged, so as to fuse large masses of material requiring high temperature, provided the Siemens method of cooling his electrode with water is dispensed with. Bell in 1861 had electrolyzed cryolite, and Gauduin in 1869 decomposed aluminum salts, by the electric current, in crucibles, by means of external heat. As the aluminum was extracted, fresh material was added. This is also done by complainant's process, and by that of the defendant, when necessity requires. Other patents are in evidence from which it appears that the decomposition of metallic compounds was old in the art. In every case external heat was used. No electrolytic heat generated in the crucible was utilized for continuous heating. That seems not to have been practical until the discovery by Hall of a suitable bath, which would, when fused, dissolve alumina. I think that these patents quite clearly show the state of the art with reference to electrolysis and internal heating of ores or compounds. They disclose the state of the art to be such that what Bradley did was to adopt a well-known process for heating to the special purpose of fusing—a carrying forward or new application of what others had already done or attempted in reducing refractory metals by similar means. His claims must, therefore, be narrowly construed. * * *

"The complainant's argument is that by the Bradley patents an electrolytic current is employed sufficiently powerful to do two things. to wit, to electrolyze and to develop sufficient heat to keep the ore fused. * * *

"True, Bradley explicitly states that by his invention external heating is dispensed with. To do that, as already stated, simultaneous and progressive fusion and electrolysis are relied upon; but, in the light of the heat which is incidentally generated by the Hall method to perform this work in his process and the prior state of the art, a construction cannot be placed upon the Bradley patent sufficiently broad to permit his claim with regard to simultaneous fusion and electrolysis to inure to his benefit as against the claims of Hall. * * *

"From the experiment of Dr. Morton, made on April 26, 1899, and from other measurements of counter-electromotive force made by Mr. Davis, Prof. Geyer, and Prof. Rogers, it is argued that the defendant uses an electric current of sufficient strength and density to decompose cryolite, and that it uses a greater voltage than would be required for electrolysis alone. Defendant's experts do not agree with this contention. I am constrained to defer to the judgment of defendant's expert witnesses, in view of the vast amount of corroborating evidence found in the case, showing that Hall, in experimenting with his process, never contemplated the use of an electric current of greater voltage than to produce decomposition. He was primarily of the opinion that the heat produced by the electrical energy necessarily used to decompose the metal in the crucible would be entirely sufficient for both fusion and decomposition. Indeed, in a letter written to his sister, as early as August, 1886, he said:

"'In some respects this invention is going to be better than I anticipated. Thus, the resistance of the liquid is exceedingly low. Also, it is evident from the experiments that the waste heat of electricity, which must be used anyway, will be nearly, if not, quite, enough to keep the solvent melted.'

"The proofs show that Hall's anticipations in that regard proved true. The current strength sufficient for electrolysis, as applied by the Hall process, is sufficient to fuse and decompose. The development of heat is an adjunct to the process, or, as said in the argument, it is incidental thereto. This fact, of course, aids in minimizing the voltage and amperage required to keep the bath fused and to perform electrolysis. Obviously, this renders it unnecessary that Hall should use an excessive current

for fusion of the ore. By Bradley's method, it is distinctly stated that the current must be sufficiently powerful both to keep the ore in a proper state of fusion and to perform the required electrolytic work. It appears that in securing this result by his process a double strength of current is required. Cryolite is the ore cited by Bradley as an illustration in his patent, and doubtless was in his mind when he conceived his invention. Its fusion requires, as has been said, a current of greater strength and intensity than would be required to produce decomposition alone. In the case of Pittsburgh Reduction Co. *v.* Cowles Electric Smelting & Aluminum Co., *supra*, the defendants sought to distinguish their process then employed by denying infringement of the Hall patent, for the reason that they used the electric current internally applied to fuse their bath material. The Court said:

"'This defense is based on a narrow and highly impossible construction of the Hall patent.'

"The application of that decision to the case at bar would certainly compel the conclusion that, if the only alleged infringement by Hall is the application of internal heat, then in reality no infringement exists. * * *

"The argument and briefs of complainant's counsel most strenuously insist that Bradley was a pioneer in the art, that he was the first to fuse and electrolyze by simultaneous application of electrical energy, and that by his method progressive fusion and electrolysis are made practicable. Doubtless that is so. It is not disputed that Bradley pointed out a way by which the electric current, when regulated as described by the patent, will perform two essential features of his process. This was new in the art, although Sir Humphry Davy by his experiments suggested electricity as the common agent for fusion and electrolysis. The conception and practicability of utilizing the electric current for these purposes simultaneously was unlike the prior art. Hall, ambitious, vigorous, and intellectually strong, competed, experimented, and produced a process in aid of decomposition of refractory ores not contemplated by the complainant's patents. The same purpose that Bradley had in view is accomplished by the joint action of certain compounds when subject to certain chemical and electrical action. The admixture of material and the chemical and electrical action applied thereto by Hall's process are essentially different. * * *

"It must, therefore, be held that the process used by defendant under the patent issued to Hall, No. 400,766, does not infringe patents granted to Bradley, Nos. 464,933 and 468,148. The bill is dismissed."

2—THE CASE ON APPEAL

We have now brought our series of illustrative cases through the following steps: *First*, the suit by the Hall Company against the Cowles Company on Hall Patent No. 400,766, in which the patent was held valid and the Cowles Company were held to be infringers and were ordered to pay the Hall Company $292,000 damages and profits arising from said infringement, noting that this sum was never paid because of a rehearing being finally allowed. *Second*, the litigation of the Cowles Company to obtain title to the Bradley patents, which were believed to dominate the Hall patent, in which litigation the Cowles Company was defeated in the lower court but was victorious on appeal. *Third*, the suit by the Cowles Company against the Hall Company on the Bradley patents in which, in the lower Court, the Cowles Company was defeated and the Hall Company held not to be an infringer.

We now proceed to the final step of the long litigation, in which the Cowles Company appealed from the decision of the lower Court finding that the Hall Company did not infringe the Bradley patents. The result of this appeal was that the Court held that the principal Bradley patent, No. 468,148, was valid, and infringed by the Hall Company and awarded an injunction and an accounting against them.

The decision on appeal was rendered October 20, 1903 (125 Fed. Rep. 926), the Court saying in part as follows:

"*Coxe, Circuit Judge.* The patent in controversy was granted February 2, 1892, to Charles S. Bradley for an improvement in processes for separating, by the electric current, aluminum from its ores or compounds. * * * * *

"The Circuit Court found that the claims were not infringed and dismissed the bill. The complainant assigns error, contending that the Court erred in placing a narrow construction upon the claims, and in holding that the defendant's process did not infringe. The complainant also contends that the Court erred in holding that the success of defendant's process was due to the invention of Hall and not to Bradley. * * * *

"The application for the patent in suit was filed February 23, 1883, which may be taken as the date of Bradley's invention. Prior to this date it was known that metals contained in ores which are conductors could be separated therefrom by electricity, but the problem of separating metals from non-conducting ores by this method had not been solved. The compounds of aluminum at ordinary temperature are non-conductors. It had, therefore, been the custom to place these refractory ores in a crucible, apply external heat until the ore was melted and then pass an electric current through the melted mass. In this way a pure product was obtained in small quantities, but as the specification states, the intense heat soon destroyed the crucible and the process could not be worked upon a successful commercial basis. This controversy relates solely to the separation of aluminum from its ores; three of the claims are designed to cover the process when so limited and the remaining claims relate to highly refractory ores of which the compounds of aluminum are a type. The defendant is engaged in producing aluminum. The investigation may, therefore, be confined to this one metal, for, if the patent, when so limited, be valid and if the claims cover the defendant's process it matters not what else they cover or fail to cover.

"We start, then, with the undisputed fact that prior to Bradley's invention no one had ever succeeded in separating aluminum from its compounds solely by the use of electricity, or, in other words, no one had dispensed with external heat.

"The reference principally relied on to anticipate or limit the claims is the description of an experiment made by Sir Humphry Davy in 1807 and published the following year in *Philosophical Transactions of the Royal Society of London*. Davy tried several experiments on the electrization of potash rendered fluid by heat and attained his object only by employing electricity as the common agent for fusion and decomposition. A small piece of potash, which had been exposed for a few seconds to the atmosphere for the purpose of producing moisture, was placed on an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4 in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. The potash soon began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the negative surface there was no liberation of elastic fluid, but small globules having a high metallic luster, like quicksilver, appeared, some of which burned with explosion and bright flame as soon as they were formed, others remained, were merely tarnished and were finally covered with a white film. Numerous experiments soon showed that these globules of sodium and potassium were the substances of which Davy was in search. Here, then, was an interesting experiment but nothing more. It was not made with the ores of aluminum, but with minute pieces of soda and potash which were rendered conductive by moisture induced by previous exposure to the atmosphere.

"In a work on aluminum, published by Tissier in 1858, it is

stated that, in 1807, Davy undertook to decompose alumina by the battery, as he had decomposed potash and soda, 'but he failed completely.' In fact, Davy himself admits that his experiments in this regard were without substantial results. His method was incapable of producing results upon a commercial scale. He had no conception of progressive feeding or of a fused bath, or regulating the strength of the electric current. The experiment was undoubtedly a brilliant one, but it can no more be regarded as an anticipation of the Bradley process than it could be regarded as an infringement if made to-day for the first time. That such a claim of infringement might be asserted is, perhaps, conceivable, but that it could be sustained is an unthinkable proposition.

"Davy suggested the possibility of producing metal from certain ores conductive in a fused state, and this hint, for it was hardly more, undoubtedly set the chemists and electricians thinking, just as the discovery of Franklin put the idea of the telegraph into the brain of Morse and as the discovery of Watt made possible the inventions of Stephenson and Fulton. Judged by its practical results, the contribution of Davy was not as valuable as it now appears when read in the light of subsequent achievement. For three-quarters of a century chemists and electricians all over the world, with Davy's work before them, were endeavoring to find a method of producing aluminum commercially, and they all failed. After Davy's experiment no further effort of the inventive faculties was required, says the defendant. All that a manufacturer needed to do was to operate the Davy process on a large scale. To do this no expert knowledge was required. And yet not only manufacturers, but the most learned specialists of the age, permitted this treasure of inestimable value to remain in plain view before them and would not even stoop to pick it up. The fact that Davy's experiment was permitted to lie dormant during 76 years of intense activity in chemistry, electricity and metallurgy is almost conclusive evidence that the defendant has greatly overestimated its importance.

"Duvivier's experiment of 1854 has even less bearing upon the present controversy. A small piece of disthene was exposed to the electric flame, undoubtedly an electric arc, disengaged from a carbon point about as large as a drawing pencil. It was melted at the end of three or four minutes and the aluminum, freed from its oxygen, showed itself at the surface of the molten material. A small globule set on the outer edge flattened out as it cooled and, when scratched with the point of a knife, it showed silver white and in hardness it resembled pure silver. That this was aluminum is not shown and cannot be shown, as the only test to which it was subjected was the one above stated. The entire description is meager and uncertain and by no means as definite and satisfactory as the prior experiment of Davy.

"The Siemens British patent of 1879 also describes the use of an electric arc for the fusion of metals, but electrolysis cannot be so accomplished.

"The United States patent to Ball and Guest, of January, 1881, is for an improvement in 'electrical carbonizing apparatus.' It does not relate to the separation of aluminum, or any other metal, from its ores by electricity.

"Faure's French patent, of 1880, describes an invention, the object of which is 'the manufacture of metallic sodium, of the cyanides, by fixing atmospheric nitrogen, and in general the treatment, at high temperature, of alkaline salts or metals.' He employs electric arcs and external heat to produce high temperatures, and secures the sodium by chemical reaction.

"The British patent to Lane Fox, of 1878, is for 'improvements in the application of electricity to lighting and heating purposes,' and discloses nothing more than the Ball and Guest patent, *supra*. It has no application to electrolyzing refractory ores.

"The article printed in the *Transactions of the American Institute of Mining Engineers*, in May, 1882, describes the process of some unknown inventor as it was explained to the Institute by Prof. Howe. Assuming this to be a 'publication' within the meaning of the law it is too indeterminate to be of value as an anticipation. Prof. Howe did not pretend to have any personal knowledge of the facts and merely gave a brief statement of what had been told him. That he had reference to an arc process is evident from the following language: 'A voltaic arc is then thrown across from another electrode against the carbon crucible,' which is described as the cathode. It seems to be conceded on all hands that the use of an arc constitutes 'a radical and fatal departure' from the process involved in this controversy. The person who actually practiced the method of producing aluminum described by Prof. Howe may have accomplished something of practical value and he may not. No one knows. Had he done so it is, perhaps, fairly inferable that something more would have been heard of it in the art of electrolysis. The name, at least, of so eminent an inventor would not have been permitted to remain long in obscurity. It might have taken time and persuasion but, eventually, his reluctance to being enrolled among the immortals would have been overcome.

"The Court understands that the foregoing are all the references relied on by the defendant to anticipate the Bradley claims. * * * * It is thought that they describe the only instances where, in the prior art, there was an attempt to dispense with external heating and to utilize the electric current for the double purpose of fusion and electrolysis. That they do not anticipate, or materially restrict, the Bradley patent seems self-evident. * * * *

"Not only did the electricians of the earlier art fail to produce aluminum by electricity alone, but the wrecks which strew the pathway, which Davy pointed out nearly a century ago, offer mute but impressive proof of the genius of the man who first surmounted its many obstacles and reached the destination in safety. Indeed, after numerous abortive attempts and repeated failures the electrical world seemed to have settled down into the belief that aluminum could not be produced by the sole agency of electricity. Accordingly, the effort of inventors was directed to the perfection of processes in which external heat was employed to melt the ore and keep it in a fused state. The record abounds in such instances. Patent after patent is introduced claiming new methods of separating aluminum from its ores, but in every instance external fire is used to fuse the bath and maintain it in a fused condition. Many of these inventions were long after the introduction of dynamos and they continued to be made and practiced for several years after the Bradley invention. Indeed, so strongly was the inventive trend towards the employment of external heat that even the defendant's inventor, Hall, could not be induced to dispense with its use until 1889. When the defendant's works were started at Pittsburgh, in December, 1888, the pots were built to be externally heated and they were so heated for some time thereafter. The Hall patent of April 2, 1889 (No. 400,766), which was applied for July 9, 1886, three years after the Bradley application, was for improvements in the 'process of reducing aluminum by electrolysis.' In this patent externally heated crucibles are shown in the drawing and described in the specification.

"Since the Bradley invention, aluminum, which formerly was regarded as one of the precious metals, has become as common as copper and brass and its price has been reduced from $15 per pound to 25 cents per pound. We do not intend to intimate that this marvelous change was due solely to Bradley's invention, but simply, at this time, to emphasize the fact that it took place after Bradley's invention. If he has done nothing to produce this result he is, of course, entitled to no consideration

whatever, but if he has contributed something he is entitled to protection to the extent of that contribution, be it much or little.

"We have proceeded thus far to the conclusion that we are dealing with a patent which discloses a meritorious process for producing aluminum in large quantities, the essential features of which are, *first*—dispensing with external heat, and, *second*—the use of the same electric current to produce and maintain fusion and electrolyze the ores of aluminum. We are unable to discover anything in the prior art describing this process or anything closely approximating thereto. The patent is, therefore, not anticipated and its claims are entitled to a liberal construction.

"The judge of the Circuit Court, after careful and painstaking research, reached the conclusion that Bradley had made a valuable invention, but he failed to grant relief to the complainant upon the theory that the process which the defendant uses was an entirely separate invention, neither dependent upon nor subsidiary to the invention of Bradley. In this we think there was error. Hall's achievement should be considered in the light of an improvement upon Bradley's fundamental discovery. There can be little doubt that the defendant's process is a valuable one and that to it is largely due the cheap aluminum of the present day. There is not the least disposition to detract from the merits of Hall or minimize his contribution to the art. Indeed, it may be conceded that, if the novel features so introduced be secured by a valid patent, he can hold the monopoly against all, Bradley included. This concession does not permit him, however, to appropriate the broad invention. He does not acquire the right to use the Bradley process simply because he has improved that process. He is entitled to enjoy what is his, but in so doing he cannot appropriate the property of another. The record discloses nothing unusual in this regard. It is rarely that an invention develops ultimate perfection in the hands of the inventor. The test of actual use discovers defects to be remedied and suggests improvements to be made. If the inventor produces a new and useful result he does not lose his reward because he, or some one else, subsequently renders it more useful. * * * *

"Considerable time has been devoted, in the Court below and in the briefs, to a consideration of the patent to Hall, under which the defendant is said to operate. It is thought this discussion is irrelevant, for the reason that the patent was not granted until 1889 and does not disclose the process which the defendant uses and of which the complainant complains. The process patented to Hall adopts external heat to produce fusion, the specification showing and describing an iron or steel carbon-lined crucible which is 'placed in a suitable furnace, B, and subjected to a sufficient heat to fuse the materials placed therein.' It was only when the defendant abandoned the 'furnace, B,' and adopted the Bradley method of fusing by means of the electric current that the charge of infringement was made. It seems evident that the defendant may practice the invention of the Hall patent with perfect impunity so far as the Bradley patent is concerned. Neither is it important to determine whether Hall knew of Bradley's invention when he made the discovery which induced him to dispense with his melting pots. It is enough that it was at least three years after Bradley's invention. Whether Hall was an independent inventor or appropriated Bradley's idea, is utterly immaterial. * * * *

"Hall starts by fusing cryolite and maintaining fusion by means of the electric current; so does Bradley; at least in the example given in the patent cryolite is the ore mentioned. If no other ore were added by Hall the processes up to this point would be identical. But Hall found that alumina, which is just as much an ore of aluminum as is cryolite, dissolves readily with cryolite as a solvent or flux, and he was thus enabled to produce a more efficient and cheaper electrolyte. The Bradley process is not confined to cryolite or alumina; it relates to all ores or compounds of aluminum and all other refractory ores of a like type. Cryolite is mentioned as an illustration in the specification, but it might as well have mentioned alumina or any other similar ore. That there is nothing in the patent, or out of the patent, requiring the limitation of the claims to cryolite seems too plain for debate. The process may be used with cryolite alone or alumina alone or with both together, whether applied synchronically or successively. In either case the essential features of the process are appropriated.

"Again, it is argued that the claims are limited to an electric current twice as strong as that formerly employed when external heat was used and that defendant does not use such a current, and, therefore, does not infringe. We are not satisfied that this proposition has been established. * * * *

"A current must be employed sufficiently powerful to do the work in hand and, as more work is required, the current must be of greater strength than that used when electrolysis alone was required of it. No amount of scientific theory can overthrow the plain fact that when additional work is required additional power must be provided. If one horse is to carry the load of two he must be stronger than either of those whose place he takes. He need not necessarily be 'twice as strong,' although such a standard of comparison would be a wise one to follow. After a few trials his owner will know what changes to make in harness and load in order to economize 'horse power.' So a current which is to fuse, maintain fusion and electrolyze must be of greater power than one whose sole vocation is to electrolyze. It has two additional burdens laid upon it which require expenditure of energy; relieved of these there is more strength for electrolysis. * * * *

"There is not a word in the claims limiting them to a current double the old capacity, and we are unable to perceive any reason why the claims should be eviscerated by importing into them the statements of a formula intended only as an illustration. The patentee undoubtedly does say that, as compared with the old method, a more powerful current is employed, but he does not say that this result can be produced only by increasing the voltage. It may be accomplished by decreasing the resistance of the bath, and this is apparently what the defendant has done. * * * *

"The fact that the defendant has made mechanical changes in the containing vessels and thus gets a greater proportion of heat from the electrodes than from the fused ore is a mere incident of the new construction and immaterial upon the question of infringement. A patented process cannot be appropriated because the infringer practices it with new, enlarged and improved apparatus. * * * *

"Various other limitations upon the claims are urged by which the defendant seeks to avoid infringement. They are of the same general nature and proceed upon the same initial fallacy, namely, that in a generic process patent every phenomenon observed during operation and every minute detail described must be read into the claims and that the least departure from the claims as so construed avoids infringement. Neither position is tenable. In a patent like Bradley's the claims should be as broad as the invention and, even if unnecessary and unreasonable limitations are incorporated in the claims, the Court should interpret them liberally and not permit a defendant to escape who reaches the same result by analogous means, though he may employ additional elements and improve mechanical appliances. * * * *

"It is asserted that the Bradley process is not operative. Having found that the defendant is using the process and it appearing that the annual output of its works is now over 7,000,000 pounds, it seems unnecessary to enter upon an extended discussion of this proposition. There is, however, ample proof that the patented process when practiced experimentally

produced aluminum and there is also proof that practically the same process was commercially operated for short periods both in this country and in Europe. The owners of the patent have not attempted to operate under it of late years, but the reasons are obvious. Some of the more important of these reasons are as follows: The protracted litigation over the title, the suit based upon the Hall patent, the present suit and the impossibility of commercial competition with the defendant without using the so-called Hall improvement or some other improvement equally cheap and effective. The cryolite-alumina electrolyte cannot be used so long as the decision sustaining the validity of the Hall patent remains undisturbed.

"To attempt a discussion of all the questions mooted in the briefs would extend this decision beyond all reasonable length and would serve no beneficial purpose. Even were it possible to do so it is surely unnecessary to follow all of the excursions of the experts into the occult realms of electrochemical science. Some of these trails seem to vanish into thin air, others are lost in a desert of technicalities and of others still it is true that he who attempts to travel them is quite likely to find himself wandering aimlessly 'through caverns measureless to man.'

"Although the appeal included both patents the argument has been confined wholly to No. 468,148.

"It follows that the decree, in so far as it relates to letters patent No. 464,933, must be affirmed with the costs of this appeal, and in so far as it relates to No. 468,148 the decree is reversed with the costs of this appeal and the cause is remanded to the Circuit Court with instructions to enter a decree in favor of the complainant for an injunction and an accounting, with costs."

The rehearing ordered April 4, 1903, in the case of the Hall Company against the Cowles Company was never had because the decision of October 20, 1903, of the U. S. Circuit Court of Appeals in the case of the Cowles Company against the Hall Company made it unnecessary and because, as a result of this latter decision, a settlement was arrived at between the two companies wherein the Hall Company paid the Cowles Company a large sum for past infringement and a royalty on all aluminum to be produced up to the end of the life of the Bradley patent. The Bradley patent being held to dominate the Hall patent and process made it impossible for the Hall Company to continue in business without coming to an agreement with the Cowles Company, while the Hall patent, being an improvement patent on the Bradley patent, prevented the Cowles Company from using said improvement without consent of the Hall Company. The only conclusion possible was a mutual adjustment.

The discussion of these various litigations has been somewhat lengthy but has been entered into to give an idea of how the Courts apply some of the rules of law heretofore discussed, to give a concrete idea of the vagaries of patent litigation and to serve as an illustration of the difficulties which sometimes meet the inventor in the development of his enterprise.

As was stated at the outset of these lectures, they are not addressed to lawyers but to chemists and chemical engineers. They do not pretend to cover the whole range of patent law but to merely point out some of the rules of law which if kept in mind will enable you to form an intelligent opinion concerning some of the problems you will surely have to meet.

2 Rector Street, New York

# CURRENT INDUSTRIAL NEWS

## JAPANESE RADIUM

According to *Engineering*, Dr. Ishidzu of the Tokyo Hygienic Laboratory has been investigating the hot and mineral springs of Japan with a view to ascertaining the quantity of radium in them. As the result of his researches, the doctor declares that Japan is the richest radium country in the world. The cold mineral spring which has been hitherto considered to contain the largest quantity of radium is Joachimsthal in Austria, which issues from a radium mine and contains 2000 maches of radium emanation. Dr. Ishidzu's investigation has revealed the fact that a mineral spring in Yamanashi Prefecture is impregnated with 800 maches of radium-bearing water, while another spring at Chuggoka, Japan, has 300 maches.—A. McMillan.

## INDIAN SESAMUM CROP

A forecast of the 1915–6 sesamum crop issued by the Department of statistics, India, and based upon reports from the eight provinces which contain on an average 78 per cent of the entire area under Sesamum in British India, states that in northern and western India the late arrival of the monsoon delayed sowing operations; in the central provinces, Madras and Bengal, conditions at sowing time were favorable. The present condition of the crop is reported to be generally good. The returns of acreage received up to date are incomplete, owing mainly to the absence of any estimate for the united provinces, and only a general comparison of the figures with those of the previous year can be made. The total area reported amounts to 1,811,000 acres as against 1,954,000 acres for the same tracts at this date last year, a decrease of 7 per cent.—M.

## RADIUM AS A FERTILIZER

For the past two years experiments have been instituted at Reading, England, to investigate the power of radium as a fertilizing agent. As a result of the above experiments it is made clear that while in some cases plants dressed with radioactive ore have given better results than the control plants, the improvement has not been of such a nature as to warrant the assumption that so expensive a commodity as radium could be profitably applied to crops. Accepting these investigations as conclusive, the farmer and gardener, says the *Times*, need look for no material benefit from radium. The chief result has been to emphasize the value of farmyard manures and artificial fertilizers. —M.

## A NEW PHOSPHATIC ORE

M. B. De Prolliere asserts in a letter to a French contemporary that he has discovered in one of the departments of France a considerable deposit of a new variety of ore, extremely rich in phosphorus, containing more than 50 per cent. The exact analysis is given as:—phosphoric acid, 50.10; lime, 0.005; silica, 4.75; potash, iron, manganese, nil; soda, 0.005; free alumina, 8.30; combined alumina, 22.80; fluorine, 4.15; water of combination, 5.60; loss, 4.79; total, 100.00. An ore of this description should render great service to chemical industry for the preparation of phosphorus, phosphoric acid, metallic phosphides and also for the improvement of the manufacture of phosphates. If it is worth while to extract the phosphorus from bones containing 13 per cent, it should be much more advantageous to obtain it from inexhaustible ore yielding 50 per cent. —M.

## ACETIC ACID MANUFACTURE IN CEYLON

The threatened shortage of acetic acid supplies for the rubber industry consequent upon the outbreak of war, says the *Chemical Trade Journal*, has stimulated the endeavors to produce this product from material to hand. Coco juice, coconut water and coconut vinegar were all found to be suitable coagulants, es-

pecially coconut water, which is now being used regularly on rubber estates. At Peradeniya, pyroligneous acid from the destructive distillation of wood and of coconut shells was produced by an improvised still and the results made public. Acetic acid can be made cheaply and in ample quantity from coconut shells. It is not sufficiently clear in color for the coagulation of rubber to be made into first latex crepe but good clear smoked sheet can be and is being made with it. Ceylon has an abundance of coconut shells and it is calculated that the cost of acid per pound of dry rubber is 0.08 c. in the case of crude acetic acid from coconut shells as compared with 0.39 c. to 0.65 c. when ordinary acetic acid is used.—M.

### MUCILAGE FOR PARAFFIN PAPER

According to the *Papermaker*, a suitable mucilage for paraffin and similar papers, which binds well and resists the weather, consists of a mixture of dextrine, rice-starch acetate lacquer and beeswax. The proportions vary according to the character of the paper for which the mucilage is used. For normal paraffin paper of medium weight, the following mixture is used, heating being effected by direct steam, by a flame or a hot plate. Dextrine 30 parts, rice starch 30 parts, acetate lacquer 20 parts, beeswax 20 parts. The mixture, well stirred, produces an extremely viscous, yet transparent mass with good weather-resisting qualities.—M.

### OIL PURCHASE

It is reported that the property of the Venezuelan oil concessions was likely to be acquired by the Shell Transport Interests. The terms of the sale, according to the *Petroleum World*, seem to have been completed and the deal will result in the formation of a new company with capital, $15,000,000, which will provide a working capital for the new company of $5,000,000. Shareholders in the existing Venezuelan concessions, if the arrangements are sanctioned, will receive one 7 per cent preferred share and three ordinary shares in the new company.—M.

### ACTION OF ULTRAVIOLET RAYS ON GLYCERIN

Glycerin is decomposed on exposure to ultraviolet radiation; formaldehyde and traces of other aldehyde substances are among the decomposition products. The presence of water aids the decomposition.—M.

### BRITISH EXPORT PROHIBITION

By an order in Council issued recently, the exportation of magnesite and magnesite bricks is prohibited to all destinations; compounds of chromium and oil fuel except for ships' use to all destinations other than British possessions and protectorates; formic acid and sodium carbonate to all foreign countries in Europe and on the Mediterranean and Black Seas other than France, Russia, Italy, Spain and Portugal.

Amendments and additions to the proclamation of July, 1915, with regard to prohibition of exports are made "Antipyrene (phenazone)" is deleted and there is substituted therefor "Antipyrene (phenazone) and its derivatives." "Mica (including mica splittings), and micanite," is to read "mica (including mica splittings and mica chimneys) and micanite." "Coal (including anthracite and steam, gas, household and all other kinds of coal) and coke" is to read "Coal (all kinds) and coke, but not including that allowed by the Commissioners of Customs to be shipped as bunker coal."—M.

# NOTES AND CORRESPONDENCE

### AMERICAN CHEMICAL SOCIETY—SPRING MEETING

The Fifty-Second General Meeting of the American Chemical Society will be held in Urbana, Illinois, April 18 to 21, 1915.

At that time the new chemical laboratory of the University of Illinois, said to be the largest in the world, will be dedicated.

The regular Council Meeting of the Society will convene on the evening of April 17th. C. L. PARSONS, *Secretary*

### SECOND PAN-AMERICAN SCIENTIFIC CONGRESS SECTION VII: MINING AND METALLURGY, ECONOMIC GEOLOGY AND APPLIED CHEMISTRY

The Second Pan-American Scientific Congress will meet in Washington under the auspices of the Government of the United States on Monday, December 27, 1915, and adjourn on Saturday, January 8, 1916.

EXECUTIVE COMMITTEE

William Phillips, A.B., Third Assistant Secretary of State, CHAIRMAN, *ex officio*.
James Brown Scott, J.U.D., Secretary, Carnegie Endowment for International Peace, *Vice-Chairman*.
William H. Welch, M.D., LL.D., President, National Academy of Sciences, *Honorary Vice-Chairman*.
John Barrett, LL.D., Director-General, Pan-American Union.
W. H. Bixby, Brigadier-General, U. S. A., Retired.
Philander P. Claxton, LL.D., Commissioner of Education.
William C. Gorgas, M.D., Sc.D., Surgeon-General, U. S. A.
William H. Holmes, B.S., Head Curator, Smithsonian Institution.
Hennen Jennings, C.E., former President, London Institution Mining and Metallurgy.
George M. Rommel, B.S., Chief, Animal Husbandry Division, Bureau of Animal Industry, Department of Agriculture.
L. S. Rowe, Ph.D., President, American Academy of Political and Social Science.
Robert S. Woodward, Ph.D., President, Carnegie Institution of Washington.

ORGANIZATION OFFICERS

John Barrett, LL.D., *Secretary-General*.
Glen Levin Swiggett, Ph.D., *Assistant Secretary-General*.
HEADQUARTERS—Pan-American Union, Washington, D. C.

The nine main Sections of the Program of the Congress, with the names of the Chairman in charge of each Section, are a follows:

I—Anthropology, Mr. William H. Holmes.
II—Astronomy, Meteorology, and Seismology, Mr. Robert S. Woodward.
III—Conservation of Natural Resources, Agriculture, Irrigation and Forestry, Mr. George M. Rommel.
IV—Education, Mr. P. P. Claxton.
V—Engineering, General W. H. Bixby.
VI—International Law, Public Law, and Jurisprudence, Mr. James Brown Scott.
VII—Mining and Metallurgy, Economic Geology, and Applied Chemistry, Mr. Hennen Jennings.
VIII—Public Health and Medical Science, General Wm. C. Gorgas.
IX—Transportation, Commerce, Finance, and Taxation, Mr. L. S. Rowe.

Each Section is divided further into sub-Sections. There are forty-five of the latter in all, each with a special Committee and Program. The deliberations of the Congress will be based, in consequence, according to the subject-matter to be discussed in the various sub-Sections. In addition to the general sessions of the Congress, there will be joint sessions between the different Sections and sub-Sections. Several of the leading national associations of the United States, concerned with the investigation of subjects of pertinent interest to some of the Sections of the Congress, have received and accepted invitations from the Executive Committee of the Second Pan-American Scientific Congress to meet in Washington at the same time and hold one or more joint sessions with a Section or sub-Section of corresponding interest.

MEMBERS OF THE CONGRESS

The following persons will be members of the Congress:

The official delegates of the countries represented.
The representatives of the universities, institutes, societies, and scientific bodies of the countries represented.
Such persons in the countries participating in the Congress as may be invited by the Executive Committee, with the approval of the countries represented.
All writers of papers.

All members of the Congress shall be entitled to attend its ses-

sions, to take part in the debates and to receive a copy of such publications as the Executive Committee may issue. There will be no membership fee of any character.

Section VII comprises the following subjects: Mining and Metallurgy, Economic Geology, and Applied Chemistry. It will consider especially the mineral resources of the several republics, the methods by which these resources can be developed and used, and the manifold applications of chemistry in the production and utilization of materials of benefit to man. The Chairman of this Section is Mr. Hennen Jennings, a former President of the London Institute of Mining and Metallurgy and member of the Institute of Civil Engineers (London), the American Institute of Mining Engineers, the South African Association of Engineers, and other national and international societies of scientific and mining interests. Mr. S. Sanford, mining engineer and editor, the United States Bureau of Mines, Washington, D. C., is the Secretary of this Section.

COMMITTEES OF THE FOUR SUB-SECTIONS IN SECTION VII

1—MINING—Mr. Van H. Manning, director of the U. S. Bureau of Mines, Washington, D. C., *Chairman*. Mr. J. F. Callbreath, secretary of the American Mining Congress, Washington, D. C. Dr. C. H. Lindley, lawyer, authority on mining law, San Francisco, Cal. Mr. E. W. Parker, statistician, Wilkes-Barre, Pa. Mr. H. C. Perkins, mining engineer, Washington, D. C. Mr. G. S. Rice, chief mining engineer of the U. S. Bureau of Mines, Pittsburgh, Pa. Mr. W. L. Saunders, engineer, President of the American Institute of Mining Engineers, New York, N. Y. Mr. B. B. Thayer, past president of the American Institute of Mining Engineers, New York, N. Y.

2—METALLURGY—Mr. W. R. Ingalls, president of the Mining and Metallurgical Society of America, and editor of the *Engineering and Mining Journal*, New York, N. Y., *Chairman*. Dr. F. G. Cottrell, chief chemist of the U. S. Bureau of Mines, San Francisco, Cal. Dr. R. N. Richards, professor emeritus of mining engineering and metallurgy, Massachusetts Institute of Technology, Boston, Mass., former president of the American Institute of Mining Engineers. Mr. Bradley Stoughton, metallurgical engineer, Secretary of the American Institute of Mining Engineers, New York, N. Y. Dr. L. D. Ricketts, mining and metallurgical engineer, New York, N. Y. Mr. Karl Eilers, metallurgical engineer, New York, N. Y. Mr. W. R. Walker, metallurgist, New York, N. Y. Dr. G. H. Clevenger, professor of metallurgy, Stanford University, Cal.

3—ECONOMIC GEOLOGY—Dr. Geo. Otis Smith, director of the U. S. Geological Survey, Washington, D. C., *Chairman*. Dr. J. C. Brenner, president of Stanford University, Stanford University, Cal.; former president of the Geological Society of America. Dr. J. F. Kemp, professor of geology, Columbia University, New York, N. Y., former president of the American Institute of Mining Engineers. Mr. Waldemar Lindgren, professor of economic geology, Massachusetts Institute of Technology, Boston, Mass. Dr. C. R. Van Hise, president of the University of Wisconsin, Madison, Wis.; former president of the Geological Society of America. Mr. David White, chief geologist of the U. S. Geological Survey, Washington, D. C. Dr. I. C. White, state geologist of West Virginia, Morgantown, W. Va.; formerly chief of the Brazilian Coal Commission. Dr. Bailey Willis, consulting geologist to Argentine Government; professor of geology, Leland Stanford, Jr., University.

4—APPLIED CHEMISTRY—Dr. Charles E. Munroe, authority on explosives; dean of graduate studies, George Washington University, Washington, D. C.; former president of the American Chemical Society, *Chairman*. Dr. Carl L. Alsberg, chief of the Bureau of Chemistry, Department of Agriculture, Washington, D. C. Dr. C. H. Herty, president of the American Chemical Society, Chapel Hill, N. C. Dr. B. C. Hesse, chemist, New York, N. Y. Dr. W. F. Hillebrand, chief chemist of the U. S. Bureau of Standards, Washington, D. C.; former president of the American Chemical Society. Mr. Lawrence Addicks, electrochemist; president of the American Electrochemical Society, Douglas, Ariz. Dr. P. C. McIlhiney, chemist; Secretary of the New York Section, Society of Chemical Industry, New York, N. Y. Dr. Harvey W. Wiley, chemist; former president of the American Chemical Society, Washington, D. C.

Some of the most distinguished scientists in Pan-America have been invited to prepare papers for Section VII on the different subjects described in the Preliminary Program, edition of April 15th, a copy of which may be obtained on request to the Secretary-General of the Congress.

Mr. Jennings has proposed for the series of special Pan-American conferences to be discussed by all of the participating countries the following topics:

MINING—The mining laws of each country and the changes that may be made to aid the development of mineral resources. History of the mining industry in each country, with special reference to the beginnings of that industry.

METALLURGY—Development of the patio process. Present methods of concentrating ores and the development of concentration methods.

MINING AND METALLURGY—Development of hydroelectric power for mining and metallurgy, the amount probably available, and specific benefits from its utilization.

MINING, METALLURGY AND ECONOMIC GEOLOGY—A bibliography on economic geology, mining, and metallurgy, each country to coöperate by assembling references to its own mineral resources and their development.

## THE WILLARD GIBBS PROFESSORSHIP OF RESEARCH IN PURE CHEMISTRY

In course of the academic year 1914–1915, a new department was established on a permanent basis in the Mellon Institute of Industrial Research of the University of Pittsburgh, namely, a Department of Research in Pure Chemistry. The headship of this Department is to be known as the Willard Gibbs Professorship of Research in Pure Chemistry, "to ever proclaim the ideal which the incumbents of the chair and the groups of research workers to be associated with them will be expected to follow." It constitutes a chair in the Graduate School of the University of Pittsburgh as well as in the Mellon Institute.

Dr. Martin A. Rosanoff, who had built up and for years headed the Graduate Department of Chemistry in Clark University, was formally inaugurated as the first permanent incumbent of this Professorship, at exercises held in the Assembly Hall of the Mellon Institute on October 26th. The exercises included addresses by Professors James McKeen Cattell and Marston Taylor Bogert, both of Columbia University, and by Dr. Rosanoff, followed by a reception and an inspection of the Mellon Institute.

Chancellor Samuel Black McCormick presided at the exercises. He explained the circumstances connected with the establishment of the chair and thanked the donors whose generosity had made possible the endowment, of which the income, amounting to $5,000 per annum, is to constitute the salary of the incumbent of the chair. He then introduced Professor Cattell, who spoke on "The Support of Scientific Research in a Democracy." Professor Bogert, who was introduced by Dr. Raymond F. Bacon, Director of the Mellon Institute, spoke on "The Especial Value of Research in Pure Chemistry."

## SECOND NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES—NEW YORK, SEPTEMBER 25 TO 30, 1916

At the Chemists' Club, 52 East 41st Street, New York, Wednesday evening, November 10th, was a notable gathering of the following well-known industrial chemists, at a dinner attended by the management of the exposition, to discuss plans for the next National Exposition of Chemical Industries: Raymond F. Bacon, Charles H. Herty, Henry B. Faber, A. D. Little, E. F. Roeber, George D. Rosengarten, T. B. Wagner, L. H. Baekeland, M. C. Whitaker, B. C. Hesse, Adrian Nagelvoort and Charles F. Roth; also R. G. Hollaman and F. W. Payne, of the International Exposition Company, were present, all of whom will serve on the Advisory Committee for the 1916 National Exposition of Chemical Industries, to be held at the Grand Central Palace, New York City, during the week of September 25, 1916. At this meeting Dr. Charles H. Herty was elected to serve as chairman of this committee for the coming year.

Plans for enlarging and increasing the scope of the coming exposition were laid, which will assure a very large exposition both from the attendance standpoint as well as exhibits. The plans include using several floors of the Grand Central Palace, with speakers in the evening and motion pictures during the day from 11 A.M. to 7 P.M. Next year an entirely new set of motion pictures will be shown, covering a very much wider field of industrial activities than was represented during this year's exposition.

## STATIC ELECTRICITY AS A CAUSE OF EXPLOSIONS

*Editor of the Journal of Industrial and Engineering Chemistry:*

Referring to the report of Major A. Cooper-Key, H.M., Chief Inspector of Explosives, on an explosion of cordite which recently

occurred in a Stowmarket factory, attributing the cause to a spark produced from the generation of static electricity, his theory is not at all far-fetched to those well informed on the subject, as many can testify who handle combustibles or products, the vapors of which mix with the atmosphere to form an explosive combination. This is frequently the cause of fires and explosions in the dry cleaning industry, and this is unfortunate when we consider that in most cases the remedy consists merely of grounding the machinery or its insulated parts, thus allowing any static electricity to escape to the ground.

Several years ago I was able to observe this phenomenon personally and I shall endeavor to describe the incident as it occurred. Some silk fabrics were being "French" or dry cleaned, the process being conducted in a washer similar to those used in laundries. This machine is simply a revolving wooden cylinder enclosed in a wooden or metal shell. In practice the material is placed in the inner cylinder, the door of which is then closed and the solvents are admitted to fill the machine to about one-fourth of its capacity. The door of the outer shell is closed, the inner cylinder is set in motion and cleansing is accomplished by agitation with the solvents which are later extracted by means of centrifugals. In this case the inner wooden cylinder was perfectly insulated and had no metal fittings on the inside that made connections with the outside of the machine. The solvents, consisting almost entirely of a light petroleum ether, were in a perfectly anhydrous condition having been filtered through dry calcium chloride, hence they offered no means of escape for the electricity. Consequently, during the time the material was in motion (the process required about forty-five minutes) a considerable charge of static electricity had accumulated, and on grasping the silk fabrics with the hand a spark was emitted at the point of contact and a crackling sound was produced. Slight agitation with the hands caused a continuation of the crackling sound but no more sparks were produced.

The air within the machine had been entirely displaced by the vapor of petroleum ether, consequently no explosion was possible. At the time, no fan was in operation and the air in the room perfectly quiet. Had there been a current of air circulating through the room to make possible the formation of an explosive mixture of air and vapor, an explosion would undoubtedly have resulted.

60 Beaver St., Schenectady, N. Y. Herbert Zschiegner
October 27, 1915

## NOTE ON ARTIFICIAL ZEOLITE-PERMUTITE

*Editor of the Journal of Industrial and Engineering Chemistry:*

In reference to the note on the above subject which appeared in the November (1915) issue of your paper (p. 1103), I wish to say that I started the work on the problem about eight years ago, while a student in the Technical University of Budapest, and arrived at positive results in December, 1914.

I have never had the pleasure of meeting Mr. Bachler or any of the chemists with whom he discussed freely the results of his work.

Stephen J. Kocsor
17 Madison Avenue, New York City,
November 10, 1915

## PAPER REAGENT—A CORRECTION

In my article under the above title [This Journal, **7** (1915), 1002] the amount of distilled water to be used is "80 cc." instead of "80 cm.," as printed.

November, 8, 1915 Wm. J. Schepp

# PERSONAL NOTES

The New York Section of the A. C. S. has arranged a series of meetings for the season 1915–1916, at which representatives of the universities and the industries will speak. The object of these meetings is to impress anew upon the chemists and the educators of this country, upon capital, manufacturers, the public and the press, the necessity of coöperation between the universities and the industries. The first of this series was held on November 12th, the subject for the evening being "University and Industry." The speakers were: Nicholas Murray Butler, President of Columbia University; M. C. Whitaker, Professor Chemical Engineering, Columbia University; W. J. Gies, Professor Biological Chemistry, Columbia University; and C. E. Lucke, Professor Mechanical Engineering, Columbia University. Two of these addresses appear in full in this issue.

Dr. Charles H. Herty, President of American Chemical Society, spoke on "National Self-Containedness in Chemical Industry," before the Rochester Section of the A. C. S. on November 8th.

Prof. M. C. Whitaker, Columbia University, gave an address on "The Outlook for the Chemical Engineering Profession," before the Philadelphia Section of the A. C. S. on November 18th.

Prof. John Ferguson has resigned the regius chair of chemistry at Glasgow University to which he was appointed in 1874. He had previously for nine and a half years been a junior teacher in the department and has thus been a member of the staff for more than fifty years.

At a lecture before the Royal Botanic Society, London, Prof. W. B. Bottomley, of King's College, showed fine specimens of fruits and vegetables grown in soil mixed with bacterized peat, and expressed the hope that the peat would soon be obtainable at cost price. Sir Malcolm Morris, who presided, believed that by its use, the food supply of the country could be doubled in a short time.

A Joint Meeting of the Pittsburgh Sections of the American Electrochemical Society and the American Chemical Society was held in Thaw Hall, University of Pittsburgh, on October 21st. The attendance was 125 members and guests. Before the meeting an informal dinner, at the University Club, was attended by 52 members and guests. Mr. F. T. Snyder, of the Snyder Electric Furnace Company, of Chicago, delivered an illustrated lecture on "Electric Furnaces for High Temperature Industrial Chemical Work." He described furnaces claimed to be capable of working for long periods of time at 2500° C. There was a lively discussion, lasting until late in the evening.

Dr. Frank K. Cameron, whose resignation from the United States Bureau of Soils was reported in this column last month, has accepted the position of chemical engineer with the Utah Potash Company, Marysvale, Utah, an operating company which will produce potash and by-products from the alunite deposit on the property of the Florence Mining and Milling Company. Dr. Cameron is now at Marysvale, Utah, at the head of a Bureau of Research, developing the different products of the alunite deposits controlled by this company.

Dr. Bernhard C. Hesse announces that the business he has conducted for the past ten years, with offices at 90 William Street, New York City, will be discontinued at the end of the present year and that thereafter his services will be at the exclusive command of the General Chemical Company.

The Indiana Section of the A. C. S. has recently issued a fifteen-page pamphlet containing a directory of its members. In general, the name, position, business and home addresses of the member are given.

Wirt du Vivier Tassin, for many years chief chemist and assistant curator of the division of mineralogy of the National Museum, died in Washington, D. C., on November 2nd, of heart failure, at the age of forty-six years. He was a graduate of

the Universities of Cornell and Harvard, and a member of the American Chemical Society, the American Society for Testing Materials, and the Cosmos Club of Washington. Since 1908 Mr. Tassin had been a consulting metallurgist and chemical engineer at Chester, Pa., and was well known for his contributions to mineralogy and metallurgy.

Professor Emeritus Nathan Frederick Merrill, of the University of Vermont, died on October 26th at the age of sixty-six years. He had formerly been professor of chemistry at the medical school of Boston University, assistant in chemistry courses at Harvard, and professor at Denison University, and was for thirty years professor of chemistry in the University of Vermont. He was a member of the American Chemical Society since 1892.

George L. Ringel, of Fritzsche Bros., New York, addressed the 8th regular meeting of the Maryland Section of the A. C. S. on November 13th, on "The Distillation of Essential Oils from Antiquity to Modern Days."

On October 25th, Professor M. T. Bogert addressed the staff and students of the School of chemistry of the University of Pittsburgh and of the Mellon Institute upon "Reminiscences of Famous European Chemists and Chemical Laboratories."

Louis Gottschalk, an expert chemist and the inventor of a recently patented process to synthesize rubber, has died at his home in Newark, N. J., at the age of sixty-seven years.

Dr. A. W. Davison spoke on "Some Recent Developments in Nitrogen Fixation," before the November 10th meeting of the Cincinnati Section of the A. C. S.

Prof. C. H. Fulton, head of the mining engineering department of Case School of Applied Science, addressed the Cleveland Section of the A. C. S. on "The Flotation Process of Ore Concentration," at their November 8th meeting.

Mr. Leonard W. Cronkhite, of Boston, Mass., addressed the Rhode Island Section of the A. C. S. on November 11th, on "Some Problems of the Chemical Industry during the Past Year."

The newly formed Ames Section of the American Chemical Society held its first meeting October 21, 1915, and the following officers were elected for the ensuing year: J. A. Wilkinson, *President;* P. E. Brown, *Vice-President;* W. G. Gaessler, *Secretary-Treasurer;* W. F. Coover, *Councilor.* The Ames Section starts out with 32 charter members, only two of whom are not connected directly with the Iowa State College, and prospects for a successful year are very bright.

The December meeting of the Section was held on the 2nd, when Prof. Homer F. Staley, of the Department of Ceramics, Iowa State College, spoke on "Peculiarities in the Chemistry and Physics of the Silicate Industries."

Dr. Charles F. Chandler, professor emeritus of Columbia University, has concluded a series of three illustrated lectures on "The Art of Photography," before the department of arts and sciences of the university.

Sir Andrew Noble, F.R.S., distinguished for his scientific work on artillery and explosives, died on October 22nd, at eighty-four years of age.

The Nobel Prizes for chemistry for the years 1914 and 1915, according to a Reuter dispatch from Stockholm, have been awarded respectively to Prof. Theodore William Richards, of Harvard University, for fixing the atomic weights of chemical elements, and to Dr. Richard Willstätter, of the University of Berlin.

Charles H. Kiessig has died at his home in New York City at the age of sixty-five years. The deceased was born in Saxony, Germany, and in 1879 came to the United States to establish the business of manufacturing ultramarine blue. From 1885 to 1895 he was the representative of Dr. Eugen Schaal, of Fuerbach, Germany, and introduced Ester Gum products to the domestic trade, but for the last twenty years he conducted a business as importer's agent. Mr. Kiessig was well known in paint and chemical circles and was a member of the Chemists' Club, on whose House Committee he served as chairman for a number of years.

Prof. Vivian B. Lewis, until last year professor of chemistry in the Royal Naval College, England, died on October 23rd, aged sixty-three years.

Siegfried S. Hartig died in Pittsburgh, Monday, November 15th, as the result of burns received at one of the plants of the Aetna Chemical Company. Mr. Hartig was a graduate of Columbia University, Class of 1915 Chemical Engineering, and has been working as a chemical engineer with the Aetna Company since his graduation.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

### BUREAU OF STANDARDS

**Specific Heat and Heat of Fusion of Ice.** H. C. Dickinson and N. S. Osborne. Scientific Paper 248. 34 pp. "The present investigation is one of a series undertaken, at the request of the refrigeration industries, for the determination of constants which are of fundamental importance in the design and operation of refrigeration machinery.

"By means of a calorimeter of the aneroid type—that is, employing the thermal conductivity of copper instead of the convectivity of a stirred liquid to distribute heat supplied electrically—the specific heat and heat of fusion of ice were determined.

"The specific heat was determined upon four samples of ice, all of a high but yet of different degrees of purity. A variation in the specific heat of ice is found which depends upon the degree of purity.

"It is found that at a given temperature $\theta$, between —40° and —2°, for the purest ice experimented on, the specific heat in 20° calories per gram per degree is represented within the limit of experimental accuracy by the equation:

$$s = 0.5057 + 0.001863\,\theta$$

and that from —2° to —0.05° the specific heat does not exceed the value given by the above equation by more than $0.004/\theta^2$.

"The specific heat of impure ice at any temperature $\theta$ above —40° is greater than that of pure ice by $1L/\theta^2$ where L is the heat of fusion and 1 the initial freezing point.

"The value found for the heat of fusion of ice is 79.76 (20°) calories per gram, which is within 1/4000 of the value previously determined at the Bureau by a different method employing a stirred water calorimeter."

**Characteristics of Radiation Pyrometers.** George K. Burgess and Paul D. Foote. Scientific Paper 250. 86 pp. In this article there are given "an account of the principles which form the basis for the operation of total radiation pyrometers, descriptions in some detail of representative types of this in-

strument, together with the results of an experimental study of their calibration and behavior under various conditions of use, and as modified by changing the several factors which may influence the readings of such pyrometers. A considerable portion of the text is devoted to the examination of the sources of error and their elimination or correction. In all, there were carefully examined some 20 instruments, including all the ordinary types commonly met with in practice, such as the Féry, Foster, Thwing, and Brown pyrometers.

"The discussion has, however, been limited, in the main, to those types of instruments which are portable and which are in general use as pyrometers, although it is recognized that there are other special energy receiving and measuring devices which have been of great service in the laboratory and which could be or have been adapted to the measurement of temperature."

**Effective Resistance and Inductance of Iron and Bimetallic Wires.** JOHN M. MILLER. Scientific Paper 252. 62 pp.

**A Study of the Quality of Platinum Ware.** GEORGE K. BURGESS AND P. D. SALE. Scientific Paper 254. 27 pp. A new thermoelectric method for determining the purity of platinum is described and results of tests on 164 samples reported in detail. The method does not mar the material which is tested. [See THIS JOURNAL, 7 (1915), 561.]

**Construction of Primary Mercurial Resistance Standards.** F. A. WOLFF, M. P. SHOEMAKER AND C. A. BRIGGS. Scientific Paper 256. 89 pp. Paper, 25 cents. The theory of the design and computation of these standards and experimental details of construction of such standards are given together with the results of inter-comparison of tubes prepared by the Bureau of Standards and by certain foreign laboratories.

**A Method of Measuring Earth Resistivity.** FRANK WENNER. Scientific Paper 258. 10 pp. A method is given for measuring earth resistances such as might be of value in determining the composition or condition of soil, especially such items as moisture content, or ore content, or in the study of damage due to stray currents.

**Value of the High-Pressure Steam Test of Portland Cements.** R. J. WIGG AND H. A. DAVIS. Technologic Paper 47. 34 pp. The following conclusions indicate the scope of the work and the nature of the results obtained:

"1—The high-pressure steam test should be made on all cements that are incorporated in cement, mortar, or concrete products that are to be cured in steam at pressures above atmospheric.

"2—The high-pressure steam test may be of value as forecasting the behavior of neat cement or a very rich mortar when exposed under normal conditions in dry air, but it will not forecast the behavior of cements in concretes as normally exposed.

"3—The cement passing the high-pressure steam test is not superior in cementing quality, as determined from the compressive strength of concretes, to cement that fails to pass this test.

"4—The cement passing the high-pressure steam test does not make more permanent or durable concrete than cement which meets the requirements of the standard specification but fails to pass this test.

"5—Cement failing to pass the standard specification atmospheric steam test but meeting the other requirements of the standard specification shows in some instances a normal strength in concrete.

"6—For practical work under normal conditions of construction, the results of this investigation fail to show that the high-pressure steam test is of value as a means of determining the ultimate soundness of concrete."

**An Air Analyzer for Determining the Fineness of Cement.** J. C. PEARSON AND W. H. SLIGH. Technologic Paper 48. 74 pp. This report describes the preliminary experiments and the results of the development of an apparatus devised for separation of cement and other finely divided materials for mechanical analysis. The distinguishing features of the new elutriator are as follows: "The introduction of an unretarded air stream into a conical-shaped bulb in such manner that the sample under examination is completely and continuously exposed to the action of the air; a separating chamber of considerable height which permits no lodgment of either fine or coarse particles; a tapping device to minimize the adherence of fine dust to any part of the apparatus; and a collector which catches and holds all material passing through the separating chamber."

**Emergent Stem Correction for Thermometers in Creosote Oil Distillation Flasks.** R. M. WILHELM. Technologic Paper 49. 20 pp. "The purpose of this investigation was primarily to ascertain the magnitude of the emergent stem correction error which may occur in the use of thermometers in the distillation of creosote, a question which has arisen at various times in connection with the testing of thermometers for use in distillation flasks."

The importance of this investigation is evident from the fact that in actual application of the method's neglect of the proper stem correction may introduce errors of as much as 15°.

**Viscosity of Porcelain Bodies High in Feldspar.** A. V. BLEININGER AND C. S. KINNISON. Technologic Paper 50. 7 pp. "The object of the work was to determine the range of compositions showing greatest rigidity, at the highest kiln temperatures, information which should be useful in selecting bodies subject to minimum deformation in firing, and hence causing least loss in manufacture due to deformed ware."

**Use of Sodium Salts in the Purification of Clays and in the Casting Process.** A. V. BLEININGER. Technologic Paper 51. 40 pp. "The present work was undertaken for the purpose of studying the effect of the alkalies upon the behavior of clay suspensions, embracing the materials commonly used in the manufacture of the finer clay products, with special reference to the purification of clays and the casting process."

Results include data on the effect of alkali upon American kaolin and clays such as are used in the pottery industry, indicating viscosity of clays, suspensions, absorption of reagents, strength of treated mixtures in the dry state, and the influence of time on the stability of the system.

**An Investigation of Fusible Tin Boiler Plugs.** GEORGE K. BURGESS AND PAUL D. MERICA. Technologic Paper 53. 37 pp. "An explanation has been sought for the 'failure' by oxidation of fusible tin boiler plugs during service. These failures are of two types: (*a*) those in which the oxide forms as an interlocking 'network' throughout the tin of the filling; (*b*) those in which the oxide forms as a solid hard mass at the fire end of the plug.

"About 950 new and 100 used plugs were examined, the latter classified according to the type of change of deterioration which had taken place in them during service, and a number were tested for purity of the tin, both by determination of the melting point of the latter, and by chemical analysis. Lead and zinc were found to be the principal impurities present.

"The relation of these findings to existing specifications for fusible plugs is discussed and more rigorous inspection of the product of licensed manufacturers suggested." [See THIS JOURNAL, 9 (1915), 824.]

**Difference in Weight between Raw and Clean Wools.** WALTER S. LEWIS. Technologic Paper 57. 5 pp.

**The Testing of Rubber Goods.** ANONYMOUS. Circular 38, 3rd Ed. 89 pp. This issue supersedes the 2nd edition, issued two years ago. "The purpose of this circular is to describe the methods of testing used at the Bureau of Standards, with the hope that sufficient interest may be aroused among manufacturers and purchasers of rubber goods to assist in bringing

about that concerted action which is necessary for the standardization of tests, and to furnish the general public with information which will enable users of rubber goods to determine the quality of materials they secure."

**Standardization of Bomb Calorimeters.** ANONYMOUS. Circular 11, 2nd Ed. 17 pp. This revised edition discusses the principles of construction and use of bomb calorimeters.

**Measurements for the Household.** ANONYMOUS. Circular 55. 1st Ed. 149 pp. Paper, 45 cents. This circular gives a popular exposition of units, instruments, and methods of measurement of household quantities. In addition to such common measurements as length, weight, and capacity of ordinary commodities of trade, there are also sections upon gas, electricity and water meters, humidity, time, temperature, fuels, illumination, etc. The style is distinctly nontechnical, and over 60 illustrations make it still more readable.

**Tolerances and Specifications for Weights and Measures and Weighing and Measuring Devices.** Unnumbered publication. 29 pp. This reports on the specifications adopted by the Tenth Annual Conference on the Weights and Measures of the United States held at the Bureau of Standards, May 25–28, 1915.

### COMMERCE REPORTS—OCTOBER, 1915

A résumé of the "antidumping" legislation in force in Canada, South Africa and Australia is given. (P. 1.)

Use of sulfuric acid as a preservative in the **adhesive** has been found by the Bureau of Standards to cause deterioration of envelopes to which it was applied. (P. 13.)

The **palm and palm-kernel oil** industry of British West Africa is described. The nuts are cracked by hand and the oil extracted by primitive methods. Total annual exports amount to $23,000,000, the oil being used for soap, etc., and for edible oils. (P. 22.)

The Japanese Diet has passed a bill granting subsidies for a period of 10 years to companies engaged in the manufacture of **dyestuffs, drugs, and explosives** from coal tar. More than half the capital must be subscribed by Japanese subjects. (P. 25.)

Two factories have been established in Indo-China for the manufacture of **paper pulp.** (P. 75.)

A **cement plant** with a daily capacity of 500 barrels, has started operation in Rigal, P. I. (P. 84.)

Numerous **rubber** plantations have been formed in Ecuador, though the present production is small because of low prices. (P. 88.)

Increased taxes on **alcohol** are proposed in France, including a Government monopoly of denatured alcohol. (P. 97.)

Production of **nitrate** in Chile is far short of the exportation. (P. 98.)

Efforts are being made to develop the **paper industry** of Australia by special government contracts. (P. 107.)

The United States consumes annually 86 lbs. *per capita* of **sugar,** amounting to one-fifth of the world's production. Exports of sugar from the United States have increased from 72,000,000 lbs. in 1913–14, to 582,000,000 lbs. in 1914–15. (P. 114.)

There is prospect of developing a **shale-oil** industry in Australia. (P. 117.)

In the effort to develop the natural **indigo** industry of India, stress is being laid upon the selection of seed, and upon standardization of the dye produced. (P. 151.)

The demand for **mercury** and **vermillion** in China has increased so that it is proposed to import from the United States.

Experiments are to be made in the United States upon possible commercial uses of Hawaiian **kukui oil,** obtained from the kukui nuts. The oil has a specific gravity of 0.82 and is a drying oil, similar to linseed oil or Chinese wood oil. It has also been used as an edible and medicinal oil. (P. 187.)

Efforts of the last year to raise **hemp** in Germany have proven successful. (P. 194.)

The first shipment of 50 tons of **dyes,** consigned to the Secretary of Commerce on account of the National Association of Cotton Manufacturers, has arrived. (P. 194.)

In Germany **five-pfennig pieces** are to be made of iron for temporary circulation. (P. 215.)

In addition to quebracho, a number of other woods high in **tannin** are found in Paraguay. (P. 236.)

Among the **natural dye** materials produced in Ecuador, are the following: "archilla," a lichen from which archil and litmus are obtained; "achiota" or "annatto," from the seeds of which the color annatto is obtained; "cascol" (brown); the nut of the "avocado" (black); "chanche berries" (black); "anil" (blue); "croton sanguefluum" (red); "jocte" (black); "mangle" (brown); "colcas" (yellow); and "chilca" (brown). (P. 264.)

The Chinese government has organized a Bureau to control the output of **gold, silver, copper, and other metals.** (P. 314.)

**Copper** mining is being revived in Sweden, having fallen off greatly in recent years. (P. 331.)

China is suffering seriously from lack of **lead.** (P. 352.)

Several **cottonseed oil** factories in the South have started the production of peanut oil. (P. 358.)

Among new fibers proposed for **paper making,** are the "neuquen pine" from Argentine; "hedychium coronarium," a plant of the ginger family, found in swamp lands in Central America, West Indies, Brazil and India; and hop vines, now proposed for this purpose in Germany. (P. 360.)

**Tanning materials** used in Brazil include "carbatimao bark," containing 60 per cent of tannin; "angico bark," with 28 per cent of tannin; and "mangue bark" (mangrove). (P. 363.)

The largest **paper mill** in Sweden has just been constructed at Hallsta. (P. 388.)

In a study in Germany of the medicinal uses of animal charcoal, it has been found possible to absorb from the system recently administered **poisons** such as morphine, strychnine, carbolic acid, etc., and also poisonous products of germ action, *e. g.*, in cholera, etc. (P. 397.)

Special supplements, containing statistics of imports, exports, manufactures, etc., were issued as follows:

| | |
|---|---|
| Austro-Hungary—1*b* | Brazil—40*c* |
| Germany—6*f* | Ecuador—43*a* |
| Russia—13*d* | British South Africa—66*d* and *e* |
| Spain—15*e* | British West Africa—67*a* |
| Turkey—18*d* | Egypt—68*a* |
| Danish West Indies—37*a* | Libya—74*a* |

STATISTICS OF EXPORTS TO THE UNITED STATES

| AUSTRIA—Sup. 1*b* | BERLIN—Sup. 6*f* | TURKEY—Sup. 18*d* |
|---|---|---|
| Aluminum | Aluminum | Chromium ore |
| Chemicals | Carbon electrodes | Emery |
| Drugs | Lactic acid | Glue |
| Enameled iron ware | Dextrin | Gum mastic |
| Glassware | Glycerine | Gum tragacanth |
| Magnesite | Lanolin | Licorice root |
| Hides | Thorium nitrate | Olive oil |
| Sugar beet seed | Earthenware | Sesame |
| Ozocerite | Glassware | |
| BATUM, RUSSIA—Sup. 13*d* | Glue | ECUADOR—Sup. 43*a* |
| Licorice root | Hides | Gold |
| Manganese ore | Enameled ware | Hides |
| Potassium carbonate | Tungsten | Ivory nuts |
| SPAIN—Sup. 15*e* | Mica | Kapok |
| Argols | Linoleum | Rubber |
| Pyrites | Paper | |
| Licorice root | Artificial silk | |
| Olive oil | Tin | EGYPT—Sup. 68*a* |
| Copper | COLOGNE—Sup. 6*f* | Gum arabic |
| Cork | Aniline dyes | Hides |
| | Chemicals | Iron ore |
| | Paper | Senna |

Among the methods for increasing the **potash supply** of the United States, the extraction from feldspar by heating with limestone and iron oxide to 2200° F. is suggested; and also the recovery of potash from distillery residues where molasses is used. (P. 403.)

Several plants in Paraguay for the extraction of **tanning extract** from quebracho logs, which have been closed for a few years have been reopened. (P. 426.)

Owing to exhaustion of the world's supply of **tanning materials**, several South African plants are being exploited, including wattle, sumac, elandsboontjes, and bastard sumac. (P. 428.)

Zatacon grass, which grows from California and Texas to Argentine, is suggested as a valuable **paper stock.** (P. 437.)

DEPARTMENT OF AGRICULTURE

**Meats, Their Composition and Cooking.** CHARLES D. WOODS. Farmers' Bulletin 34, Revised Ed. 31 pp. Paper, 5 cents. A popular review of the subject. Revised from the issue of February, 1904.

**Principles of Nutrition and Nutritive Value of Food.** W. O. ATWATER. Farmers' Bulletin 142, 3rd Revised Ed.

**Story of the Thermometer and Its Uses in Agriculture.** ALFRED H. THIESSEN. Separate 635 from 1914 Year Book. 10 pp. Paper, 5 cents.

**The Preparation of Fertilizer from Municipal Waste.** J. W. TURRENTINE. Separate 643 from 1914 Year Book. 15 pp. Paper, 5 cents. This article summarizes in a popular way the methods and desirability of recovering valuable products from sewage, street sweepings, dead animals, and garbage collected by municipalities.

**Biochemical Decomposition of Nitrogenous Substances in Soils.** W. B. KELLEY. Hawaiian Experiment Station Bulletin 39. 25 pp. Paper, 5 cents.

**The Soils of the Hawaiian Islands.** W. B. KELLEY, WILLIAM MCGEORGE AND ALICE R. THOMPSON. Hawaiian Agricultural Experiment Station Bulletin 40. 35 pp. Paper, 5 cents.

**Grades for Commercial Corn.** J. W. F. DUVEL. Department Bulletin 168. Contribution from the Bureau of Plant Industry. 11 pp. Paper, 5 cents.

**The Toxicity to Fungi of Various Oils and Salts, Particularly Those Used in Wood Preservation.** C. J. HUMPHREY AND RUTH M. FLEMING. Department Bulletin 227. Contribution from the Bureau of Plant Industry. 38 pp. Paper, 10 cents. This bulletin gives the results of an investigation conducted in the Forest Products Laboratory at Madison, Wisconsin, on the preservative value of various oils and salts and their toxic effect in wood-destroying fungi. [See THIS JOURNAL, **8** (1915), 652.]

**The Naval Stores Industry.** A. W. SCHORGER AND H. S. BETTS. Department Bulletin 229. Contribution from the Forest Service. 58 pp. Paper, 15 cents. This article reviews the production, handling, and properties of turpentine and resin, including certain specifications of chemical interest. The information is of interest to both producers and users of naval stores.

**Oil-Mixed Portland Cement Concrete.** LOGAN W. PAGE. Department Bulletin 230. Contribution from the Office of Public Roads. 26 pp. Paper, 10 cents. This bulletin is a revision of Bulletin 46 of the Office of Public Roads and is of interest to those using moisture-proof cement concrete.

**Sugar Beets; Preventable Losses in Culture.** HARRY B. SHAW. Department Bulletin 238. 21 pp. Paper, 10 cents.

**Pasteurizing Milk in Bottles and Bottling Hot Milk Pasteurized in Bulk.** S. HENRY AYERS AND W. T. JOHNSON, JR. Department Bulletin 240. 27 pp. Paper, 5 cents. This paper is of interest to milk testers, health officials, and any others who have to do with milk supply of cities.

**Portland Cement Concrete Pavements for Country Roads.** CHARLES H. MOOREFIELD AND JAMES T. VOSHELL. Department Bulletin 249. Contributions from the Office of Public Roads. 34 pp. Paper, 15 cents.

**Studies on Changes in the Degree of Oxidation of Arsenic and Arsenical Dipping Baths.** ROBERT M. CHAPIN. Department Bulletin 259. Contribution from the Bureau of Animal Industry. 12 pp. Paper, 5 cents.

**A Study of the Soft Resins in Sulfured and Unsulfured Hops in Cold and in Open Storage.** G. A. RUSSELL. Department Bulletin 282. Contribution from the Bureau of Plant Industry. 19 pp. Paper, 5 cents. "This bulletin presents the results obtained from experiments conducted to determine the extent and character of the changes in the soft resins in hops under varying conditions of curing and storage. The soft resins, or so-called bitter acids, are a principal factor in determining the commercial value of hops."

**The Production of Sulfuric Acid and a Proposed New Method of Manufacture.** WILLIAM H. WAGGAMAN. Department Bulletin 283. Contribution from the Bureau of Soils. 39 pp. Paper, 10 cents. "This method is based on the fact that if a mixture of warm gases is drawn downward through a special flue their resistance to the downward pull, together with the constant change of their course, will tend to mix them very intimately and unless the internal diameter of the flue is too great there will be practically no zones of inactivity in the apparatus. Moreover, the constant impinging of the gases on the walls of the spiral flue, which can be cooled either by air or water, makes it practicable to maintain the gases at a temperature most favorable for the efficient yield of sulfuric acid."

A very complete tabulation is included in which the author has classified all American patents on the manufacture of sulfuric acid both on the contact and chamber process. Many details in the development of these processes are made clear by this summary.

**Strength Tests of Structural Timbers Treated by Commercial Wood-Preserving Processes.** H. S. BETTS AND J. A. NEWLIN. Department Bulletin 286. Contribution from the Forest Service. 15 pp. Paper, 5 cents. This report is of interest to users of timber where strength is of importance.

**Effect of Alkali Salts in Soils on the Germination and Growth of Crops.** FRANK S. HARRIS. Journal of Agricultural Research, **5** (1915), 1–54.

**Effect of Temperature on the Movement of Water Vapor and Capillary Moisture in Soils.** G. J. BOUYOUCOS. Journal of Agricultural Research, **5** (1915), 141–173.

**Journal of Agricultural Research.** Beginning with the first number of Volume 5, which is dated October 4, 1915, this Journal will be issued weekly.

GEOLOGICAL SURVEY

**The Fractional Precipitation of Some Ore-Forming Compounds at Moderate Temperatures.** ROGER C. WELLS. Bulletin 609. 46 pp. "The experiments described in this bulletin were made to aid in elucidating the chemistry of ore deposition. They were confined to aqueous solutions at moderate temperature, and they have shown the order of solubility of the compounds of each of the classes investigated—sulfides, hydroxides, carbonates, and silicates.

"The present experiments do not show the behavior of solutions that may exist in magmas or that may constitute magmatic exudations."

The general results of the investigation are summarized in a table which gives the order of solubility for each class of compounds investigated, as deduced from the experiments reported on fractional precipitation.

**Contributions to Economic Geology, 1915.** The following seven reports are separate from this annual summary. Each contains information of economic interest but very little material of purely scientific significance. The nature of the deposits, chemically and geologically, and the geographical nature of the surroundings are described in so far as they have important economic bearing.

**Gold Deposits Near Quartzsite, Arizona.** EDWARD L. JONES, JR. Bulletin 620–C. Separate from Part I, pp. 45–57; issued September 23.

**Some Cinnabar Deposits in Western Nevada.** ADOLPH KNOPF. Bulletin 620–D. Separate from Part I, pp. 59–68; issued September 14

**The Healdton Oil Field, Carter County, Oklahoma.** C. H. WEGEMANN AND K. C. HEALD. Bulletin 621–B. Separate from Part II, pp. 13–30; issued September 10.

**The Loco Gas Field, Stephens and Jefferson Counties, Oklahoma.** C. H. WEGEMANN. Bulletin 621–C. Separate from Part II, pp. 31–42; issued August 30.

**The Duncan Gas Field, Stephens County, Oklahoma.** C. H. WEGEMANN. Bulletin 621–D. Separate from Part II, pp. 43–50; issued August 30.

**A Reconnaissance in Palo Pinto County, Texas, with Special Reference to Oil and Gas.** C. H. WEGEMANN. Bulletin 621–E. Separate from Part II, pp. 51–59; issued September 11.

**Possibilities of Oil in the Porcupine Dome, Rosebud County, Montana.** C. F. BOWEN. Bulletin 621–F. Separate from Part II, pp. 61–70; issued September 24.

**Mineral Resources of Alaska.** Bulletin 622. 380 pp. This bulletin includes 16 scientific and technical reports on various phases of the Alaskan mining industry as developed by the investigations made by the Geological Survey during 1914. A general summary of the Alaskan mining industry is given and the following, among other topics, are discussed. The future of gold placer mining; tin mining; mineral deposits (for several districts); auriferous gravels and copper deposits (of various regions); mineral deposits and mining conditions (for several regions); quicksilver deposits; and iron ore deposits near Nome.

**Silver, Copper, Lead, and Zinc in the Central States in 1914.** B. S. BUTLER AND J. P. DUNLOP. Mineral Resources, Part I, 27–124. Separate published July 19. (Mines Report.) The total mine production of silver, copper, lead and zinc in the Central states in 1914 was distributed as follows:

| | Quantity | Value |
|---|---|---|
| Silver (fine ounces) | 482,983 | $267,089 |
| Copper (pounds) | 164,398,821 | 21,865,043 |
| Lead (short tons) | 203,845 | 15,899,910 |
| Zinc (short tons) | 168,032 | 17,139,264 |

Practically all of the silver and copper of these states was produced in Michigan, and Missouri contributed practically all of the lead and two-thirds of the zinc.

"The total value of the mine production of silver, copper, lead and zinc in the Central States in 1914 was $55,171,306, a decrease of $2,840,686 from the value for 1913. The total value of the production of these metals for the years 1907 to 1914, inclusive, was $518,267,549, of which $238,395,086 was for copper, $153,883,998 for zinc, $124,151,390 for lead, and $1,837,075 for silver.

"Nearly all the silver that is produced in the Central States is recovered incidentally to the production of other metals. Of the 1914 production 413,500 ozs. came from the copper lodes of Michigan, an increase of 118,327 ozs., resulting from a much larger copper output. About 25 per cent of the concentrates from lead ores mined in southeastern Missouri were desilverized and yielded nearly all the production of silver from that State recovered in 1914; a small output of silver was also derived from copper ore, and the total recovery from Missouri amounted to 61,168 ozs.

"All but a very small proportion of the ore from the Central States is of such tenor that it requires concentration."

**Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1914.** J. P. DUNLOP. Mineral Resources, Part I, 139–63. Separate Published August 20. (Mines Report.) "There were 81 producing mines reported to the Survey in 1914, of which 36 were deep and 45 were placer properties. The latter are mostly small, many of them yielding only nominal and occasional outputs of gold. In 1913 there were 90 reported producers, of which 42 were deep mines. Of the 36 deep mines in 1914, those producing copper numbered 7, those producing zinc (and in one case lead also) numbered 7, and the remainder were gold mines. The largest number of operating properties in 1914 were in Georgia, where there were 26 gold placers and 11 deep mines, or 37 in all. In 1914 North Carolina had 21 producers, of which 12 were placers.

"The following table shows concisely the quantity of ore sold or treated and the recoverable metals of the Eastern or Appalachian States in 1914:

| | | | |
|---|---|---|---|
| Ore sold or treated | 1,842,890 short tons | Copper | 19,555,362 lbs. |
| Gold | $173,589 | Lead | 254,000 lbs. |
| Silver | 100,727 fine ozs. | Zinc | 169,716,954 lbs. |
| | | TOTAL VALUE | $11,437,707" |

**The Production of Manganese and Manganiferous Ores in 1914.** D. F. HEWETT. Mineral Resources, Part I, 165–81. Separate published August 21. "The production of manganese ores for 1914 was 2,635 tons, which represents a decline of 1,413 tons from that of 1913, although it compares favorably with the average production of the five preceding years, 2,394 tons. The production of all grades of manganiferous ores was 445,827 tons, of which 60,414 tons contained more than 15 per cent of manganese, and was used in the manufacture of low-grade ferromanganese and manganiferous pig iron. The production of this class of ore in 1913 was 672,146 tons, of which 35,850 contained more than 15 per cent manganese.

"Imports of manganese ore declined 61,796 tons—from 345,090 tons in 1913 to 283,294 tons in 1914. Imports from Russia were only about two-fifths of those of the preceding year on account of Turkey entering into the war in October and the closing of the Dardanelles to Russian traffic, and imports from India declined about 30 per cent. This decrease was partly offset by the increased importation from Brazil.

"With the manganese alloys, the imports of ferromanganese decreased 35 per cent, although there was an increase in the imported tonnage of spiegeleisen. The prices of these materials have undergone great fluctuations during the year.

"For several months prior to August 1 the price of standard 80 per cent ferromanganese was constant at about $40 a ton. During August prices ranged from $110 to $140 a ton, and although the material was quoted as low as $62 in November, the price advanced to $80 in December."

The marketed production and imports into the United States of manganese alloys and ores from important foreign sources in 1914 were:

| Long tons | Ferromanganese | Spiegeleisen | Manganese ore |
|---|---|---|---|
| Production | 100,731 | 76,625 | 2,635 |
| Imports | 82,997 | 2,870 | 283,294 |

**The Production of Bauxite and Aluminum in 1914.** W. C. PHALEN. Mineral Resources, Part I, 183–209. Separate published September 9. "The production of bauxite in the United States in 1914 was 219,318 long tons, valued at $1,069,194, an increase of 9,077 tons, or 4.3 per cent, in quantity, and of $71,496, or 7.1 per cent, in value, as compared with the production in 1913.

"The states which produced bauxite were, as usual, Alabama, Arkansas, Georgia, and Tennessee. Arkansas was the largest producer, owing to the extensive operations of the American Bauxite Company in Saline County.

"The average price of bauxite per long ton at the mines was, in 1914, $4.87."

A consideration of the world's production shows that the United States far exceeded all other producers except France, for which no statistics are available.

"The chief uses of bauxite were outlined in this report for 1913, as follows: (1) As raw material in the production of metallic aluminum; (2) in the manufacture of aluminum salts; (3) in the manufacture of bauxite bricks; (4) in the manufacture of alundum (fused alumina) for use as an abrasive. The use of bauxite in the manufacture of calcium aluminate to give a quick set to plaster compositions should be added, as well as the extended use which alundum is finding in the refractory industries."

The methods for preparing pure alumina from bauxite are described.

The 1914 consumption of aluminum amounted to 79,000,000 lbs.; during the same period the world's production was 45,700 metric tons. The exports were valued at $1,550,000.

A discussion is included as to the sources of alumina and aluminum other than bauxite and particular attention is given to the preparation of aluminum from alunite. The aluminum market conditions are also reported and uses of the metal and its alloys discussed.

**Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1914.** CHARLES W. HENDERSON. Mineral Resources, Part I, 211–38. Separate published September 23. (Mines Report.) "The value of the production of gold, silver, copper, lead, and zinc from New Mexico ores and gravels for 1914, as reported from 139 productive mines, 24 of which were placers, amounted to $11,049,932. As compared with $11,694,002 in 1913, this shows a decrease in value for 1914 of $644,070. The gold yield was 56,680.79 fine ozs., valued at $1,171,696, an increase in 1914 of 14,017.62 fine ozs. in quantity and of $289,770 in value. The yield of silver was 1,777,445 fine ozs., valued at $982,927, an increase of 146,172 fine ozs. in quantity, but a decrease of $2,362 in value. The copper output was 59,307,925 lbs., an increase in 1914 of 2,999,219 lbs., the lead output (calculated as lead in lead bullion and lead in zinc-lead oxide) was 18,403,392 lbs., an increase of 1,880,231 lbs. The value of the base metals showed a decrease of $839,896 for copper, a decrease of $104,858 for lead, and an increase of $13,276 for zinc (valued at the average yearly price of spelter for each year)."

**Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1914.** CHARLES W. HENDERSON. Mineral Resources, Part I, 239–54. Separate published September 24. (Mines Report.) "The total value of the production of gold, silver, and lead in South Dakota in 1914, as reported from 30 productive mines, 10 of which were placers, amounted to $7,431,343. This is an increase of only $7,010 over the yield of 1913. The gold output in 1914 was 354,758.45 fine ozs., valued at $7,333,508, nearly 99 per cent of the total value. The increase in gold yield for the year was 687.60 fine ozs. in quantity and $14,214 in value. The production of silver also increased from 172,702 to 176,642 fine ozs. Smelting ore from South Dakota carried no copper and only 3,897 lbs. of lead, against 1,793 lbs. of copper and 10,205 lbs. of lead in 1913. The output of placer gold amounted to only 68 ozs.

"The consumption of quicksilver and cyanide in South Dakota mills in 1914 was 13,500 lbs. of quicksilver,[1] 89,649 lbs. of potassium cyanide,[2] and 425,397 lbs. of sodium cyanide.[2]

"The total value of the production of gold, silver, and copper in the State of Wyoming in the calendar year 1914 was only $7,387 as against $84,474 in 1913."

**Gold, Silver, Copper, Lead, and Zinc in Colorado in 1914.** CHARLES W. HENDERSON. Mineral Resources, Part I, 255–313. Separate published October 16. (Mines Report.) "The total value of the production of gold, silver, copper, lead, and zinc in Colorado in 1914, as reported from 866 mines, of which 35 were placers, amounted to $33,460,126, as compared with $35,450,585 in 1913, a decrease of $1,990,459. Of the total value 59 per cent represented gold, the output of which was $19,883,105, an increase of $1,736,189, as compared with the yield of 1913. There was a decrease in silver output of 529,190 fine ozs. The production of copper, which is merely incidental to the recovery of other metals, decreased 588,653 lbs. The quantity of lead produced in 1914 was 74,211,898 lbs., a decrease of 13,685,875 lbs. The quantity of zinc produced was 96,774,960 lbs., a decrease of 22,571,469 lbs."

**Quicksilver in 1914: Production and Resources.** H. D. MCCASKEY. Mineral Resources, Part I, 315–22. Separate published October 12. "Complete and revised figures for 1914 of the United States Geological Survey gives a domestic production of 16,548 flasks, valued at $811,680, of which 11,303 flasks were produced in California and 5,245 flasks came from Arizona, Nevada, and Texas, combined.

"The prevailing prices of quicksilver from January to July, 1914, inclusive, were so low that there was little profit in the industry, and undoubtedly many properties were worked at a loss and others were worked at reduced capacity, if not actually closed down; but upon the outbreak of the European war the prices rose so high that producers in a position to profit were encouraged to make their maximum output. The total productive capacity of the country, as at present known, is by no means unlimited, and although high prices may bring increased activity and new ore bodies may at any time be discovered, the outlook is not for excessive domestic production. These facts, the present difficulties in receiving supplies from Europe, and the improbability of large imports from any surplus stocks in Mexico, indicate high prices throughout the war at least."

The uses of quicksilver are discussed.

**The Production of Platinum and Allied Metals in 1914.** JAMES M. HILL. Mineral Resources, Part I, 333–52. Separate published October 18. "In 1914 California produced 463 ozs. of crude platinum which was about 80 per cent fine—that is, it contained 350 ozs. of refined platinum-group metals—and Oregon produced 107 ozs. of crude platinum considered 70 per cent fine, containing 75 ozs. refined platinum-group metals. The total of 570 ozs. crude sands sold for $18,240, or approximately $32.00 an oz.

"During 1914 the average price per troy oz. of the various platinum-group metals was approximately as shown below, which figures have been used by the United States Geological Survey in all computations:

| | | | |
|---|---|---|---|
| Platinum | $45.00 | Iridosmine (osmiridium) | $33.00 |
| Iridium | 65.00 | Palladium | 44.00 |

"No quotations of prices of the remaining metals of the platinum group—osmium, rhodium, and ruthenium—are available, and probably any sales were private. These metals are scarce and have little commercial use, and it seems probable that very small quantities, if any, were marketed in 1914.

"The world's output of new platinum is given approximately in the following table:

| | |
|---|---|
| Russia, crude *a* | 244,200 |
| Canada, crude *a* | 50 |
| New South Wales and Tasmania, crude *b*, *a* | 1,248 |
| Colombia, crude(*a*) | 17,500 |
| United States, domestic crude | 570 |
| United States, refined from foreign and domestic matte and bullion | 2,905 |
| Borneo and Sumatra and other crude(*d*) | (*e*) |
| Total | 263,453 |

(*a*) Estimated.
(*b*) Chiefly iridosmine.
(*c*) Does not include refined platinum from domestic crude.
(*d*) Includes small production in Madagascar.
(*e*) No basis for estimate."

**Gold, Silver, Copper, Lead, and Zinc in California and Oregon in 1914.** CHARLES G. YALE. Mineral Resources, Part I, 353–414. Separate published October 30. (Mines Report.) "There was a decrease in California in 1914 in number of productive mines, in total quantity of ore treated, and in output of copper and zinc, but an increase in yield of gold, silver, and lead, the total value of the output for the year being $1,101,842 less than in 1913. The value of the gold increased $246,538, the silver increased by 93,460 ozs., and the lead by 737,581 lbs. The decline in copper was 4,067,315 lbs., and in zinc, 668,014 lbs."

**The Production of Asbestos in 1914.** J. S. DILLER. Mineral

Requirement: 1 lb. of mercury per 16.20 ozs. of gold, or 1 lb. of mercury per 117 tons of ore.

[2] Potassium and sodium cyanide were used at a ratio of 0.26 lb. of cyanide per ton of ore or tailings treated, and for every lb. used there was recovered 0.259 oz. of gold.

Resources, Part II, 93–102. Separate published July 20. "The total asbestos mined and sold in the United States in 1914 was 1,247 short tons, valued at $16,810 a gain as compared with 1,100 short tons, valued at $11,000 in 1913, of 13 per cent in quantity and of more than 52 per cent in value.

"Nearly all the asbestos sold in the United States comes from Canada, and it is evident that the Canadian market controls prices in this country. The range in prices of the various grades of Canadian fiber in New York is shown in the accompanying table:

| | | | |
|---|---|---|---|
| No. 1 crude | $350–375 | No. 1 fiber | $100–125 |
| No. 2 crude | 225–250 | No. 2 fiber | 75–100 |
| | | Shorter fibers | 10– 30 |

"The average price of the Arizona crude No. 1 and No. 2 in New York should accord closely with Canadian crude of the same grades. The price of crude fiber continued to rise during the early months of 1915. The amphibole variety averaged nearly $10 a ton in 1914."

**The Production of Mineral Paints in 1914.** JAMES M. HILL. Mineral Resources, Part II, 103–22. Separate published July 21. "The mineral paints treated in this chapter are divided into three groups—(1) natural mineral pigments, (2) pigments made directly from ores, and (3) chemically manufactured pigments.

"The total quantity and value of pigments sold during 1914 and considered in this report were greater than in 1913. There was a slight decrease in the production of the natural mineral pigments, but in both the other classes there was a marked increase in output. The output of the pigments made directly from ores increased 9.45 per cent and the production of pigments made chemically increased about 12.09 per cent. The decrease in the quantity of natural mineral pigments amounted to 5.4 per cent.

"The following table shows the total marketed production of the three groups of pigments for 1914:

| | Short tons | Value |
|---|---|---|
| Natural mineral pigments | 66,766 | $473,036 |
| Pigments made directly from ores | 106,791 | 9,978,710 |
| Chemically manufactured pigments | 246,206 | 27,630,829 |
| TOTAL | 419,763 | $38,082,575 |

"The following table gives the marketed production and value of the natural pigments during 1914, and price per ton at point of production:

| PIGMENT | Short tons | Value | Price per ton |
|---|---|---|---|
| Ocher | 14,387 | $136,185 | $ 9.47 |
| Umber and sienna | 790 | 21,070 | 26.67 |
| Metallic paint | 30,947 | 179,653 | 5.81(a) |
| Mortar colors | 5,371 | 47,723 | 8.88 |
| Slate and shale, ground | 15,271 | 88,405 | 5.79 |
| TOTAL | 66,766 | $473,036 | |

(a) Includes crude iron ore sold for paint, which accounts in part for the low value per ton.

"This table represents approximately the output of natural mineral pigments; the figures are the best obtainable under present conditions but are known to be inaccurate, probably being at least 25 per cent below the actual output.

"The prices per ton of metallic paints and mortar colors apparently advanced 12 cents and $2.26, respectively. The other pigments decreased in price, the decrease being 12 cents for umber and sienna, 82 cents for ground slate and shale, and 43 cents for ocher.

"In order to conceal individual returns, the statistics of production of zinc oxide, leaded zinc, and of white lead and blue lead produced by sublimation have to be combined. The total quantity of these pigments marketed amounted in 1914 to 106,791 short tons, valued at $9,978,710. As compared with the production of 1913, this was an increase of 9,218 tons, or 9 per cent in quantity and of $957,814, or 10 per cent in value.

"The chemically manufactured pigments treated in this report include basic carbonate white lead, both dry and in oil, red lead, litharge, and orange mineral among the lead pigments, and lithopone and Venetian red. The last two pigments contain no lead, but are chemically precipitated pigments.

"The following table shows the marketed production and value of chemically prepared pigments during 1914:

| PIGMENT | Short tons | Value |
|---|---|---|
| Basic carbonate of white lead { In oil | 130,398 | $16,983,587 |
| Basic carbonate of white lead { Dry | 29,076 | 2,959,652 |
| Red lead | 18,697(a) | 2,151,054 |
| Litharge | 27,345 | 2,856,092 |
| Orange mineral | 426 | 70,019 |
| Lithopone | 32,819 | 2,490,530 |
| Venetian red | 7,445 | 119,895 |
| TOTAL | 246,206 | $27,630,829 |

(a) A small quantity of orange mineral is included with red lead."

**The Production of Fluorspar in 1914 with a Note on Cryolite.** ERNEST F. BURCHARD. Mineral Resources, Part II, 123–9. Separate published July 26. "The total quantity of domestic fluorspar reported to the Survey as marketed in 1914 was 95,116 short tons, valued at $570,041, as compared with 115,580 short tons, valued at $736,286, marketed in 1913, a decrease in quantity of 20,464 short tons and in value of $166,245. This decrease represents 17.7 per cent of the quantity and about 22.5 per cent of the value of the product marketed in 1913. The average price per ton for the whole country, considering all grades of fluorspar—gravel, lump, and ground—was approximately $5.99 in 1914, as compared with $6.37 in 1913, a decrease of 38 cents a ton, or about 5.97 per cent. This value represents the selling price on board cars or barges at railroad or water shipping points.

"No cryolite is produced in the United States, the entire supply used in this country being imported from Ivigtut, an Eskimo hamlet on the southern coast of Greenland.

"The quantity of cryolite reported to have been imported for consumption in the United States in 1914 was 4,612 long tons, valued at $94,424, as compared with 2,559 long tons, valued at $55,557, in 1913. The average price per ton declared in 1914 was apparently $20.47 as compared with $20.54 in 1913. Cryolite is now imported free of duty."

**Sulfur, Pyrite, and Sulfuric Acid in 1914.** W. C. PHALEN. Mineral Resources, Part II, 131–49. Separate published July 26.

"The marketed production of sulfur in the United States in 1914 was 327,634 long tons, valued at $5,954,236. Compared with the quantity of sulfur marketed in 1913, which was 311,590 long tons, valued at $5,479,849, this is an increase of 16,044 long tons in quantity and of $474,387 in value.

"The table of imports given shows that in 1914 there were imported for consumption 26,135 long tons of sulfur, valued at $477,937. In this figure are included imports of all classes of sulfur—crude, refined, flowers of sulfur, and grades not specifically described. . . . . The crude sulfur imported came almost entirely from Japan. The imports from Sicily have become practically negligible, having amounted in 1914 to only 3 per cent of the imports of crude sulfur. The Japanese product enters chiefly at the Pacific coast ports.

"The marketed production of pyrite in the United States in 1914 amounted to 336,662 long tons, valued at $1,283,346, compared with 341,338 long tons, valued at $1,286,084 in 1913—a reduction of 4,676 long tons or 1.4 per cent in quantity, and of $2,738 or one-fifth of 1 per cent in value.

"The pyrite imported into the United States in 1914 amounted to 1,026,617 long tons, valued at 4,797,236, an increase of 176,025 long tons in quantity and of $1,186,189 in value, as compared with imports in 1913. It is very evident from these

figures that there has been no shortage in the supply of foreign pyrite on account of the war in Europe.

"In the following table the quantity, value, and price per ton are given of the three main grades of acid, and also similar data for other strengths of acid combined:

| Grade | Short tons | Value | Price per ton |
|---|---|---|---|
| 50° Baumé | 1,628,402 | $9,712,056 | $ 5.96 |
| 60° Baumé | 581,955 | 3,476,242 | 6.12 |
| 66° Baumé | 916,192 | 10,509,471 | 11.47 |
| Other grades | 65,890 | 882,158 | 13.39 |
| Total | 3,162,439 | 24,479,927 | 7.74 |
| Total reduced to 50° Baumé acid(a) | 3,762,417 | 24,163,331 | 6.42 |

(a) Exclusive of 21,993 short tons of fuming acid, not convertible, valued at $316,596.

"In the following table is given the quantity of sulfuric acid recovered from the gases from smelters throughout the United States. By comparison with the preceding table it will be observed that this is approximately 25 per cent of the total acid produced in the United States during the year 1914. The figures given in the table, however, do not include acid manufactured from copper-bearing Spanish pyrite:

| Source(a) | Short tons | Value | Price per ton |
|---|---|---|---|
| Copper smelters | 348,727 | $2,215,690 | $6.35 |
| Zinc smelters | 411,911 | 2,974,603 | 7.22 |
| Total | 760,638 | $5,190,293 | $6.82 |
| Total acid reduced to 50° Baumé. | 950,798 | ..... | ... |

(a) The acid reported to the Survey includes that of 50°, 53°, 55°, 60°, and 66° Baumé strengths, and a small quantity of electrolyte and oleum. All strengths, with the exception of the electrolyte, have been reduced to both 50° and 60° Baumé, as given in the table."

**The Production of Talc and Soapstone in 1914.** J. S. Diller. Mineral Resources, Part II, 151–7. Separate published July 30. "The United States produces more talc and soapstone than all the rest of the world combined. The domestic output has nearly doubled in the last decade, and the comparatively uniform development of the industry indicates its stability and gives promise for continued increasing demand.

"The total marketed production of talc and soapstone in the United States in 1914 was 172,296 short tons, a decrease of 2 per cent as compared with the production of 1913. Rhode Island and Maryland in 1914 produced soapstone alone. The other states, except North Carolina, Vermont, and Virginia, produce talc only."

**The Production of Graphite in 1914.** Edson S. Bastin. Mineral Resources, Part II, 159–74. Separate published August 20. "Graphite (both natural and manufactured) produced in the United States in 1914 was approximately 73 per cent, by value, of that imported for consumption. Of the domestic production about one-third, by value, was natural graphite and two-thirds manufactured graphite.

Production of Natural Graphite, 1914 ]

| | Quantity | Value |
|---|---|---|
| Amorphous (short tons) | 1,725 | $38,750 |
| Crystalline (pounds) | 5,220,539 | 285,368 |
| Total (short tons) | 4,336 | 324,118" |

**The Production of Mineral Waters in 1914.** R. B. Dole. Mineral Resources, Part II, 175–219. Separate published August 20. "Though reports were received for the first time from 78 springs, the active springs were fewer and the production and value of both medicinal and table water were less in 1914 than in 1913. The total quantity sold in 1914 was 54,358,466 gals., valued at $4,892,328, whereas in 1913 the sales were 57,867,399 gals., valued at $5,631,391. The decrease in production was 3,508,933 gals., or 6 per cent, and the decrease in value was $739,063, or 13 per cent."

This report includes also a historical sketch of the mineral water trade and full information regarding producers in each state.

**The Cement Industry in the United States in 1914.** Ernest F. Burchard. Mineral Resources, Part II, 221–59. Separate published August 23. "The total quantity of Portland, natural, and puzzolan cement marketed, or shipped from the mills in the United States, in 1914, was 87,257,552 bbls., valued at $80,533,203, as compared with 89,541,348 bbls., valued at $89,550,527, in 1913. This represents a decrease in quantity of 2,283,796 bbls., or nearly 2.6 per cent, and in value of $9,017,324, or 10.1 per cent.

"In the following table the production of Portland cement in the United States is classified according to the kinds of raw materials from which the cement is manufactured.

| | Barrels | Percentage |
|---|---|---|
| Type 1—Cement rock and pure limestone | 24,907,047 | 28.2 |
| Type 2—Limestone and clay or shale | 50,168,813 | 56.9 |
| Type 3—Marl and clay | 4,038,310 | 4.6 |
| Type 4—Blast-furnace slag and limestone | 9,116,000 | 10.3" |

**The Gypsum Industry in 1914.** G. F. Loughlin. Mineral Resources, Part II, 261–70. Separate published August 23. "The production of gypsum in 1914 was marked by a decrease in quantity but an increase in value, the latter due to a strong advance in the price of calcined gypsum which more than offset a decline in price of crude gypsum, so that the total value broke all previous records.

"The number of short tons of raw gypsum mined in 1914 was 2,476,465, a decrease of 123,043 tons from the 2,599,508 tons mined in 1913. The gypsum sold without calcining and used principally as an ingredient in Portland cement, in paint, and as land plaster, amounting to 443,687 short tons and valued at $646,799, showed a decrease in quantity of 19,449 tons and in value of $50,267, as compared with 463,136 short tons, valued at $697,066, in 1913. The material calcined for plaster decreased in quantity 117,783 short tons, but increased in value $171,434. The total value of gypsum and gypsum products produced in 1914 was $6,895,989, as compared with $6,774,822 in 1913, an increase of $121,167."

**The Production of Sand and Gravel in 1914.** G. F. Loughlin. Mineral Resources, Part II, 271–83. Separate published August 26.

**The Production of Borax in 1914.** Charles G. Yale and Hoyt S. Gale. Mineral Resources, Part II, 285–90. Separate published September 4. "In 1914 the production of crude borate materials in the United States was 62,400 short tons, valued at $1,464,400, as compared with 58,051 short tons in 1913, valued at $1,491,530, an increase of 7.49 per cent in quantity and a decrease of 1.82 per cent in value. All of the crude borate material now used in this country is the mineral colemanite (calcium borate), and the output in 1914 was from three mines in southern and southeastern California. The value of the product given is estimated on a basis of $1 per unit per cent of anhydrous boric acid (boron trioxide, $B_2O_3$) in the raw material, which basis is believed to approximate very closely the price of the ore at the time or point of shipment.

"According to the available statistics concerning the world's production of borates, or basic acid and borax, prior to 1914, it appears that Chile and the United States lead the industry with approximately equal output of these materials."

**The Production of Salt, Bromine, and Calcium Chloride in 1914.** W. C. Phalen. Mineral Resources, Part II, 291–306. Separate published September 20. "The marketed production of salt in the United States in 1914, including Porto Rico, was 34,804,683 bbls. of 280 lbs. each, or 4,872,656 short tons, valued at $10,271,358, an increase in 1914 of 405,385 bbls., or 56,754 short tons, or 1.18 per cent in quantity and of $148,219, or 1.46 per cent in value.

"The production of bromine during 1914 amounted to 577,000 lbs., valued at $203,000.

"In connection with the salt and bromine industry in Michigan, Ohio, and West Virginia, a considerable quantity of the calcium chloride contained in the natural brines is recovered."

# BOOK REVIEWS

**Test Methods for Steam Power Plants.** By EDWARD H. TENNEY, B.A., M.E. D. Van Nostrand Co. Price, $2.50 net.

This book forms a valuable addition to the testing or operating engineer's library. It emphasizes the chemical side of power-plant testing which has heretofore been more or less neglected in books on this subject.

The first chapter takes up the purchase of coal on the B. t. u. basis and the percentage of ash basis, and describes clearly the methods of sampling, making proximate and ultimate analyses, and determining the heat value of coal. It also describes the methods used in determining the calorific value of the combustible matter left in the ash.

The second chapter deals with the chemistry of combustion and the requirements for furnace and boiler economy and describes some of the tests necessary to check the operations occurring in the furnace. In this chapter the writer expounds a rather novel theory as to the reason for the benefit derived in the combustion of certain grades of coal, from the presence of surface moisture. No mention is made of the influence on clinker formation of the chemical combination of impurities in the fuel with constituents of the furnace lining. It is unfortunate that this subject was omitted as it has an important bearing on the economy of a plant on account of its intimate relation to the cost of maintaining the furnaces.

The third chapter gives an unusually clear and concise description of the various salts that cause trouble in boiler feed-waters and the established methods used in determining their presence and in removing them from the water. It, however, fails to mention several methods that differ decidedly from the standard lime and soda ash methods. These methods have recently been widely advertised and engineers would appreciate reliable information about them.

The fourth and fifth chapters, on capacity and efficiency and operating tests of steam boilers and prime movers, deal briefly with the methods and apparatus used in making these tests. The amount of space devoted to apparatus for flue gas analysis is rather out of proportion to the rest of Chapter IV. Exception will be taken by most engineers to the statement in Chapter V that "Determinations with the flow meter, especially on large units, are more reliable than those made by actual measurement of the condensation in calibrated tanks." Some space might well have been devoted to the method of obtaining the derived results given in the "Typical Engine Test Report" and the turbine test given in this chapter. In the paragraph titled "Estimation of the Amount of Steam from Indicator Diagram," more emphasis should have been placed on the fact that the formula there stated gives absolutely no idea of the actual amount of steam used by the engine. The method described for testing indicator springs is faulty in that the standard used is the steam gauge which itself is subject to error. The paragraphs on the testing of condensers, oiling systems and ventilating systems is one of value.

Chapter VI gives in very concise form some excellent information with regard to the value of different classes of lubricants and the methods of testing the same. The tables given in the appendix are well selected.

A valuable feature of the book is the well selected list of references at the end of each chapter.

With the increased interest now taken by operating engineers in the boiler room as including a factory for the chemical production of heat on a large scale, this book with its emphasis on the chemical side of power-plant testing is very opportune.

G. B. PRESTON

**The Raw Materials for the Enamel Industry and Their Chemical Technology.** By J. GRUENWALD, translated by H. H. Hodgson. London: C. Griffin & Co. 225 pp. 8s., 6d.

The enameled iron industries are showing a remarkable growth and are daily increasing in importance. The literature dealing with the problems in this field of technology is meagre and has been confined chiefly to the pages of *Sprechsaal* and the *Transactions of the American Ceramic Society*. The present volume deals with the sources and methods of preparation of the many constituents entering into the composition of enamels such as clay, quartz and flint, feldspar, fluorspar, cryolite, soda ash, the lead compounds, whiting, tin oxide, antimony oxide, cobalt oxide, etc. The task has been well done and a comprehensive store of information is offered to the readers interested in this topic. The author has not confined himself to the subject of his title, but introduces information dealing with the application of the enamels throughout the book.

Mooted questions such as the function of cobalt oxide in the ground coat are discussed, as well as the methods of grinding, length of storage, etc. Reference is made to the properties of the enamels such as the coefficient of expansion and the work of Mayer and Havas is quoted fully.

The topic of the composition of the enamels is touched upon, but here the writer confines himself chiefly to the literature quoting the work of Vondrácek, Shaw, Staley and others. No attempt has been made to reduce this information to its simplest terms. A set of useful tables has been appended. The book undoubtedly is a valuable addition to the literature and should be indispensable to the workers in this field. It has made available information which hitherto could be found only in the pages of journals accessible to few.

A. V. BLEININGER

**Purchasing: Its Economic Aspect and Proper Methods.** By H. B. TWYFORD, of Otis Elevator Co., with charts, diagrams and forms. New York: D. Van Nostrand Co. Price, $3.00.

The author of this most interesting book has evidently had large experience as a buyer. As he points out, very few works have been produced on this subject, yet it is one of the most important factors in any business. For, as he says, regulated and right buying is a study in economics and vast savings can be effected by efficient and proper methods of performing this vital function. Perhaps the author has the frame of mind to consider the functions of the purchasing agent somewhat too seriously. Most purchasing agents apparently do feel that the works or institutions would go to ruin if the purchasing agent did not hold his protecting arms around the business affairs. Fortunately most works and institutions do have heads of departments, superintendents, foremen, etc., who intelligently try to hold down the outlay to a judicious point.

The author gives valuable information about ways of getting the best prices. He would depend upon competitive bids only partially, and largely would secure good prices by a study of market conditions. He gives many satisfactory forms for records, methods of checking bills with goods, etc. Methods as to office organization and as to plans for keeping of stock are intelligently discussed.

The book is well written and is altogether very readable and instructive to any one having to perform the functions of a purchasing agent.

THOS. B. FREAS

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Alcoholic Fermentation: Chemie der Hefe und der alkoholischen Gaerung.** By HANS EULER AND PAUL LINDNER 8vo 350 pp Price, $4.00. Akademische Verlagsgesellschaft, Leipzig.

**Analysis: Brief Course in Metallurgical Analysis.** By H ZIEGEL 4to 72 pp Price $4.00 Chemical Publishing Co., Easton.

**Analysis: Qualitative and Volumetric Analysis.** By W. M. HOOTON. 8vo 90 pp Price $1.00 E Arnold London.

**Analytical Chemistry. Vol. 2. Quantitative Analysis.** By F. V. TEGDWELL AND W T HALL 4th Ed 8vo. 926 pp Price, $3.50 J Wiley & Sons New York

**Catalysis: Die Katalyse. Part 2. Spezieller Teil.** By GERTRUD WOKER. 8vo. 789 pp. Price, $7.00. F. Enke, Stuttgart.

**Chemistry. By F. P. ARMITAGE 8vo Price, $0.25 Longmans, Green & Co., New York.**

**Chemistry: Chemie und Chemikalienkunde fuer Drogisten.** By C. A. PETZOLD. 4th Ed. 346 pp. Price, $1.00. A. L. Herrmann, Berlin.

**Chemistry: Lehrbuch der Chemie.** By A. F. HOLLEMAN. 12th Ed. 8vo. 492 pp. Price, $2.50. Veit & Co., Leipzig.

**Chemistry: Outlines of Chemistry.** By L. KAHLENBERG. 8vo. 578 pp. Price, $2.60. Macmillan Co., New York.

**Chemistry: A Practical Elementary Chemistry.** By B. W Mc FARLAND. 12mo. 462 pp. Price, $1.25. Charles Scribner's Sons, New York.

**Concrete: Simplified Reinforced Concrete Mathematics.** By M. D. CASLER. 12mo. 66 pp. Price, $1.25. D. Van Nostrand Co., New York.

**Cork: Its Origin and Industrial Uses.** By G. E. STECHER. 8vo. Price, $1.25. E. and F. N. Spon, London.

**Economic Geology.** By H. RIES. 2nd Ed. 8vo. 722 pp. Price, $4.00 J. Wiley & Sons, New York.

**Explosives: Industrial Nitrogen Compounds and Explosives.** By GEOFFREY MARTIN. 8vo. 134 pp. Price, $2.00. Crosby Lockwood, London.

**Fluids: An Introduction to the Mechanics of Fluids.** By E. H. BARTON. 8vo. 249 pp. Price, $1.75. Longmans, Green & Co., New York.

**Forging of Iron and Steel.** By W. A. RICHARDS. 12mo. 219 pp. Price, $1.50. D. Van Nostrand Co., New York.

**Heating: District Heating.** By S. M. BUSHNELL AND F. B. ORR. 8vo. Price, $3.25. E. and F. N. Spon, London.

**Heat-Power: Answers to Problems in "Elements of Heat-Power Engineering."** By C. F. HIRSCHFELD. 8vo. 4 pp. Price, $0.10. J. Wiley & Sons, New York.

**Highway Engineering.** By A. H. BLANCHARD. 8vo. 350 pp. Price, $2.50. J. Wiley & Sons, New York.

**Inorganic Chemistry: Gmelin und Kraut's anorganische Chemie.** By FRIEDHEIM AND PETERS. 7th Ed. 189 pp. Price, $0.50. Carl Winter, Berlin.

**Iron Metallurgy: Lehrbuch der Eisenhuettenkunde.** Vol. 1. By B. OSANN. Price, $7.25. W. Engelmann, Leipzig.

**Machine Design.** By A. W. SMITH AND G. H. MARX. 4th Ed. 8vo. 500 pp. Price, $3.00. J. Wiley & Sons, New York.

**Materials: The Elements of Mechanics of Materials.** By C. E. HOUGHTON. 2nd Ed. 12mo. 216 pp. Price, $2.00. D. Van Nostrand Co., New York.

**Metallurgy.** By HENRY WYSOR. 2nd Ed. 8vo. 391 pp Price, $3.00. Chemical Publishing Co., Easton.

**Mineralogy:** Third Appendix to the Sixth Edition of Dana's System of Mineralogy. By E. S. DANA. 8vo. 87 pp. Price, $1.50. J. Wiley & Sons, New York.

**Mineralogy: Jahrbuch fuer Mineralogie.** 40 Beilageband. 2 Heft. Price, $4.00. Schweizerbart, Stuttgart.

**Mineralogy: Practical Geology and Mineralogy.** By W. D. HAMMAN. Revised Ed. 12mo. 253 pp. Price, $2.50. Way Press, S. Pasadena, Cal.

**Minerals: Handbuch der Mineralchemie.** Vol. 2. By C. DOELTER. 8vo. Price, $1.50. Theodor Steinkopff, Dresden.

**Organic Chemistry: Laboratory Experiments on the Class Reactions and Identification of Organic Substances.** By A. A. NOYES AND M. S. PARSONS. 3rd Ed. 12mo 31 pp Price, $0.50 Chemical Publishing Co., Easton.

**Organic Chemistry: Practical Organic and Biochemistry Chemistry.** By R. H. A. PLIMMER. 4to 635 pp Price $3.60. Longmans, Green & Co., New York.

**Painting by Immersion and by Compressed Air.** By A. S. JENNINGS. 8vo. 267 pp. Price, $2.75. E. and F. N. Spon, London.

**Petrol Engine.** By F. J. KEAN. 8vo. 140 pp. Price, $1.00. E. and F. N. Spon, London.

**Physical Chemistry: Lehrbuch der physikalischen Chemie.** Vol. 2 By KARL JELLINEK 8vo 939 pp Price, $8.00. F. Enke, Stuttgart.

**Potash: Its Distribution, Commercial Sources and Agricultural Value.** By A. SMETHAM. 8vo. Toulmin, Preston.

**Structures: The Theory of Structures.** By C. M. SPOFFORD. 2nd Ed 8vo 483 pp Price, $4.00. McGraw-Hill Book Co., New York.

**Tables: Logarithmische Rechentafeln fuer Chemiker, Pharmazeuten, Etc.** By F. W. KUESTER. 15th Ed. 8vo. 107 pp. Price, $0.60. Veit & Co., Leipzig.

**Thermodynamics: Einfuehrung in die Thermodynamik.** By R. BLONDOT. Tr. from the 2nd French Ed. 8vo. Price, $1.00. Theodor Steinkopff, Dresden.

## RECENT JOURNAL ARTICLES.

**Aluminum: Recovering Aluminum Chips by Melting.** By H. W. GILLETT. *Iron Trade Review*, Vol. 57 (1915), No. 20, pp. 942-943.

**Asphalt: Chemie der Asphalte.** By PAUL GOEDRICH. *Monatshefte fuer Chemie*, Vol. 36 (1915), No. 6/7, pp. 535-548.

**Case Hardening: Materials Employed in Case Hardening.** By R. A. MILLHOLLAND. *The Iron Age*, Vol. 96 (1915), No. 19, pp. 1041-1042.

**Cellulose: Applications of Cellulose in the Arts.** By A. D. CONLEY. *Paper*, Vol. 18 (1915), No. 8, pp. 17-19.

**Copper-Nickel Ore: Ueber die Roestung von Kupfernickelerzen.** By H. MANZ. *Chemiker-Zeitung*, Vol. 39 (1915), No. 111, pp. 693-694.

**Crushing: Coarse-Crushing Plant of 1000 Tons Capacity.** By G. O. BRADLEY. *Mining and Scientific Press*, Vol. 111 (1915), No. 16, pp. 592-598.

**Cyanide Plant Design.** By S. A. WORCESTER. *Engineering and Mining Journal*, Vol. 100 (1915), No. 16, pp. 631-633.

**Essential Oils: Fortschritte auf dem Gebiet der Chemie der aetherischen Oele und Riechstoffe.** By A. RECLAIRE. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 72, pp. 369-374.

**Fertilizing Theories before Liebig.** By C. ELSCHNER. *The American Fertilizer*, Vol. 43 (1915), No. 8, pp. 25-28.

**Flotation: Why Do Minerals Float?** By O. C. RALSTON. *Mining and Scientific Press*, Vol. 111 (1915), No. 17, pp. 623-627.

**Glass: Die Beurteilung der Alkali-Kalk-Glaeser nach der Tscheuschner'schen Formel.** By J. KOERNER. *Sprechsaal*, Vol. 48 (1915), No. 38, pp. 333-334.

**Glass: The Relation of Chemistry and Mechanical Manipulation to the Evolution of the Glass Industry.** By R. L. FRINE. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 13, pp. 800-802.

**Hydrocellulose: Ueber die Hydrocellulose.** By O. HAUSER AND H HERZFELD. *Chemiker-Zeitung*, Vol. 39 (1915), No. 109-110, pp. 689-690.

**Iron: Carburizing Iron in Blast Furnace Gases.** By T. H. BYROM. *Steel and Iron*, Vol. 49 (1915), No. 28, pp. 1001-1003.

**Iron: Das Gluehen von Eisen bei der gravimetrischen Eisenbestimmung.** By E. SELCH. *Zeitschrift fuer analytische Chemie*, Vol. 45 (1915), No. 9, pp. 457-463.

**Liquid Jets.** By C. TERRY DU RELL. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 12, pp. 714-716.

**Mercury: The Determination of Mercury in Cyanide Solution and Precipitate.** By W. J. SHARWOOD. *Mining and Scientific Press*, Vol. 111 (1915), No. 18, pp. 663-665.

**Metals: Die Umwandlungen der Metalle.** By E. JAENECKE. *Zeitschrift fuer physikalische Chemie*, Vol. 90 (1915), No. 3, pp. 313-339.

**Nitrogen: Fixation of Atmospheric Nitrogen.** By J. E. CLENNELL. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 12, pp. 756-758.

**Pipes: Wrought-Iron or Steel Pipes.** By L. C. WILSON. *Engineering Magazine*, Vol. 50 (1915), No. 2, pp. 247-254.

**Porcelain: Die Eigenschaften des technischen Porzellans der Berliner koeniglichen Porzellan-Manufaktur.** By R RIEKE. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 72, pp. 374-376.

**Recorders in the Power Plant.** By J. C. SMALLWOOD. *Engineering Magazine*, Vol. 50 (1915), No. 2, pp. 262-275.

**Resins: Die loeslichen Kunstharze und ihre Verwendbarkeit.** By HUGO KUEHL. *Kunststoffe*, Vol. 5 (1915), No. 17, pp. 196-197.

**Sherardizing as a Manufacturing Problem.** By S. TROOD. *Steel and Iron*, Vol. 49 (1915), No. 27, pp. 958-961.

**Textile Fibers: Neurungen in der chemisches Technologie der Spinnfasern.** By R. LOEWENTHAL. *Chemiker-Zeitung*, Vol. 39 (1915), No. 106, pp. 669-670.

**Tin: Fortschritte in der Metallurgie des Zinns und Wolframs waehrend der Jahre 1913-1914.** By HANS MENNICKE *Elektrochemische Zeitschrift*, Vol. 22 (1915), No. 5/6, pp. 101-106.

**Vanadium: The Romantic Story of Vanadium.** By C. J. STARK. *Iron Trade Review*, Vol. 57 (1915), No. 17, pp. 781-784.

# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. Parker

Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Softening Water. K. Schrempp, May 11, 1915. U. S. Pat. 1,139,378.** The water to be softened is subjected to pressure by heating it in a chamber and then suddenly relieving the pressure on the water by passing the latter into a chamber; where the pressure is considerably lower than in the first chamber, insoluble carbonates are precipitated in the second chamber.

**Inalterable White Pigment. R. Bonastre, May 11, 1915. U. S. Pat. 1,139,427.** A pure stable sulfate of zinc solution is treated with an aqueous solution of barium sulfid whereby a lithopone product containing pure stable sulfid of zinc is precipitated. The zinc is dried and calcined at below a red heat out of contact with the air.

**For Recovering Elemental Sulfur from Sulfur-Gases. W. F. Lamoreaux and C. W. Renwick, May 18, 1915. U. S. Pat. 1,140,310.** Sulfur dioxid mixed with atmospheric oxygen is passed through a bed of incandescent carbon and maintained in contact with such carbon for a predetermined period. The increment of heat required to secure practically complete reduction of the sulfur dioxid is secured by passing an electric current through the bed of incandescent carbon.

**Steel. G. E. Weissenburger, May 25, 1915. U. S. Pat. 1,140,550.** A charge of iron low in oxidizable agents is heated within a Bessemer converter until oxidation of the carbon begins. The application of the heat is then discontinued and the blast of air is directed against the charge until substantially all of the oxidizable agents have been eliminated by oxidation.

**Hardening Iron. S. L. Brown, May 25, 1915. U. S. Pat. 1,140,568.** Iron is heated and immersed in a vat of boiling sodium chlorid.

**Flotation of Minerals. R. F. Bacon, May 25, 1915. U. S. Pat. 1,140,865.** Sulfid minerals are separated from associated gangue by subjecting the mixture in a finely divided condition to the flotation action of colloidal sulfur, the flotation solution being produced by the reaction between a soluble sulfid and sulfur dioxid, the sulfur dioxid being admitted in such excess as to make the solution of colloidal sulfur faintly acid.

**Alcoholic Fermentation. R. de Fazi, May 25, 1915. U. S. Pat. 1,140,882.** Sugared liquids and liquids obtained by saccharification from amylaceous substances are exposed to ultraviolet rays during fermentation, yeast being employed which has been cultivated under the action of ultraviolet rays.

**Treating Lead. C. Ellis, June 1, 1915. U. S. Pat. 1,141,177.** Melted lead is forced into two or more streams which are caused to mutually impinge under substantial pressure whereby the metal is comminuted.

**Potash, Etc., from Kelp. S. R. Oppenheim, June 1, 1915. U. S. Pat. 1,141,482.** Dry kelp is placed in a horizontal layer and a flame applied directly to the top of the layer to ignite only the upper portion. The flame is then extinguished and the blazing portion of the kelp allowed to subside to a glowing condition. This combustion is continued by means of a downward draft until the whole charge is charred but not incinerated. The charred mass is then treated to extract the potash.

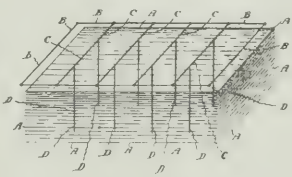
**Treating Cottonseed Meal, Etc. J. G. Falls, June 8, 1915. U. S. Pat. 1,142,243.** The purpose of this process is to produce a palatable food product from cottonseed meats, meal or flour by subjecting them to a temperature sufficiently high to remove their disagreeable odor and flavor.

## BRITISH PATENTS

A. W. Millan, Chemist, Glasgow, Scotland

The following abstracts are taken direct from the patent specifications, as soon as these are published by the British Patent Office. The date given at the end of the abstract is date of acceptance.

**Manufacture of Aluminum Sulfate. J. Boulton, Sept. 26, 1914. Brit. Pat. 20,227.** Crude materials containing alumina are treated with sulfuric acid by a process of electrolysis with the assistance of magnetism. Iron and other impurities are deposited and perfectly clear solutions result. "B" is a system of steel wires which are magnetized before fixing up with the cross wires "C" of copper. Zincs "D" are connected to the copper wires "C" and the whole is immersed in the vat "A" containing the liquors.—July 29, 1915.



**Apparatus and Process for the Purification of Liquids. B. B. Crombie and C. J. A. Dalziel. Oct. 26, 1914. Brit. Pat. 21,513.** This invention relates to an improvement in plant, used for the purification of liquids containing solids in solution or suspension, in which aluminum alloy plates have been employed in conjunction with an electrolytic process. It is found that plates made of an alloy, aluminum 5 lbs., platinum 15 grains, reduce very considerably the time taken for the sedimentation of solids. The figure shows a sectional view of the treatment box with the arrangement of plates.

**Vulcanization of Caoutchouc. P. A. Newton, May 22, 1914. Brit. Pat. 12,661.** The above refers to the use of ammonia derivatives of basic reaction (other than those which readily give off $NH_3$) or such bases as have dissociation constant higher than $1 \times 10^{-8}$ in place of piperidine for purposes of vulcanization. Example, 100 parts para-caoutchouc are vulcanized at 130–135° C. (3 atm. steam pressure) for 30 minutes with 10 parts of sulfur and 1 part acetaldehyde ammonia. A well vulcanized rubber is obtained.—Sept. 9, 1915.

**New Fuel for Internal Combustion Engines. T. Franke. Aug. 1, 1914. Brit. Pat. 18,226.**—The above refers to a mixture of unrefined carbinols from the distillation of raw peat ($66^2/_3$ per cent) and benzene ($33^1/_3$ per cent), the mixture being effected as gases during distillation. It leaves no carbon and has very low freezing point.—Sept. 1, 1915.

**Tanning Extracts. W. E. Horrocks and J. K. Tullis. Aug. 7, 1914. Brit. Pat. 18,332.** Wood extracts obtained as waste products in cellulose manufacture are converted into tanning extracts by treatment with neutral salt or salts. The extract may be used as a liquid, paste or powder.—Sept. 7, 1914.

**Trinitrotoluene. Società Italiana Prodotti Explodenti and Ferdinando Quartieri. Sept. 9, 1914. Brit. Pat. 19,566.** Pure dinitrotoluene is obtained by fractional liquefaction and heated to 110° C. with 4 to 5 times its weight of nitric-sulfuric mixture (20 to 30% $HNO_3$). Pure trinitrotoluene crystallizes from the mass obtained by slow cooling and acid impurities are removed by melting it *in vacuo*.—Sept. 9, 1915.

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON NOVEMBER 20TH.

## INORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetate of Lime, gray | 100 Lbs. | 4.50 | @ | 4.55 |
| Alum, lump | 100 Lbs. | 4.00 | @ | 5.00 |
| Aluminum Sulfate, high-grade | 100 Lbs. | 2.50 | @ | 3.00 |
| Ammonium Carbonate, domestic | Lb. | 8 1/2 | @ | 9 1/2 |
| Ammonium Chloride, gray | Lb. | 8.25 | @ | 8.50 |
| Ammonium Phosphate, commercial, 98–100% | Lb. | 10 1/4 | @ | 10 3/4 |
| Aqua Ammonium, 16°, drums | Lb | 2 1/4 | @ | 2 1/2 |
| Arsenic, white | Lb. | 3 3/4 | @ | 4 |
| Barium Chloride | Ton | 90.00 | @ | 100.00 |
| Barium Nitrate | Lb. | 15 | @ | 16 |
| Barytes, prime white, foreign | Ton | 19.00 | @ | 23.00 |
| Bleaching Powder, 35 per cent | 100 Lbs. | 4.00 | @ | 5.00 |
| Blue Vitriol | Lb. | 6 1/2 | @ | 6 3/4 |
| Borax, crystals, in bags | Lb. | 5 3/4 | @ | 6 |
| Boric Acid, powdered crystals | Lb. | 10 | @ | 10 1/2 |
| Brimstone, crude, domestic | Long Ton | 22.00 | @ | 22.50 |
| Bromine, technical, bulk | Lb. | 1.50 | @ | 1.75 |
| Calcium Chloride, lump | Ton | — | @ | 11.78 |
| Calcium Chloride, granulated | Ton | — | @ | 14.78 |
| Caustic Soda, 70 @ 76 per cent | 100 Lbs. | 5.25 | @ | 5.50 |
| Caustic Soda, powdered or granulated, 76 per cent | 100 Lbs. | 5.50 | @ | 5.75 |
| Chalk, light precipitated | Lb. | 4 3/4 | @ | 5 1/2 |
| China Clay, imported | Ton | 11.00 | @ | 16.00 |
| Feldspar | Ton | 8.00 | @ | 12.00 |
| Fuller's Earth, foreign, powdered | 100 Lbs. | 80 | @ | 1.05 |
| Glauber's Salt, in bbls | 100 Lbs. | 60 | @ | 75 |
| Green Vitriol, bulk | 100 Lbs. | 70 | @ | 80 |
| Hydrochloric Acid, commercial, 18° | 100 Lbs. | 1.75 | @ | 2.00 |
| Hydrochloric Acid, C. P., conc., 22° | 100 Lbs. | 2.25 | @ | 2.50 |
| Iodine, resublimed | Lb. | 4.25 | @ | 4.30 |
| Lead Acetate, white crystals | Lb. | 11 5/8 | @ | 12 1/8 |
| Lead Nitrate | Lb. | 11 1/2 | @ | 12 |
| Litharge, American | Lb. | 6 1/2 | @ | — |
| Lithium Carbonate | Lb. | 90 | @ | 1.00 |
| Magnesium Carbonate | Lb. | 13 | @ | — |
| Magnesite, "Calcined" | Ton | 30.00 | @ | 35.00 |
| Mercuric Chloride, commercial | Lb. | 1.50 | @ | — |
| Nitric Acid, 36° | Lb. | 6 1/4 | @ | 7 |
| Nitric Acid 42° | Lb. | 8 1/2 | @ | 9 1/4 |
| Phosphoric Acid, sp. gr. 1.750 | Lb. | 28 | @ | 31 |
| Phosphorus | Lb. | 40 | @ | 1.00 |
| Plaster of Paris | Bbl. | 1.50 | @ | 1.70 |
| Potassium Bichromate, casks | Lb. | 30 | @ | — |
| Potassium Bromide | Lb. | 2.50 | @ | 2.51 |
| Potassium Carbonate, calcined, 80 @ 85% | 100 Lbs. | 24 | @ | 26 |
| Potassium Chlorate, crystals, spot | Lb. | 45 | @ | 50 |
| Potassium Cyanide, bulk, 98–99 per cent | Lb. | 28 | @ | 32 |
| Potassium Hydroxide | Lb. | 47 | @ | 52 |
| Potassium Iodide, bulk | Lb. | 3.70 | @ | 3.75 |
| Potassium Nitrate | Lb. | 20 | @ | 22 |
| Potassium Permanganate, bulk | Lb. | 1.25 | @ | 1.50 |
| Quicksilver, flask, 75 lbs | | 100.00 | @ | 105.00 |
| Red Lead, American, dry | Lb. | 7 | @ | — |
| Salt Cake, glass makers' | 100 Lbs. | 55 | @ | 65 |
| Silver Nitrate | Oz. | 32 | @ | 34 |
| Soapstone in bags | Ton | 10.00 | @ | 12.00 |
| Soda Ash, 48 per cent | 100 Lbs. | 1.00 | @ | 1.10 |
| Sodium Acetate | Lb. | 7 1/4 | @ | 7 3/4 |
| Sodium Bicarbonate, domestic | 100 Lbs. | 1.20 | @ | — |
| Sodium Bicarbonate, English | Lb. | 3 1/2 | @ | 3 5/8 |
| Sodium Bichromate | Lb. | 17 1/2 | @ | 18 |
| Sodium Carbonate, dry | 100 Lbs. | 1.25 | @ | — |
| Sodium Chlorate | Lb. | 50 | @ | — |
| Sodium Fluoride, commercial | Lb. | 13 | @ | — |
| Sodium Hydroxide, 60 per cent | 100 Lbs. | | 2.25 | |
| Sodium Hyposulfite | 100 Lbs. | 2.25 | @ | 2.50 |
| Sodium Nitrate, 95 per cent, spot | 100 Lbs. | 2.95 | @ | 3.00 |
| Sodium Silicate, liquid | 100 Lbs. | 85 | @ | 1.10 |
| Sodium Sulfide, 30%, crystals, in bbls | Lb. | 2 | @ | 2 1/2 |
| Sodium Sulfite, crystals | Lb. | 2 1/2 | @ | 2 5/8 |
| Strontium Nitrate | Lb. | 21 | @ | 22 |
| Sulfur, flowers, sublimed | 100 Lbs. | 2.20 | @ | 2.60 |
| Sulfur, roll | 100 Lbs. | 1.80 | @ | 2.15 |
| Sulfuric Acid, chamber, 60° | 100 Lbs. | 1.00 | @ | 1.25 |
| Sulfuric Acid, conc., sp. gr. 1.842 | 100 Lbs. | 1.75 | @ | 2.50 |
| Sulfuric Acid, oleum (fuming) | 100 Lbs. | 1.75 | @ | 2.50 |
| Talc, American | Ton | 9.00 | @ | 13.00 |
| Terra Alba, American, No. 1 | 100 Lbs. | 75 | @ | 80 |
| Tin Bichloride, 50° | Lb. | 12 1/2 | @ | 12 3/4 |
| Tin Oxide | Lb. | 46 | @ | 47 1/2 |
| White Lead, American, dry | Lb. | 6 | @ | — |
| Zinc Carbonate | Lb. | 13 | @ | 15 |
| Zinc Chloride, commercial | Lb. | 8 | @ | 8 1/2 |
| Zinc Oxide, American process | Lb. | 8 5/8 | @ | 8 7/8 |
| Zinc Sulfate | Lb. | 6 1/2 | @ | 7 |

## ORGANIC CHEMICALS

| | | | | |
|---|---|---|---|---|
| Acetanilid, C. P., in bbls | Lb. | 1.10 | @ | 1.15 |
| Acetic Acid, 28 per cent, in bbls | 100 Lbs. | 3.50 | @ | 4.50 |
| Acetic Acid, glacial, 99 1/2%, in carboys | Lb. | 25 | @ | 30 |
| Acetone, drums | Lb. | 28 | @ | 30 |
| Alcohol, denatured, 180 proof | Gal. | 46 | @ | 47 |
| Alcohol, grain, 188 proof | Gal. | 2.58 | @ | 2.60 |
| Alcohol, wood, 95 per cent, refined | Gal. | 50 | @ | 52 |
| Amyl Acetate | Gal. | 3.50 | @ | — |
| Aniline Oil | Lb. | 1.05 | @ | 1.50 |
| Benzoic Acid, ex-toluol | Lb. | 3.75 | @ | 4.00 |
| Benzol, 90 per cent | Gal. | 75 | @ | 85 |
| Camphor, refined in bulk, bbls | Lb. | 42 | @ | — |
| Carbolic Acid, U. S. P., crystals, drums | Lb. | 1.75 | @ | 1.80 |
| Carbon Bisulfide | Lb. | 6 1/2 | @ | 7 1/2 |
| Carbon Tetrachloride, drums, 100 gals | Lb. | 19 | @ | 21 |
| Chloroform | Lb. | | 40 | |
| Citric Acid, domestic, crystals | Lb. | 55 | @ | 55 1/2 |
| Cresol, U. S. P. | Gal. | 1.15 | @ | 1.25 |
| Dextrine, corn (carloads, bags) | 100 Lbs. | 2.80 | @ | — |
| Dextrine, imported potato | Lb. | 10 | @ | 12 |
| Ether, U. S. P., 1900 | Lb. | 15 | @ | 20 |
| Formaldehyde, 40 per cent | Lb. | 9 1/2 | @ | 10 |
| Glycerine, dynamite, drums included | Lb. | 60 | @ | 62 |
| Oxalic Acid, in casks | Lb. | 50 | @ | 51 |
| Pyrogallic Acid, resublimed bulk | Lb. | 1.25 | @ | 1.45 |
| Salicylic Acid | Lb. | 3.75 | @ | 4.00 |
| Starch, cassava | Lb. | 3 1/2 | @ | 4 1/8 |
| Starch, corn (carloads, bags) | 100 Lbs. | — | @ | 2.00 |
| Starch, potato | Lb. | 6 3/4 | @ | 7 |
| Starch, rice | Lb. | 7 | @ | 8 |
| Starch, sago | Lb. | 3 | @ | 3 1/2 |
| Starch, wheat | Lb. | 5 | @ | 5 1/2 |
| Tannic Acid, commercial | Lb. | 75 | @ | 76 |
| Tartaric Acid, crystals | Lb. | 50 | @ | 50 1/2 |

## OILS, WAXES, ETC.

| | | | | |
|---|---|---|---|---|
| Beeswax, pure, white | Lb. | 47 | @ | 55 |
| Black Mineral Oil, 29 gravity | Gal. | 12 1/2 | @ | 13 |
| Castor Oil, No. 3 | Lb. | 10 3/4 | @ | 11 1/4 |
| Ceresin, yellow | Lb. | 10 | @ | 14 |
| Corn Oil, crude | 100 Lbs. | 7.50 | @ | 7.60 |
| Cottonseed Oil, crude, f. o. b. mill | Gal. | 50 1/2 | @ | 51 |
| Cottonseed Oil, p. s. y. | Lb. | 7 7/8 | @ | 8 |
| Creosote, beechwood | Lb. | 3.50 | @ | 4.50 |
| Cylinder Oil, light, filtered | Gal. | 20 | @ | 25 |
| Fusel Oil, crude | Lb. | 2.90 | @ | 3.25 |
| Japan Wax | Lb. | 12 3/4 | @ | 13 |
| Lard Oil, prime winter | Gal. | 92 | @ | 96 |
| Linseed Oil, raw (car lots) | Gal. | 64 | @ | — |
| Menhaden Oil, crude (southern) | Gal. | 45 | @ | |
| Naphtha, 68 @ 72° | Gal. | 22 | @ | 24 |
| Neat's-foot Oil, 20° | Gal. | 94 | @ | 96 |
| Paraffine, crude, 117 & 119 m. p. | Lb. | 3 1/2 | @ | 4 |
| Paraffine Oil, high viscosity | Gal. | 23 | @ | 24 |
| Rosin, "F" Grade, 280 lbs. | Bbl. | | 5.45 | |
| Rosin Oil, first run | Gal. | — | @ | 32 |
| Shellac, T. N. | Lb. | 17 1/2 | @ | 18 |
| Spermaceti, cake | Lb. | 25 | @ | 26 |
| Sperm Oil, bleached winter, 38° | Gal. | 70 | @ | 72 |
| Spindle Oil, No. 200 | Gal. | 18 | @ | 19 |
| Stearic Acid, double-pressed | Lb. | 13 1/2 | @ | 14 |
| Tallow, acidless | Gal. | 70 | @ | 72 |
| Tar Oil, distilled | Gal. | 30 | @ | 31 |
| Turpentine, spirits of | Gal. | | 58 1/2 | |

## METALS

| | | | | |
|---|---|---|---|---|
| Aluminum, No. 1, ingots | Lb. | 55 | @ | 57 |
| Antimony, Hallets' | Lb. | | nominal | |
| Bismuth, New York | Lb. | | 3.00 | |
| Copper, electrolytic | Lb. | 19 1/4 | @ | 19 1/2 |
| Copper, lake | Lb. | 19 1/4 | @ | 19 1/2 |
| Lead, N. Y. | 100 Lbs. | | 5.25 | |
| Nickel, electrolytic | Lb. | 50 | @ | — |
| Nickel, shot and ingots | Lb. | 45 | @ | — |
| Platinum, refined | Oz. | 45.00 | @ | 50.00 |
| Silver | Oz. | | 51 7/8 | |
| Tin | 100 Lbs. | 40.00 | @ | — |
| Zinc, N. Y. | Lb. | | 18 1/4 | |

## FERTILIZER MATERIALS

| | | | | |
|---|---|---|---|---|
| Ammonium Sulfate | 100 Lbs. | | 3.55 | |
| Blood, dried | Unit | | 3.40 | |
| Bone, 4 1/2 and 50, ground, raw | Ton | | 35.00 | |
| Calcium Cyanamid | Unit of Ammonia | | 2.45 | |
| Calcium Nitrate, Norwegian | 100 Lbs. | | — | |
| Castor Meal | Unit | | — | |
| Fish Scrap, domestic, dried, f. o. b. works | Unit | 3.75 | & | 10 |
| Phosphate, acid | Unit | 75 | @ | 80 |
| Phosphate rock; f. o. b. mine: | | | | |
| Florida land pebble, 68 per cent | Ton | 2.75 | @ | 3.00 |
| Tennessee, 70–80 per cent | Ton | 5.00 | @ | 5.50 |
| Potassium "muriate," basis 80 per cent | Ton | | 435.00 | |
| Pyrites, furnace size, mported | Unit | — | @ | 13 |
| Tankage, high-grade; f. o. b. Chicago | Unit | 3 10 | & | 10 |

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